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Cadmium(II) Complexes of 4-(4-Pyridyl)Pyrazole: A Case of Two Conformational Supramolecular Isomers Polythreaded in the Same Crystal and a Rare Example of 5-Connected **nov** NetGuang Yang,<sup>†,\*</sup> Raphael G. Raptis,<sup>\*,‡</sup> and Peter Šafář<sup>§</sup>

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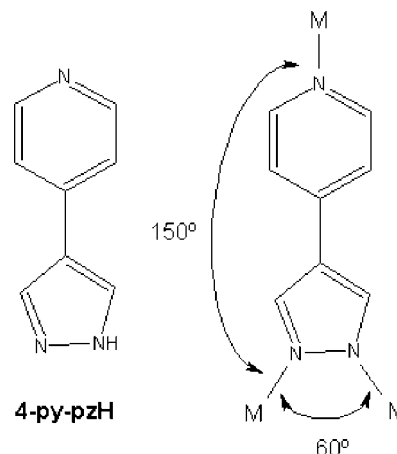
**ABSTRACT:** Stoichiometric control of the reactions of  $\text{Cd}(\text{BF}_4)_2$  with 4-(4-pyridyl)pyrazole (4-py-pzH) led to the isolation of four different crystalline products: a mononuclear complex  $[\text{Cd}(\text{4-py-pzH})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2$  (**1**), a polythreaded two-dimensional (2D) + one-dimensional (1D) complex  $[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})_2]_n$  (**2**), a 1D chain  $\{[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2][\text{Cd}(\text{NCS})_4]\}_n$  (**3**), and a 3D  $[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})]_n$  (**4**). Complex **2** consists of stacked 2D square layers penetrated by columns of 1D ribbons. The 2D and 1D components of **2** are conformational supramolecular isomers of formula  $[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})_2]_n$ . The topology underlying **4** represents a rare example of a 5-connected **nov** net observed in metal–organic frameworks.

## Introduction

The expansion of the field of metal–organic frameworks (MOFs) of predetermined structure depends on the judicious choice of new linkers and nodes of appropriate coordination algorithms.<sup>1</sup> Rigid, polydentate N-donor ligands are typical linkers employed in such work.<sup>2</sup> Bidentate *N,N'*-pyrazole, as well as substituted pyrazoles, with an ideal 60° angle formed between the *N-sp*<sup>2</sup> donor orbitals, are convenient bridging ligands for the synthesis of cyclic trinuclear complexes.<sup>3</sup> Substitution of the pyrazole 4-position with a 4-pyridyl group renders the 4-(4-pyridyl)pyrazole (4-py-pzH, Scheme 1) a potentially tridentate ligand with either 60° or 150° bites, allowing new coordination motifs and opening up further extended lattice geometries. Some of these possibilities have been demonstrated in the case of cobalt and zinc complexes where two different coordination modes of 4-(4-pyridyl)pyrazole have been identified:  $\eta_1\text{-4-Hpy-pzH}^+$  and  $\mu_3\text{-4-py-pz}^-$ .<sup>4</sup>

The term “supramolecular isomerism” was first proposed by Zaworotko to define the existence of more than one superstructure for a given set of molecular components in a supramolecular system.<sup>5</sup> Even though several examples have been described in the literature,<sup>6</sup> supramolecular isomerism and its manifestation upon structure and bulk properties has not yet been fully understood. Although the existence of isomeric forms can be anticipated to some extent, the preparation of a specific isomer relies on serendipity. Several parameters may contribute to supramolecular isomerism in coordination polymers. Zaworotko has described a case of supramolecular isomerism caused by variable ligand conformation: 1,2-bis(4-pyridyl)ethane can adopt *gauche* (angular) or *anti* (linear) conformations where the conformational flexibility of the bridging bipyridyl ligand results in three entirely different polymeric structures in the corresponding cobalt(II) complexes.<sup>7</sup> Geometrical isomerism around the metal ions is another cause of supramolecular isomerism in coordination polymers: Two quite similar infinite chains coexist

Scheme 1. 4-(4-Pyridyl)-pyrazole and the Angles It Provides upon Binding to Metals



in the crystal structure of a cadmium(II) thiocyanate complex with phenylthiourea, the difference between them being the *cis*- versus *trans*- $\text{N}_2\text{S}_4$  coordination geometry of the Cd-centers.<sup>8</sup> Supramolecular isomers can exist even for given coordination mode and conformation of the ligands, as well as given coordination geometry around the metal ions. An example of the latter case is the copper(II)-5-nitro-1,3-benzenedicarboxylate, which exhibits two isomeric forms: hexagon and zigzag chain.<sup>9</sup> Hydrogen bonding and weak interactions (such as  $\pi$ – $\pi$  stacking, etc.) may also contribute to favoring one isomeric form over another. The recognition of new cases of supramolecular isomerism and the identification of the factors that determine the various isomeric forms is a critical stage of development before we attain predictive ability over this phenomenon.

In this paper, we report the synthesis and X-ray crystal structures of four Cd(II)-4-(4-pyridyl)pyrazole complexes: mononuclear  $[\text{Cd}(\text{4-py-pzH})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2$  (**1**), polythreaded  $[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})_2]_n$  (**2**), one-dimensional (1D)  $\{[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2][\text{Cd}(\text{NCS})_4]\}_n$  (**3**), and three-dimensional (3D)  $[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})]_n$  (**4**) with a rare **nov** topology. Complex **2** contains

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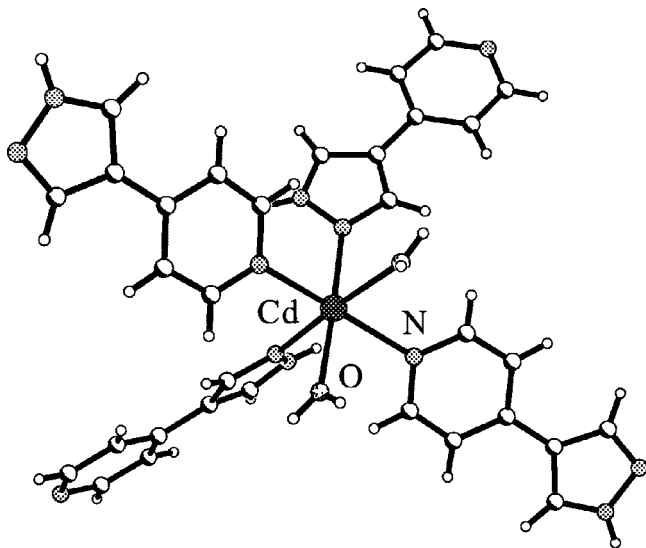


Figure 1. Molecular structure of 1.

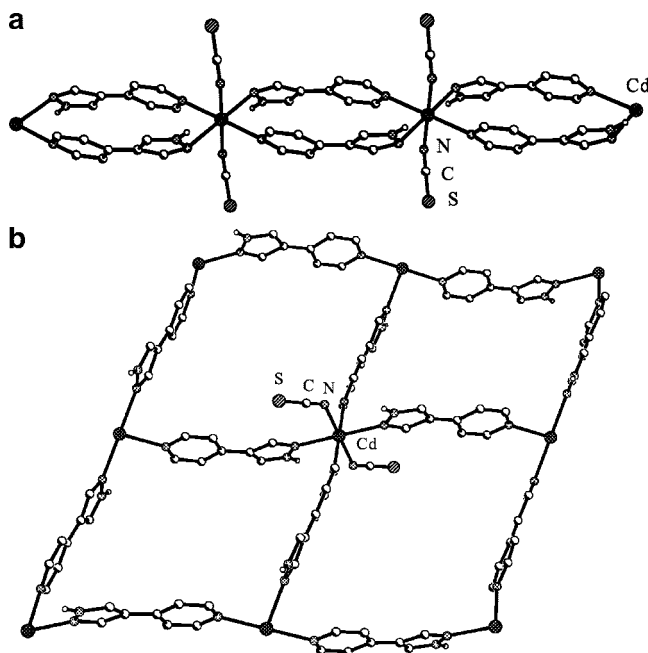


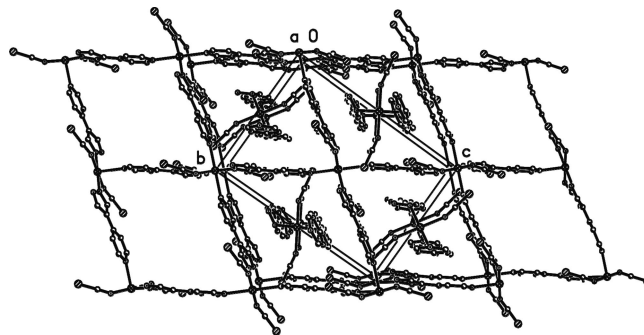
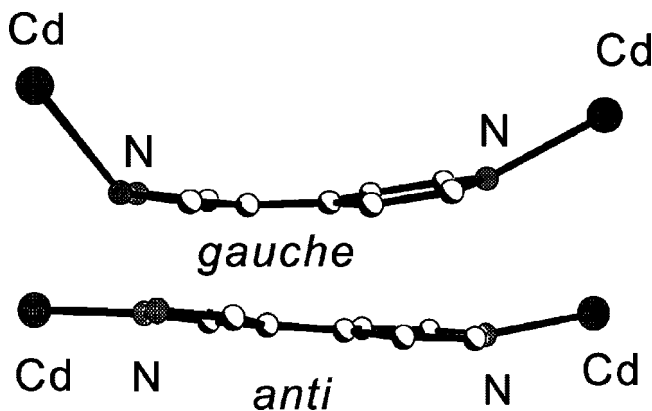
Figure 2. (a) 1D chain of  $[\text{Cd}(\text{NCS})_2(4\text{-py-pzH})_2]_n$  (**2**). Only N-bound H-atoms are shown. (b) 2D grid of  $[\text{Cd}(\text{NCS})_2(4\text{-py-pzH})_2]_n$  (**2**); the distance of  $\text{Cd}\cdots\text{Cd}$  bridged by 4-py-pzH is 10.758(8) Å. Only N-bound H-atoms are shown.

two conformational supramolecular isomeric forms: a 2D (4,4)-net and an 1D-chain interlocked into a single crystalline lattice.

### Experimental Section

4-(4-Pyridyl)pyrazole was prepared by a literature method.<sup>10</sup> All other reagents are commercially available and were used as received. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN). IR spectra were recorded on a Nicolet Magna-IR 750 spectrophotometer.

**Synthesis.**  $[\text{Cd}(4\text{-py-pzH})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2$  (**1**). 4-py-pzH (0.1 mmol, 14.5 mg) in ethanol was mixed with  $\text{Cd}(\text{BF}_4)_2$  (0.1 mmol, 29 mg). After that,  $\text{Et}_3\text{N}$  (0.1 mmol) was added into the mixture under stirring. The resulted solution was allowed to evaporate slowly to give colorless polyhedral crystals within two weeks in ca. 15% yield (based on Cd).  $\text{C}_{32}\text{H}_{32}\text{B}_2\text{CdF}_8\text{N}_{12}\text{O}_2$  (902.7): calcd. C 42.58, H 3.57, N 18.62; found C, 42.42; H, 3.54; N, 18.83.

Figure 3. Packing diagram of **2**, viewed along the *a*-axis.Figure 4. Two conformations, *gauche* and *anti*, of Cd-4-py-pzH-Cd observed in the 1D chain and 2D grid of **2**, respectively.

$[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})_2]_n$  (**2**). 4-py-pzH (0.2 mmol, 29 mg) dissolved in a small volume of ethanol was mixed with  $\text{Cd}(\text{BF}_4)_2$  (0.1 mmol, 29 mg) and  $\text{NH}_4\text{SCN}$  (0.2 mmol, 15 mg) dissolved in water. The resulting solution was allowed to evaporate slowly. After one week, colorless cubic crystals of **2** formed in 50% yield (based on Cd).  $\text{C}_{18}\text{H}_{14}\text{CdN}_8\text{S}_2$  (518.9): calcd. C 41.66, H 2.72, N 21.59, S 12.36; found C 41.20, H 2.75, N 21.46, S 12.70. IR (KBr,  $\text{cm}^{-1}$ ): 3451 (s, br), 3276 (s), 3101 (m), 2057 (vs), 1614 (s), 1571 (m), 1550 (m), 1435 (w), 1389 (w), 1224 (m), 1146 (w), 1047 (m), 1033 (m), 956 (m), 823 (m), 720 (w), 697 (s), 614 (w), 526 (m).

$\{[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2][\text{Cd}(\text{NCS})_4]\}_n$  (**3**) and  $[\text{Cd}(\text{NCS})_2(\mu\text{-4-py-pzH})_2]_n$  (**4**). 4-py-pzH (0.1 mmol, 14.5 mg) dissolved in a small volume of ethanol was mixed with  $\text{Cd}(\text{BF}_4)_2$  (0.2 mmol, 58 mg) and  $\text{NH}_4\text{SCN}$  (0.4 mmol, 30 mg) dissolved in water. The resulting solution was allowed to evaporate slowly. A small amount of colorless needles of **3** appeared on the wall of the vial within two days. Pale yellow plates of **4** formed slowly after the crystallization of **3**. Yield for **4**: ca. 30% (based on Cd). For **3**: IR (KBr,  $\text{cm}^{-1}$ ): 3130 (s, br), 2100 (m), 2071 (m), 2049 (m), 1618 (m), 1401 (vs), 1084 (s), 1042 (s), 824 (w), 749 (w), 534 (m), 522 (m), 483 (w). For **4**:  $\text{C}_{10}\text{H}_7\text{CdN}_5\text{S}_2$  (373.7): calcd. C 32.14, H 1.89, N 18.74; found C 31.74, H 1.94, N 18.56. IR (KBr,  $\text{cm}^{-1}$ ): 3305 (s), 3118 (w), 3108 (w), 2108 (vs), 2084 (vs), 1616 (s), 1572 (m), 1552 (m), 1471 (w), 1433 (m), 1388 (m), 1334 (w), 1304 (w), 1220 (m), 1145 (m), 1047 (s), 1016 (m), 954 (s), 873 (m), 821 (s), 699 (s), 615 (w), 525 (m), 458 (m).

**Crystallography.** Diffraction measurements were carried out with a Bruker SMART 1K CCD diffractometer and graphite monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073$  Å) radiation. Data reductions were performed with the SAINT software, which corrects for Lorentz and polarization effects.<sup>11a</sup> Absorption corrections were applied using the SADABS empirical method. The structure was solved by the direct methods and refined by least-squares on  $F^2$  using the SHELXTL package of crystallographic programs.<sup>11b</sup> All non-hydrogen atoms were refined anisotropically, while H-atom positions were generated geometrically and treated as isotropic contributions.

**Crystallographic Data.** **1**:  $\text{C}_{32}\text{H}_{32}\text{B}_2\text{CdF}_8\text{N}_{12}\text{O}_2$ ,  $M = 902.72$ , orthorhombic, *Pcca* (No. 54),  $a = 17.557(2)$ ,  $b = 12.4349(17)$ ,  $c = 17.814(2)$  Å,  $V = 3889.0(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.542$  g cm<sup>-3</sup>,  $\mu = 0.647$  mm<sup>-1</sup>, 19 147 reflections collected, 3441 independent ( $R_{\text{int}} = 0.0773$ ), 258 parameters, 7 restraints,  $R_1 = 0.0597$  for 2439 observed

Table 1. Selected Bond Lengths and Torsion Angles for 1–4

complex		bond distances (Å)			torsion angles (°)	
		Cd–N <sub>NCS</sub>	Cd–N <sub>pz</sub>	Cd–N <sub>py</sub>	Cd–N <sub>pz</sub> –C–C	Cd–N <sub>py</sub> –C–C
1			2.339(5)	2.311(5)	175.60(38)	179.27(51)
2	chain	2.265(3)	2.447(3)	2.341(3)	132.74(26)	157.55(28)
	2D	2.318(3)	2.370(2)	2.345(2)	177.28(19)	167.54(25)
3	cationic	2.300(5)	2.307(5)		163.49(38)	
		2.327(5)	2.311(5)			
	anionic	2.276(5)				
		2.360(5)				
		2.391(5)				
4		2.316(2)	2.328(2)	2.3212(19)	179.86(17)	174.87(21)
		2.365(2)				

reflections with  $I > 2(\sigma)I$  (0.0822 for all data),  $wR_2 = 0.1755$ ,  $S = 1.071$ ,  $\max \Delta\rho = 1.102 \text{ e } \text{\AA}^{-3}$ .

2:  $\text{C}_{18}\text{H}_{14}\text{CdN}_8\text{S}_2$ ,  $M = 518.89$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 9.7821(13)$ ,  $b = 12.1686(17)$ ,  $c = 17.221(2) \text{ \AA}$ ,  $\beta = 103.282(2)^\circ$ ,  $V = 1995.0(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.728 \text{ g cm}^{-3}$ ,  $\mu = 1.327 \text{ mm}^{-1}$ , 9591 reflections collected, 3520 independent ( $R_{\text{int}} = 0.0276$ ), 265 parameters, 2 restraints,  $R_1 = 0.0286$  for 2646 observed reflections with  $I > 2(\sigma)I$  (0.0444 for all data),  $wR_2 = 0.0665$ ,  $S = 1.035$ ,  $\max \Delta\rho = 0.356 \text{ e } \text{\AA}^{-3}$ .

3:  $\text{C}_{22}\text{H}_{16}\text{CdN}_{12}\text{S}_6$ ,  $M = 865.63$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 5.7016(11)$ ,  $b = 15.523(3)$ ,  $c = 17.355(3) \text{ \AA}$ ,  $\alpha = 93.514(3)$ ,  $\beta = 94.945(3)$ ,  $\gamma = 95.979(3)^\circ$ ,  $V = 1518.1(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.894 \text{ g cm}^{-3}$ ,  $\mu = 1.851 \text{ mm}^{-1}$ , 9697 reflections collected, 5308 independent ( $R_{\text{int}} = 0.0517$ ), 379 parameters, 0 restraints,  $R_1 = 0.0444$  for 3558 observed reflections with  $I > 2(\sigma)I$  (0.0758 for all data),  $wR_2 = 0.0980$ ,  $S = 0.960$ ,  $\max \Delta\rho = 0.844 \text{ e } \text{\AA}^{-3}$ .

4:  $\text{C}_{10}\text{H}_7\text{CdN}_5\text{S}_2$ ,  $M = 373.73$ , monoclinic,  $P2_1/c$  (No. 14),  $a = 8.7825(9)$ ,  $b = 9.4521(10)$ ,  $c = 16.1029(17) \text{ \AA}$ ,  $\beta = 99.437(2)^\circ$ ,  $V = 1318.7(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.882 \text{ g cm}^{-3}$ ,  $\mu = 1.960 \text{ mm}^{-1}$ , 6271 reflections collected, 2325 independent ( $R_{\text{int}} = 0.0206$ ), 163 parameters, 0 restraints,  $R_1 = 0.0197$  for 2116 observed reflections with  $I > 2(\sigma)I$  (0.0231 for all data),  $wR_2 = 0.0504$ ,  $S = 1.077$ ,  $\max \Delta\rho = 0.352 \text{ e } \text{\AA}^{-3}$ .

CCDC 657475, 657472–4 (for 1–4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at <http://www.ccdc.cam.ac.uk/datarequest/cif>.

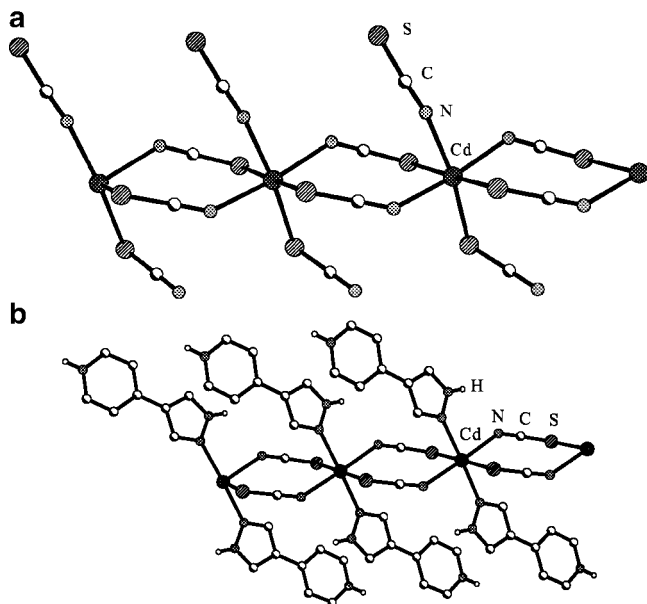
## Results and Discussion

Reaction of  $\text{Cd}(\text{BF}_4)_2$  with 4-py-pzH in a 1:1 ratio in EtOH afforded a crystalline mononuclear complex **1**, while the excess of Cd(II) ions remained in solution. The Cd-center, located on a 2-fold axis parallel to the crystallographic  $b$ -axis, is octahedrally coordinated by two *cis*- $\text{H}_2\text{O}$  molecules, two *cis*-pyrazolyl N-atoms, and two *trans*-pyridyl N-atoms (Figure 1). The four pyrazoles, 4-py-pzH, act as monodentate ligands via either their pyridyl or pyrazolyl function. Surprisingly, the pyrazole function remains protonated, even though one molar equivalent of base was used in the reaction mixture.

Reaction of  $\text{Cd}(\text{BF}_4)_2$ , 4-py-pzH, and  $\text{NH}_4\text{SCN}$  in a 1:2:2 molar ratio in an EtOH/ $\text{H}_2\text{O}$  mixture led to the isolation of cube-shaped crystals of **2**; elemental analysis demonstrated that the  $\text{Cd}^{2+}/4\text{-py-pzH}/\text{NCS}^-$  stoichiometry in **2** is also 1:2:2, the same as that of the reaction mixture. X-ray analysis revealed that two different supramolecular structures of the same chemical formula,  $[\text{Cd}(\text{NCS})_2(\mu\text{-}4\text{-py-pzH})_2]$ , coexist in **2**; one consists of 2D (4,4) nets and the other consists of 1D chains (Figure 2). The 1D chains run at an angle of  $70.8^\circ$  to the plane of the 2D nets and are located in the channels formed by the eclipsed stacking of the latter along the  $a$ -axis (Figure 3). The two crystallographically independent Cd(II)-atoms, which are located on (0, 0, 0) and (0, 0, 1/2) inversion centers generating the 2D and 1D structures, respectively, have very similar coordination environments: each Cd-atom is hexacoordinated by six N-atoms

from two monodentate  $\text{NCS}^-$ , two pyrazolyl, and two pyridyl groups. In both isomers, 4-py-pzH acts as a  $\mu_2$ -bridge between pairs of Cd-atoms via one pyridyl and one pyrazolyl N-atoms, while thiocyanates serve only as monodentate N-ligands. However, there are double  $\mu\text{-}4\text{-py-pzH}$  bridges between consecutive Cd-centers in the  $[\text{-Cd}(\mu\text{-}4\text{-py-pzH})_2\text{-Cd}]_n$  1D-structure (Figure 2a), while only single  $\mu\text{-}4\text{-py-pzH}$  bridges are present between any two Cd-centers of the 2D net (Figure 2b). In the 2D net the  $[\text{-Cd}(\mu\text{-}4\text{-py-pzH})\text{-Cd}]$  units adopt a typical, approximately coplanar, *anti*-coordination, in contrast to the clearly non-coplanar, *gauche*-coordination accommodated along the 1D chains (Figure 4). The py and pzH rings remain approximately coplanar in both the *anti* and *gauche* coordination modes, as expected for  $\pi$ -conjugated rings, but the Cd–N<sub>pz</sub> bond length is unusually long, 2.447(3) Å, in the *gauche* structure (Table 1). Therefore, the supramolecular isomerism observed here differs from that in Co(II)-complexes of 1,2-bis(4-pyridyl)ethane described by Zaworotko,<sup>7</sup> because in **2** the ligand conformation is practically identical in the two isomeric forms, the supramolecular isomerism caused by the *gauche* versus *anti* coordination modes of 4-py-pzH to Cd-atoms. The *gauche* coordination introduces strain to the chain structure, which is absent in the relaxed 2D net; however, several weak interactions may contribute to stabilize the former. First, the N<sub>pz</sub>–H $\cdots$ S hydrogen bonding is found between pyrazolyl N-atoms of the chain and the thiocyanato S-atoms of the net. Second, several  $\pi\cdots\pi$  stacking interactions exist between aromatic rings with the face-to-face distances ca. 3.11 and 3.46 Å within chains, or between chains and the 2D net.<sup>12</sup> Third, C–H $\cdots\pi$  interactions are found for some of the H-atoms of the chain pointing to the aromatic rings of the 2D net.<sup>13</sup> The shortest distance of C–H $\cdots\pi$  interactions is 2.935(3) Å for H(16) $\cdots$ N(3') (symmetry code:  $i = -x + 1, -y + 1, -z + 1$ ). The isomeric structures of  $\text{Cd}(\text{NCS})_2(4\text{-py-pzH})_2$ -MOF reported here represent a new case, in which coordination flexibility results in supramolecular isomerism. The presence of only N-bound thiocyanates in the structure of **2** is confirmed by the single absorption at 2057  $\text{cm}^{-1}$  observed in its infrared spectrum, consistent with literature values.<sup>14</sup> The entanglement of the two supramolecular isomeric lattices in **2** can be described as polythreading of 2D stacked square layers with 1D ribbons running in an approximately perpendicular direction to the layers.<sup>15</sup> As can be seen in Figure 3, the thiocyanates in the 1D ribbons interdigitate with the 2D layers, interlocking the two supramolecular lattices. Therefore, the thiocyanates serve as “stoppers” for each loop (namely, a  $\text{Cd}_4(4\text{-py-pzH})_4$ -square) in the 2D layers, as in a “polyrotaxane”. A similar polythreading of 2D and 1D supramolecular isomeric lattices has been observed in  $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ , where dca<sup>−</sup> is dicyanamide.<sup>16</sup> However, unlike **2**, the coordination mode of dca<sup>−</sup> to Mn(II) is the same in both the 2D and 1D components, while there are no “stoppers” interlocking them.





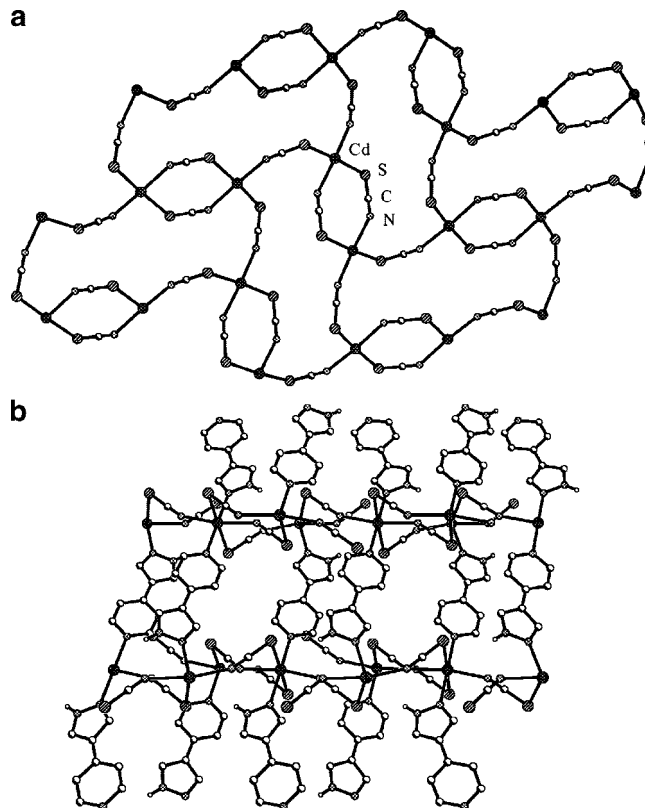
**Figure 5.** (a) Anionic chain of  $[\text{Cd}(\text{NCS})_4]^{2-}$  in **3**. (b) Cationic chain of  $[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2]^{2+}$  in **3**. Only N-bound H-atoms are shown.

When the reaction of  $\text{Cd}(\text{BF}_4)_2$ , 4-py-pzH, and  $\text{NH}_4\text{SCN}$  was conducted in a molar ratio of 2:1:4, two crystalline products were isolated: **3** (as minor product) and **4**. In the crystal of  $\{[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2][\text{Cd}(\text{NCS})_4]\}_n$  (**3**), one anionic,  $[\text{Cd}(\text{NCS})_4]^{2-}$ , and one cationic,  $[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2]^{2+}$ , infinite chains are found in a 1:1 molar ratio. In both chains, each pair of Cd(II)-atoms is bridged by two inversely related  $\mu\text{-NCS}^-$  ligands, forming chair-type eight-membered  $[\text{Cd}_2(\text{NCS})_2]$  rings. The difference lies in the remaining two *trans* positions around the six-coordinate Cd-atoms. In the anionic  $[\text{Cd}(\text{NCS})_4]^{2-}$  chains, these two positions are occupied by one S-bound and one N-bound monodentate thiocyanates (Figure 5a). In the cationic  $[\text{Cd}(\text{NCS})_2(4\text{-Hpy-pzH})_2]^{2+}$  chain these two positions are occupied by two  $\text{N}_{\text{pz}}$ -atoms (Figure 5b).

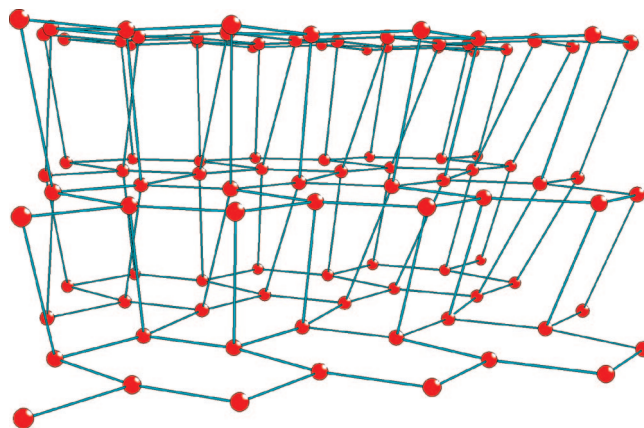
Once the thiocyanate-rich complex **3** (Cd:NCS ratio 1:3) has started crystallizing out of the reaction mixture, the formation of complex **4** with a Cd/NCS ratio of 1:2 starts forming. Complex **4** has a 3D structure with a hexacoordinate Cd(II)-atom by two thiocyanate S-atoms, two thiocyanate N-atoms, one pyrazolyl N-atom, and one pyridyl N-atom in *trans*- $\text{N}_4\text{S}_2$  pseudooctahedral geometry. The structure consists of  $[\text{Cd}(\mu\text{-NCS})_2]_n$ -2D nets connected by  $\mu$ -4-py-pzH pillars (Figure 6). There are three kinds of bridging modes in **4**, namely, singly bridging thiocyanate (Cd-NCS-Cd), doubly bridging thiocyanate (Cd-(NCS)<sub>2</sub>-Cd), and singly bridging 4-pyridylpyrazole (Cd-(4-py-pzH)-Cd) with Cd...Cd distances of 6.055(1), 5.742(1) and 10.934(13) Å, respectively. Thus, each Cd(II)-atom in **4** is connected to five neighboring Cd(II)-atoms, rendering the Cd(II)-atom a topological 5-connected node. The net underlying the structure of **4** is described as  $(4^4.6^6)\text{-nov}$  (Figure 7).<sup>17</sup> Some H-bonded organic compounds have recently been reported to have the same **nov** topology.<sup>18</sup> Compound **4** is the first example of a noninterpenetrated MOF of **nov** topology. However, there is one example of a 2-fold interpenetrated MOF of this topology.<sup>19</sup>

### Conclusions

Expectedly, in the context of the chemistry presented here,  $\text{Cd}^{\text{II}}$ -centers show a clear preference for the soft NCS ligands



**Figure 6.** (a) Layer of  $\text{Cd}(\text{NCS})_2$  network in **4**. The Cd-atoms constitute an irregular (6,3) net. (b) Packing diagram of **4**, showing the layers of  $\text{Cd}(\text{NCS})_2$  pillared by 4-py-pzH. Only N-bound H-atoms are shown.



**Figure 7.** Schematic representation of the **nov** net underlying the structure of **4**.

and for hexacoordination. In the absence, or insufficient presence of thiocyanates, the Cd/4-py-pzH stoichiometry in the reaction mixture determines the products. So, the mononuclear complex **1** was prepared in the absence of thiocyanates. Complex **3** containing only monodentate 4-Hpy-pzH<sup>+</sup> is formed initially, then, bridging 4-pypzH ligands are required in **4** as thiocyanates are depleted.

This work has revealed a new type of conformational supramolecular isomerism in the structure of complex **2**, containing two polythreaded isomeric lattices. Examples of entangled lattices have been described in the literature.<sup>20</sup> However, those of two interlocked supramolecular isomers in the same crystal are still quite uncommon.<sup>61</sup> The 4-py-pzH ligand used here, combining the functions of both pyridine and pyrazole, is expected to show a wide range of versatile coordination modes to metals upon a comprehensive study. The

effect of pH on the protonation/deprotonation of 4-py-pzH ligands has not been considered here but is the subject of further work.

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