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Synthesis and crystal structure determination of 0D-, 1D- and 3D-metal compounds of 4-(pyrid-4-yl)-1,2,4-triazole with zinc(II) and cadmium(II)

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Dedicated to Prof. Wolfgang Kaim on the occasion of his 60th birthday

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ABSTRACT

The potentially tritopic bridging ligand 4-(pyrid-4-yl)-1,2,4-triazole (pytz) reacts with cadmium(II) nitrate tetrahydrate, $Cd(NO_3)_2 \cdot 4H_2O$ and sodium dicyanamide (Na-dca) to form the molecular complex $[Cd(dca)_2(\kappa N_{pv}-pytz)_2(H_2O)_2]$ (1). The cadmium atom lies on a center of inversion and is coordinated in a slightly distorted octahedral geometry by the *trans*-oriented pytz ligands, dicyanamide anions and aqua ligands. The pytz ligand coordinates through the N_{pyridin} atom to the metal atom. The molecular complexes are connected to a 3D supramolecular network by O-H…N_{dca} and O-H…N_{triazole} hydrogen bonds. From zinc(II) bromide and pytz the compound $1D-[ZnBr_2(\mu-\kappa N_{py},N_{tz}-pytz)]$ (2) is obtained where the pytz-ligand bridges between the tetracoordinated zinc(II) atoms through coordination of its N_{pyridine}and N_{triazole}-atoms. Adjacent chains are connected through C-H…Br and C-H…N hydrogen bonds to form a 3D supramolecular structure. Single crystals of 2 crystallize homochiral in the non-centrosymmetric space group P2₁2₁2₁. The origin of the homochirality is the formation of hydrogen-bonded helices around the 2_1 screw axes with the same sense of rotation (left-handed or M in the investigated crystal). $Cd(NO_3)_2 \cdot 4H_2O$, pytz and sodium thiocyanate (NaSCN) give the framework $3D-[Cd(\mu-SCN)_2(\mu-\kappa N_{py},N_{tz}-K_{py})]$ pytz]] (**3**). Parallel layers of 2D-{Cd(μ -SCN)₂}-nets with distorted (6,3)-net topology are assembled by the bridging pytz-ligands into a 3D-structure. The pytz-ligand bridges between two cadmium atoms by N_{pvridine}- and N_{triazole}-coordination.

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1. Introduction

Coordination polymers are infinite compounds built by bridging ligands and metal ions. They are of continuous interest because of their various application oriented properties [1-3]. Current interest is mostly focused on bridging organic ligands. Coordination polymers can also refer to compounds with solely bridging inorganic ligands [4] such as μ -cyano [5], μ -thiocyanato [6,7], μ dicyanamido [8], µ-halido (µ-chloro, etc.) [9,10], µ-oxometallates [11] or to combinations of bridging inorganic and organic ligands in infinite chains or networks [12,13]. However, such compounds should preferably be called inorganic-organic hybrid materials [14]. The ligands 1,2,4-triazole and its 4-N-substituted derivatives are of current interest as bridging ligands between transitionmetal ions for the preparation of linear, 2D- and 3D-coordination polymers [8,15,16], and a wide variety of molecular polynuclear complexes [17]. 2D and 3D metal-organic frameworks (MOFs) could be obtained with the multidentate bridging ligand 1,2bis(1,2,4-triazol-4-yl)ethane [2]. Surprisingly, the coordination chemistry of the ligand 4-(pyrid-4-yl)-1,2,4-triazole [18] (pytz)

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has not been investigated unlike those of its pyrid-2-yl and pyrid-3-yl analogs (Fig. 1) [8,15,19,20]. A pytz analog with additional 2-pyridyl rings on the triazol ring has been used in coordination chemistry [21].

We report here the first three examples of the coordination chemistry of 4-(pyrid-4-yl)-1,2,4-triazole. A molecular cadmium complex and a 3D and 1D cadmium and zinc coordination polymer were synthesized and structurally investigated.

2. Experimental

2.1. General methods

Elemental analyses for C, H, N, were performed with a Perkin– Elmer 263 elemental analyzer. IR-spectra were recorded on a Nicolet Magna-IR 760 Fourier-transform spectrometer equipped with a diamond-ATR unit (ATR = attenuated total reflection). For signal intensities the following abbreviations were used: br (broad), sh (shoulder), w (weak), m (medium), s (strong), vs (very strong). Bands around 1610 and 1580 cm⁻¹ are characteristic for the pyridine ring, bands around 1530 and 630 cm⁻¹ are indicative of the triazole ring [20]. Melting points were measured in open glass capillaries according to the Tottoli method and are uncorrected.





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Fig. 1. Established metal coordination modes of 4-(pyrid-*n*-yl)-1,2,4-triazole (pytz) ligands (*n* = 2, 3, 4).

NMR-spectra were obtained with a Bruker ARX200 (200 MHz ¹H) or Bruker Advance DRX400 (400 MHz for ¹H) spectrometer with calibration to the residual proton solvent signal in MeOH-d₄ (¹H NMR: 3.31 ppm, ¹³C NMR: 49.00 ppm) DMSO-d₆ (¹H NMR: 2.52 ppm, ¹³C NMR: 39.5 ppm) against TMS with δ = 0.00 ppm. ¹³C NMR-spectra were measured at 50.32 MHz with ¹H-broadband decoupling. Multiplicities of the signals were specified s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

Chemicals were obtained from the following suppliers and used without further purification: *N*,*N*-dimethylformamide (DMF) (Roth), hydrazine monohydrate (Sigma–Aldrich), sodium dicyanamide (Aldrich), thionyl chloride, p-toluenesulfonic acid monohydrate (Merck), *N*,*N*-dimethylacetamide (DMA) (Applichem). *N*,*N*-Dimethylformamide azine was prepared from DMF and hydrazine monohydrate with thionyl chloride according to published procedures [22].

2.2. Synthesis of 4-(pyrid-4-yl)-1,2,4-triazole (pytz)



A reaction mixture consisting of *N*,*N*-dimethylformamide azine [22] (4.14 g, 19.3 mmol), 4-aminopyridine (0.900 g, 9.56 mmol), ptoluenesulfonic acid monohydrate (0.200 g, 1.05 mmol) as catalyst, and N,N-dimethylacetamide (30 ml) as solvent was refluxed for 3 days under argon (Eq. (1)). Dimethylamine was removed by a slow inert gas stream and could be detected in the exhaust gas by a wet pH-indicator paper through the color change into the basic region. Refluxing was stopped when no more NHMe2 could be detected. The solvent was then removed under vacuum. The resulting residue was dissolved in ethanol (30 ml) and the solution was refluxed with active carbon (\sim 0.2 g) for 30 min. The solution was quickly filtered while hot and the residue washed with 3×3 ml portions of hot ethanol. The volume of the combined ethanol filtrates was reduced to 10 ml and the solution was cooled to 0 °C. The white precipitate was separated by filtration, washed with cold ethanol (5 ml) and dried in air (yield 0.524 g, 38% based on 4-aminopyridine), m.p. 226–227 °C. Anal. Calc. for C₇H₆N₄ (146.15 g mol⁻¹): C, 57.53; H, 4.14; N, 38.33. Found: C, 57.38; H, 4.48; N, 39.03%. IR (ATR) $v/cm^{-1} = 451(w)$, 527(s), 628(s), 664(m), 689(s), 819(s), 872(m), 943(m), 951(w), 995(m), 1007(w), 1091(s), 1222(m), 1246(s), 1263(m), 1353(w), 1377(m), 1426(m), 1475(w), 1525(s), 1597(s), 2323(w), 3031(m), 3096(m).¹H NMR (400 MHz, DMSO-d₆): δ /ppm = 9.35 (s, 2H, H3^{*}, H3^{*'}), 8.73 ("dd", 2H, ${}^{3}J_{2,3} = 4.4$ Hz, ${}^{4}J_{2,2'} = 1.6$ Hz, H2, H2'), 7.82 ("dd", 2H, ${}^{3}J_{3,2} = 4.8$ Hz, ${}^{4}J'_{3,3} = 1.6$ Hz, H3, H3'); 13 C NMR (50.32 MHz, DMSO-d₆): $\delta/$ ppm = 152.1 (C2, C2'), 141.3 (C3*, C3*), 141.0 (C4), 115.2 (C3, C3'). 4-(Pyrid-4-yl)-1,2,4-triazole is soluble in water, methanol, hot ethanol and a range of polar organic solvents including CH₃CN.

The described method of synthesis using dimethylacetamide or dimethylformamide as a solvent (instead of typically used low-polar hydrocarbons like heptane or benzene) seems to be of a general utility for polar substrates and amines with lowered nucleophilicity[23].

2.3. Synthesis of trans-diaqua-bis(dicyanamido)-bis(4-(pyrid-4-yl)-1,2,4-triazole)cadmium (II) [Cd(dca)₂(pytz)₂(H₂O)₂] (**1**)

Cadmium(II) nitrate tetrahydrate (19.7 mg, 0.06 mmol) and sodium dicyanamide (7.9 mg, 0.09 mmol) were dissolved in de-ionized water (7 ml). Then pytz (9.2 mg, 0.06 mmol) was added as a solid to the reaction mixture which was stirred for 0.5 h at room temperature. Thereafter, the reaction mixture was heated and stirred for 3 h at 100 °C. After cooling, the reaction mixture was filtered to remove some precipitate. The filtrate was left standing under ambient conditions for slow solvent evaporation. After 3 days colorless crystals suitable for single crystal X-ray diffraction studies had formed. Yield: 8 mg, 23% based on pytz.

Anal. Calc. for $C_{18}H_{16}CdN_{14}O_2$ (572.18 g mol⁻¹): C, 37.74; H, 2.82; N, 34.23. Found: C, 36.63; H, 2.87; N, 34.51%. IR (ATR): $v/cm^{-1} = 453.8(w)$, 512.1(s), 532.4(s), 632.2(s), 653.5(m), 669.7(w), 705.6(s), 730.9(w), 756.4(w), 833.6(s), 879.6(m), 914.4(w), 954.7(w), 974.2(w), 1009.9(m), 1074.9(m), 1092.4(s), 1226(m), 1254.9(s), 1268(m), 1364.8(m), 1384.5(w), 1434.9(m), 1508.4(m), 1531.5(s), 1579.5(m), 1608.5(s), 2116.3(m, dca [8]), 2153.1(s, dca), 2215(m, dca), 2290.3(m, dca [8]), 3022.6(m), 3061.8(m), 3110.6(m) (dca = dicyanamido ligand).

2.4. Synthesis of catena-{dibromo-(μ -4-(pyrid-4-yl)-1,2,4-triazole)zinc(II)}, 1D-[ZnBr₂(μ -pytz)] (**2**)

Zinc(II) bromide (14.2 mg, 0.06 mmol) was dissolved in methanol and water (4 ml, 9:1 v:v). A smaller vial was placed in a bigger concentric vial. The first solution was filled into the smaller vial. The ligand pytz (13.3 mg, 0.09 mmol) was dissolved in 20 ml of a 9:1 (v:v) methanol:water mixture and the solution filled into the outer vial so that it also covered the open inner vial. Both solutions

Table 1

Crystal data and structure refinement for 1-3.

Compound	1	2	3
Empirical formula	C ₁₈ H ₁₆ CdN ₁₄ O ₂	$C_7H_6Br_2N_4Zn$	C ₉ H ₆ CdN ₆ S ₂
$M(g \text{ mol}^{-1})$	572.85	371.35	374.72
Crystal size (mm)	$0.20 \times 0.11 \times 0.04$	$0.09 \times 0.04 \times 0.02$	$0.10 \times 0.05 \times 0.01$
2θ Range (°)	2.74-33.14	2.17-24.70	2.36-28.30
h, k, l Range	±11; -11, 10; -25, 27	-6, 4; -8, 14; -16, 17	±10; -19, 20; ±14
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P2_1/c$
a (Å)	7.5141(2)	5.5504(2)	8.14400(10)
b (Å)	8.2155(2)	11.9815(3)	15.1775(2)
<i>c</i> (Å)	17.6711(4)	15.0684(3)	10.8767(2)
β (°)	98.5010(10)	90	105.8560(10)
V (Å ³)	1078.89(5)	1002.08(5)	1293.27(3)
Ζ	2	4	4
D_{calc} (g cm ⁻³)	1.763	2.461	1.925
F(0 0 0)	572	704	728
Absorption coefficient μ (mm ⁻¹)	1.063	10.387	2.001
Maximum/minimum transmission	0.9587, 0.8155	0.8192, 0.4549	0.9803, 0.8250
Reflections collected	19373	4919	14284
Independent reflections	$4008 [R_{int} = 0.0268]$	1711 $[R_{int} = 0.0420]$	$3209 [R_{int} = 0.0323]$
Obs. reflections $[I > 2\sigma(I)]$	3303	1562	2808
Parameters refined	168	127	163
Completeness to θ (%)	97.4	99.7	99.7
Maximum/minimum Δho (e Å $^{-3a}$)	0.646, -0.587	0.415, -0.404	0.836, -0.631
$R_1/wR_2 [I > 2\sigma(I)]^{\text{b}}$	0.0240, 0.0501	0.0267, 0.0418	0.0229, 0.0467
R_1/wR_2 (all reflections) ^b	0.0331, 0.0534	0.0313, 0.0430	0.0293, 0.0485
Goodness-of-fit on F ^{2c}	1.050	0.955	1.041
Weight. scheme w; a/b^{d}	0.0223, 0.3642	0.0000, 0.0000	0.0211, 0.6811
Absolute structure parameter (Flack value) [33]		0.051(16)	

^a Largest difference peak and hole.

^b $R_1 = [\sum(||F_0| - |F_c||) \sum |F_0|]; wR_2 = [\sum(w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$ ^c Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}.$ ^d $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3.$

Table 2

Bond lengths (Å) and angles (°) in $\boldsymbol{1.^a}$

Cd-N1	2.3314(12)	N1-Cd-01	89.08(4)
Cd-N10	2.3135(11)	N1-Cd-O1 ⁱ	90.92(4)
Cd-01	2.3492(10)	01-Cd-N10	87.29(4)
N1-Cd-N10	91.64(4)	O1-Cd-N10 ⁱ	92.70(4)
N1-Cd-N10 ⁱ	88.36(4)		
N1-Cd-N10 ⁴	88.36(4)		

^a Symmetry operation: i = 2 - x, 2 - y, 1 - z.

Table 3

Hydrogen	honds	in	1 a
nyulogen	Donus	ш	1.

D-H…A	D–H [Å]	H…A [Å]	D…A [Å]	(D–H…A) [°]
01–H…N14 _{dca} ⁱⁱ	0.85(1)	1.93(2)	2.771(2)	172(2)
01–H…N4 _{triazol} ⁱ	0.87(2)	1.94(2)	2.802(2)	173(2)

^a Symmetry operations: i = 1 + x, 1 + y, z, ii = x, 1.5 - y, 0.5 + z.

Table 4

Bond lengths (Å) and angles (°) in 2.^a

Zn-N3	2.041(4)	Zn-N1 ⁱ	2.048(4)
Zn-Br1	2.3553(8)	Zn-Br2	2.3618(8)
Br1-Zn-Br2	119.73(4)	N1 ⁱ -Zn-N3	105.41(17)
N1 ⁱ –Zn–Br2	110.81(11)	N1 ⁱ –Zn–Br1	107.27(12)
N3-Zn-Br2	106.60(11)	N3-Zn-Br1	106.04(12)

^a Symmetry operations: i = 3.5 - x, 1 - y, 0.5 + z, ii = 3.5 - x, 1 - y, -0.5 + z.

then slowly reacted by diffusion. The product was obtained as colorless crystals. Yield: 16.7 mg, 50% based on pytz.Anal. Calc. for C₇H₆Br₂N₄Zn (371.34 g mol⁻¹): C, 22.64; H, 1.63; N, 15.09. Found: C, 21.51; H, 1.74; N, 13.51%.

Table 5			
Hydrogen	bonds	in	2 . ^a

Table 6

D–H…A	D–H [Å]	H…A [Å]	D…A [Å]	(D–H…A) [°]
C7–H7…Br1 ⁱⁱⁱ	0.95	2.78	3.657(5)	154
C7–H7…N4 ⁱⁱⁱ	0.95	2.50	3.134(6)	124

^a Symmetry operation: iii = 0.5 + x, 0.5 - y, -z.

Bond lengths (Å) and	l angles (°) in 3 .ª		
Cd-S1	2.7625(6)	N5 ⁱⁱ -Cd-N6 ⁱⁱⁱ	176.38(7)
Cd-S2	2.6598(6)	S1-Cd-S2	83.270(19)
Cd-N1 ⁱ	2.3630(18)	S1-Cd-N5 ⁱⁱ	97.66(5)
Cd–N3	2.3430(18)	S1-Cd-N6 ⁱⁱⁱ	84.64(5)
Cd–N5 ⁱⁱ	2.2906(18)	S1–Cd–N1 ⁱ	81.03(5)
Cd-N6 ⁱⁱⁱ	2.3261(18)	S1-Cd-N3	168.45(4)
N1 ⁱ -Cd-N3	92.24(6)	S2–Cd–N5 ⁱⁱ	88.88(5)
N1 ⁱ -Cd-N6 ⁱⁱⁱ	89.97(7)	S2–Cd–N6 ⁱⁱⁱ	94.18(5)
N5 ⁱⁱ -Cd-N1 ⁱ	87.64(6)	S2–Cd–N1 ⁱ	163.31(5)
N5 ⁱⁱ -Cd-N3	91.39(6)	S2-Cd-N3	104.16(5)

^a Symmetry operations: i = 2 - x, 0.5 + y, 1.5 - z, ii = 1 - x, 2 - y, 2 - z, iii = x, 1.5 - y, -0.5 + z, iv = x, 1.5 - y, 0.5 + z, v = 2 - x, -0.5 + y, 1.5 - z.

IR (ATR): $v/cm^{-1} = 415.4(w)$, 456.9(m), 527.9(s), 624.1(s), 665.1(w), 624.1(s), 665.1(w), 711(s), 725.1(w), 829.6(s), 854.2(w), 863.3(m), 969.8(w), 987.4(w), 1025.7(m), 1038.5(w), 1076.9(w), 1093.4(s), 1126.9(w), 1227.3(m), 1239.8(m), 1273.0(s), 1291.9(w), 1358.7(m), 1385.6(m), 1436.8(m), 1484.4(m), 1535.7(s), 1578(m), 1612.3(s), 1698.9(w), 3022.9(w), 3063.5(w), 3103.7(m).



Fig. 2. Molecular structure of $[Cd(dca)_2(pytz)_2(H_2O)_2]$, **1** (50% probability ellipsoids, Cd as sphere of arbitrary radius); symmetry operation: i = 2 - x, 2 - y, 1 - z. Selected bond lengths and angles are given in Table 2.

2.5. Synthesis of catena-{ $bis(\mu$ -thiocyanato)-(μ -4-(pyrid-4-yl)-1,2,4-triazole)cadmium(II)} 3D-[Cd(μ -SCN)₂(μ -pytz)] (**3**)

Cadmium(II) nitrate tetrahydrate (20.3 mg, 0.065 mmol) and sodium thiocyanate (8.1 mg, 0.1 mmol) was dissolved in deionized water (7 ml). To this solution was added pytz (9.5 mg, 0.065 mmol) as a solid and stirred for 0.5 h at room temperature. Then, the reaction mixture was heated for 3 h at 100 °C. After cooling to room temperature the solution was filtered. The filtrate was allowed to stand at room temperature for slow solvent evaporation. Yellow crystals suitable for single crystal X-ray studies were obtained after 4 days. Yield: 14.4 mg, 59% based on pytz. *Anal.* Calc. for C₉H₆CdN₆S₂ (374.72 g mol⁻¹): C, 28.85; H, 1.61; N, 22.43. Found: C, 28.78; H, 1.66; N, 22.58%.

IR (ATR): $v/cm^{-1} = 453.1(m)$, 464.9(w), 472.3(w), 530.3(s), 633.1(s), 665.1(w), 670.9(w), 705.6(s), 728.6(w), 774.8(w), 827.4(s), 854.1(w), 878(m), 909.6(w), 945.2(w), 965.7(w), 986.9(w), 1015.9(m), 1029.2(m), 1075.7(w), 1094.2(s), 1228.3(m), 1248.2(s), 1280.6(m), 1305.9(w), 1358.7(w), 1383.7(w), 1434.9(m), 1507.6(m), 1531.6(s), 1584.5(m), 1608.5(s), 2092.6(s,SCN [8]), 2113.3(m, SCN [8]), 3023(w), 3111(m).

2.6. Crystal structure determinations

Crystals were carefully selected under a polarizing microscope. *Data collection*: Bruker Apex2 AXS CCD, Mo K α radiation (λ = 0.71073 Å), graphite monochromator, temperature 113(2) K, ω -scans, absorption correction with sADABS [24]. *Structural Analysis and Refinement*: The structure was solved by direct methods (SHEL-xs), refinement was done by full-matrix least squares on F^2 using the sHELXL program suite [25]; all non-hydrogen positions refined with anisotropic temperature factors; hydrogen atoms for aromatic CH groups were positioned geometrically (C–H = 0.95 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$; H atoms



Fig. 4. Section of the zig-zag chain structure in 1D-[ZnBr₂(μ -pytz)], **2** (50% probability ellipsoids, Zn as spheres of arbitrary radii); symmetry operations i = 3.5 - x, 1 - y, 0.5 + z, ii = 3.5 - x, 1 - y, -0.5 + z. Selected bond lengths and angles are given in Table 4.



Fig. 5. C-H…Br (red dashed lines) and C-H…N (orange dashed lines) hydrogen bonds between two neighboring chains in 1D-[ZnBr₂(μ -pytz)], **2**. Distances and angles of these H-bonds are given in Table 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the aqua ligands were found and refined. Graphics were done with DIAMOND [26]. Computations on the supramolecular π -interactions were carried out with PLATON for Windows [27]. Crystal data and details on the structure refinements are given in Table 1.

3. Results and discussion

The molecular complex $[Cd(dca)_2(pytz)_2(H_2O)_2]$, **1** was crystallized from an aqeous solution of cadmium(II) nitrate tetrahydrate, the pytz ligand and sodium dicyanamide. The structure is centrosymmetric with the cadmium atom coinciding with the inversion



Fig. 3. Hydrogen bonds in the supramolecular 3D-structure of 1. Distances and angles of the hydrogen bonds are given in Table 3.

center. The Cd-atom has a slightly distorted octahedral coordination with two dicyanamide, two pytz and two aqua ligands. In line with the inversion symmetry the identical ligands have to be in *trans* arrangement. The pytz ligand coordinates only through the pyridine nitrogen atom to the metal atom (Fig. 2). The angle between the triazole- and pyridine-ring plane is 10.09(7)°. The molecular complexes of **1** are connected to a 3D supramolecular framework by O–H…N_{dca} and O–H…N_{triazole} hydrogen bonds (Fig. 3).

A 1D coordination polymer of pytz with formula [ZnBr₂(μ -pytz)], **2** could be crystallized starting from zinc(II) bromide by a diffusion method from a solvent mixture of methanol and water. The zinc(II) atom in **2** has a slightly distorted tetrahedral coordination sphere of two bromine atoms, a pyridine-N and a triazole-N atom of two bridging pytz-ligands (Fig. 4). The pytz-ligand bridges between two zinc atoms through coordination with the N_{pyridine}-and one of the N_{triazole}-atoms, so that a zig-zag chain structure is formed.

Neighboring chains are oriented among others by C-H \cdots Br [2b,28,29] and C-H \cdots N [30,31] hydrogen bonds with the triazole–CH-groups as donors (Fig. 5).

Every chain is connected by the C-H--Br and the C-H--N bridges with four neighboring chains along the *b*-direction, so that a three-dimensional supramolecular network is formed (Fig. 7). If one follows either the C–H…Br or the C–H…N hydrogen bonds with the minimum number of intermediate covalent and coordinative bonds in the chain, then 21-helices exist around the crystallographic 2_1 axes parallel to the *a*-axis (Fig. 6). All the helices have the same sense of rotation, here left-handed or M in the investigated crystal (curved arrows in Fig. 6). Unlike normal 21 axes which cannot be assigned a sense of rotation, the 2_1 helices in the 3D supramolecular network of **2** have such a sense of rotation. The reason is that the repeat unit, its image and the connecting bond between them is fully displaced from the 2_1 axis. The more usual case is that the 2₁ axis passes through the connecting bond of the repeat unit and the image which then does not allow to discern a handedness. Thus, the supramolecular network in **2** is chiral as the 2_1 helices in the investigated crystal of **2** are only left handed or *M* helices. Furthermore, formation of the supramolecular network is responsible for the homochiral crystallization of the individual crystals, which crystallize in the non-centrosymmetric Sohncke [32] space group $P2_12_12_1$ with an absolute structure or a



Fig. 6. C-H···Br (red dashed lines) and C-H···N (orange dashed lines) hydrogen bonds between neighboring chains (in stick representation) in 1D-[ZnBr₂(μ -pytz)₂], **2** with the sense of rotation or handedness of the 2₁-helices along the *a*-axis (into the projection) indicated by curved arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Flack parameter of 0.051(16) [33]. In its entity the crystal ensemble is probably racemic [34].

Furthermore, the pyridine- and triazole-ring in the pytz-ligand in **2** are not co-planar but, as seen in **1**, the ring planes form an angle of $12.7(3)^\circ$. This way the pytz ligand assumes an axial chirality. In the solid state the rotation of the rings around the connecting C—N-bond is frozen. In the absence of an inversion center, mirror plane or rotoinversion axis in the non-centrosymmetric space group $P2_12_12_1$ all pytz ligands in the crystal have the same relative intra-ligand orientation of their ring planes and, thus, have the same axial chirality. This could also be a reason of the homochirality of each crystal. However, we judge the H-bonding network also as the primary origin for the axial homochirality of the pytz ligands.

An aqueous solution of cadmium(II) nitrate tetrahydrate, pytz and sodium thiocyanate yielded the compound 3D-[Cd(μ -SCN)₂(μ -pytz)], **3** with a 3D network structure based on bridging thiocyanato and pytz ligands. The cadmium atoms are coordinated in a distorted octahedral fashion by a N_{pyridine}- and a N_{triazole}-nitrogen atom in *cis* position, two *trans* NCS-nitrogen atoms and two *cis* SCN-sulfur atoms. Every pytz and SCN ligand bridges between two symmetry-related cadmium atoms (Fig. 7). The dihedral angle between the triazole-ring and the pyridine-ring plane in the pytz ligand in **3** with 21.15(12)° is the largest in all three structures presented here.

For a better understanding of the three-dimensional packing in **3**, it is helpful to construct the structure from subunits. The 2D- $\{Cd(\mu-SCN)_2\}$ network could be considered first. The SCN-ions connect the Cd atoms to slightly undulated 2D-layers with distorted six-membered rings in a topological (6,3)-network parallel to the bc plane. These 2D- $\{Cd(\mu-SCN)_2\}$ -layers are then stacked along the *a*-axis (Fig. 8).

The stacked 2D-{Cd(μ -SCN)₂}-nets are then joined by pytz ligands into a 3D-structure. A pytz-ligand bridges between two cadmium atoms by N_{pyridine} and N_{triazole} coordination, so that Cd-pytz-zig-zag chains result along the *b*-axis in between the 2D-{Cd(μ -SCN)₂} layers (Fig. 9). The perspective view in Fig. 10 differentiates the inorganic (SCN) and organic (pytz) part of the network by the color of the bonds.



Fig. 7. Building unit in 3D-[Cd(μ -SCN)₂(μ -pytz)], **3** with the color coding for the topological Cd–Cd contacts for the schematic network in Figs. 8 and 9. The ligand bridged Cd–Cd contacts are 5.77 Å (yellow), 6.47 Å (orange) and 10.79 Å (blue) (50% probability ellipsoids, Cd as spheres of arbitrary radii), symmetry operations i = 2 - x, 0.5 + y, 1.5 - z, ii = 1 - x, 2 - y, 2 - z, iii = x, 1.5 - y, -0.5 + z, iv = x, 1.5 - y, 0.5 + z, v = 2 - x, -0.5 + y, 1.5 - z. Selected bond lengths and angles are given in Table 6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Three parallel 2D-{Cd(µ-SCN)₂}-layers in **3**. Left: Ball-and-stick representation of all atoms; right: topological network of Cd-nodes. The different colors for the Cd–Cd connections refer to the two different SCN-bridging modes: yellow for an SCN-double bridge and orange for a single SCN-bridge (cf. Fig. 7). The layers are depicted in an ontop and side-on view for a clearer presentation of the (6,3)-net and the undulated topology. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. 3D-network structure in 3. Left: Ball-stick representation of all atoms; right: topological network of Cd-nodes. Yellow and orange indicate the SCN-double and -single bridges, respectively, blue indicates the pytz bridges (cf. Fig. 7). The layers are depicted in an on-top and side-on view. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. Perspective view of the network in 3 with the 2D-{Cd(μ -SCN)₂}-subnet shown with black bonds, the 1D-{Cd(μ -pytz)}-chains (running parallel to the *b*-axis) with gray bonds. Hydrogen atoms are not shown.

4. Conclusions

The new neutral ligand 4-(pyrid-4-yl)-1,2,4-triazole (pytz) can coordinate terminally to a metal atom by its N_{pyridine} donor atom or bridge between metal atoms by N_{pyridine}- and N_{triazole}-coordination. Case studies of its first metal-ligand complexes reveal the formation of a mononuclear complex, a one-dimensional chain and a three-dimensional network. For the 3D network, the bridging action of the anionic SCN-ligand was necessary, the $\{M(\mu-pytz)\}$ subunit is a zigzag chain. The molecular complexes and the 1D chain structure feature hydrogen bonds for the 3D supramolecular packing which involve the pytz N_{triazole} atom (not involved in the metal coordination) as an acceptor. This way adjacent chains in 1D- $[ZnBr_2(\mu-\kappa N_{pv},N_{tz}-pytz)]$ (2) are connected through C-H...Br and C-H...N_{triazole} hydrogen bonds to a supramolecular 3D network. The formation of 2₁ helices from the hydrogen and covalent bonds with the same handedness or sense of rotation in a single crystal leads to a homochiral network, which crystallized enantiomerically pure in the non-centrosymmetric Sohncke space group $P2_12_12_1$. In 3D-[Cd(μ -SCN)₂(μ -pytz)] (**3**) the pytz ligand participates in the 3D network with a $2D{Cd(\mu-SCN)_2}$ -subnet and 1D- $\{Cd(\mu-pytz)\}\$ -chains.

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Appendix A. Supplementary material

CCDC 814659, 814660 and 814661 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.072.

References

- [1] (a) C. Janiak, Dalton Trans. (2003) 2781;
 - (b) C. Janiak, J.K. Vieth, New J. Chem. 34 (2010) 2366;
 - (c) A.U. Czaja, N. Trukhan, U. Müller, Chem. Soc. Rev. 38 (2009) 1284;
 - (d) J.R. Long, O.M. Yaghi, Chem. Soc. Rev. 38 (2009) 1213. Introduction in 2009 special MOF issue;
 - (e) C. Janiak, Angew. Chem., Int. Ed. 36 (1997) 1431;
 - (f) K. Biradha, M.J. Zaworotko, New J. Chem. 34 (2010) 2353. Introduction in 2010 special MOF issue;
 - (g) S.-L. Zheng, X.-M. Chen, Aust. J. Chem. 57 (2004) 703;

- (h) M.P. Suh, Y.E. Cheon, E.Y. Lee, Coord. Chem. Rev. 252 (2008) 1007;
- (i) G. Férey, Chem. Soc. Rev. 37 (2008) 191;
- (j) K. Hindson, Eur. J. Inorg. Chem. (2010) 3683;
- (k) S. Kitagawa, S. Natarajan, Eur. J. Inorg. Chem. (2010) 3685. Introduction in 2010 MOF special issue.
- [2] (a) S.K. Henninger, H.A. Habib, C. Janiak, J. Am. Chem. Soc. 131 (2009) 2776;
 - (b) H.A. Habib, A. Hoffmann, H.A. Höppe, G. Steinfeld, C. Janiak, Inorg. Chem. 48 (5) (2009) 2166;
 - (c) H.A. Habib, J. Sanchiz, C. Janiak, Inorg. Chim. Acta 362 (2009) 2452;
- (d) H.A. Habib, A. Hoffmann, H.A. Höppe, C. Janiak, Dalton Trans. (2009) 1742; (e) H.A. Habib, J. Sanchiz, C. Janiak, Dalton Trans. (2008) 1734.
- [3] Examples of recent work: (a) M. Du, Z.-H. Zhang, X.-G. Wang, X.-J. Zhao, Inorg. Chim. Acta 362 (2009) 1358;
 - (b) M. Liu, Z. Yang, W. Sun, X. Li, J. Li, J. Ma, G. Yang, Inorg. Chim. Acta 362 (2009) 2884;

(c) T. Bataille, F. Costantino, P. Lorenzo-Luis, S. Midollini, A. Orlandini, Inorg. Chim. Acta 361 (2008) 9;

(d) F.F. Jian, J. Wang, T.L. Liang, X. Wang, Inorg. Chim. Acta 362 (2009) 4219; (e) G.-X. Liu, K. Zhu, S. Nishihara, R.-Y. Huang, X.-M. Ren, Inorg. Chim. Acta 362 (2009) 5103;

- (f) J. Hu, J. Li, J. Zhao, H. Hou, Y. Fan, Inorg. Chim. Acta 362 (2009) 5023;
- (g) Y.-C. Liu, W.-Y. Yeh, G.-H. Lee, T.-S. Kuo, Inorg. Chim. Acta 362 (2009) 3595; (h) S. Taheri, F. Marandi, H.-K. Fun, R. Kia, Z. Anorg. Allg. Chem. 635 (2009) 1352:
- (i) I. Stein, U. Ruschewitz, Z. Anorg. Allg. Chem. 635 (2009) 914;
- (j) J.L. Xiel, Z. Anorg. Allg. Chem. 635 (2009) 384;
- (k) M. Bröring, S. Prikhodovski, Z. Anorg. Allg. Chem. 634 (2008) 2451;
- (I) A. Kromm, Y. Geldmacher, W.S. Sheldrick, Z. Anorg. Allg. Chem. 634 (2008) 2191;
- (m) K. Müller-Buschbaum, Y. Mokaddem, Z. Anorg. Allg. Chem. 634 (2008) 2360;
- (n) H.A. Habib, J. Sanchiz, C. Janiak, Dalton Trans. (2008) 4877.
- [4] J.C. Bailar Jr., in: W.L. Jolly (Ed.), Preparative Inorganic Reactions, vol. 1, Interscience, New York, 1964, pp. 1–25.
- [5] C.D. Nicola, Effendy, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 359 (2006) 53.
- [6] (a) J. Boeckmann, C. Näther, Dalton Trans. 39 (2010) 11019;
- (b) S. Banerjee, B. Wu, P.-G. Lassahn, C. Janiak, A. Ghosh, Inorg. Chim. Acta 358 (2005) 535;
- (c) C. Sudbrake, H. Vahrenkamp, Inorg. Chim. Acta 318 (2001) 23;
- (d) G.-R. Yue, X.-Y. Lei, X.-J. Xu, G.-Q. Xue, Acta Crystallogr., Sect. E 61 (2005) m722;
- (e) H. Mori, S. Tanaka, T. Mori, Y. Maruyama, Bull. Chem. Soc. Jpn. 68 (1995) 1136. see also;
- (f) G. Bhosekar, J. Boeckmann, I. Jeß, C. Näther, Z. Anorg. Allg. Chem. 636 (2010) 2595.
- [7] (a) H. Zhang, X. Wang, H. Zhu, W. Xiao, K. Zhang, B.K. Teo, Inorg. Chem. 38 (1999) 886;
 - (b) G.J.S. Venter, R. Meijboom, A. Roodt, Acta Crystallogr., Sect. E 63 (2007) m3076;
 - (c) C. Di Nicola, Effendy, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 695.
- [8] B. Ding, L. Yi, Y. Wang, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, H.-B. Song, H.-G. Wang, Dalton Trans. (2006) 665.
- [9] (a) U. Englert, Coord. Chem. Rev. 254 (2010) 537;
- (b) C. Hu, I. Kalf, U. Englert, CrystEngComm 9 (2007) 603.
- [10] (a) M.R. Churchill, J. Donahue, F. Rotella, Inorg. Chem. 15 (1976) 2752;
 (b) G.A. Bowmaker, Effendy, J.V. Hanna, P.C. Healy, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1993) 1387;
 (c) S. Attar, N.W. Alcock, G.A. Bowmaker, J.S. Frye, W.H. Bearden, J.H. Nelson, Inorg. Chem. 30 (1991) 4166.
- [11] (a) P. DeBurgomaster, H. Liu, C.J. O'Connor, J. Zubieta, Inorg. Chim. Acta 363 (2010) 3254;
 - (b) P. DeBurgomaster, J. Zubieta, Inorg. Chim. Acta 363 (2010) 2912.
- [12] P.J. Hagrman, C. Bridges, J.E. Greedan, J. Zubieta, J. Chem. Soc., Dalton Trans. (1999) 2901.
- [13] (a) Effendy, C. Di Nicola, M. Fianchini, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 763;
 (b) A. Cingolani, C. Di Nicola, Effendy, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 748;
 (c) R. Meijboom, R.J. Bowen, S.J. Berners-Price, Coord. Chem. Rev. 253 (2009) 325.
- [14] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem., Int. Ed. Engl. 38 (1999) 2638.
- [15] (a) W. Ouellette, B.S. Hudson, J. Zubieta, Inorg. Chem. 46 (2007) 4887;
 (b) W. Ouellette, A.V. Prosvirin, V. Chieffo, K.R. Dunbar, B. Hudson, J. Zubieta, Inorg. Chem. 45 (2007) 9346.
- [16] (a) Y. Wang, B. Ding, P. Cheng, D. Liao, S. Yan, Inorg. Chem. 46 (2007) 2002;
 (b) Y. Wang, X. Zhao, W. Shi, P. Cheng, D. Liao, S. Yan, Cryst. Growth Des. 9 (2009) 2137;
 (c) Y. Wang, P. Cheng, Y. Song, D.-Z. Liao, S.-P. Yan, Chem. Eur. J. 13 (2007) 8131;

(d) O. Shakirova, A. Virovets, D. Naumov, Y. Shvedenkov, V. Elokhina, L. Lavrenova, Inorg. Chem. Commun. 5 (2002) 690;
 (e) Liu Y. Song, Z. Yu. J. Zhuang, X. Huang, X. You. Polyhedron 18 (1999) 1491

- (e) J. Liu, Y. Song, Z. Yu, J. Zhuang, X. Huang, X. You, Polyhedron 18 (1999) 1491. [17] (a) K. Drabent, Z. Ciunik, Chem. Commun. (2001) 1254;
 - (b) Y. Garcia, J. Moscovici, A. Michalowicz, V. Ksenofontov, G. Levchenko, G.

- Bravic, D. Chasseau, P. Gütlich, Chem. A Eur. J. 8 (2002) 4992;
- (c) Y. Garcia, P.J. van Koningsbruggen, G. Bravic, D. Chasseau, O. Kahn, Eur. J. Inorg. Chem. (2003) 356;
- (d) B. Liu, G.C. Guo, J.S. Huang, J. Solid State Chem. 179 (2006) 3136;
- (e) B. Ding, Y.Q. Huang, Y.Y. Liu, W. Shi, P. Cheng, Inorg. Chem. Commun. 10 (2007) 7;
- (f) H. Park, D.M. Moureau, J.B. Parise, Chem. Mater. 18 (2006) 525;
- (g) L. Yi, B. Ding, B. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, Inorg. Chem. 43 (2004) 33;
- (h) Y.Q. Huang, B. Ding, H.B. Song, B. Zhao, P. Ren, P. Cheng, H.G. Wang, D.Z. Liao, S.P. Yan, Chem. Commun. (2006) 4906.
- [18] M.C. Seidel, W.C. von Meyer, S.E. Greenflied, Rohm and Haas Company, US Patent 3 914 223, October 21, 1975.
- [19] (a) H. Li, C. Li, Z. Hu, Acta Crystallogr., Sect. E 63 (2007) m407;
 (b) Y. Liu, B. Ding, J. Coord. Chem. 60 (2007) 269;
 (c) Y.-H. Ma, P.-Z. Ma, H.-Q. Zhu, C. Cheng, Acta Crystallogr., Sect. E 62 (2006)
- m1479. [20] (a) B. Ding, L. Yi, P. Cheng, H.B. Song, H. Wang, J. Coord. Chem. 57 (2004) 771; (b) O. Shakirova, D. Naumov, Y. Shvedenkov, N. Alferova, G. Dolgushin, L. Lavrenova, J. Struct. Chem. 44 (2003) 642.
- [21] (a) J.A. Kitchen, N.G. White, M. Boyd, B. Moubaraki, K.S. Murray, P.D.W. Boyd, S. Brooker, Inorg. Chem. 48 (2009) 6670;
- (b) M.H. Klingele, S. Brooker, Inorg. Chim. Acta 357 (2004) 3413.
- [22] (a) A.D. Naik, J. Marchand-Brynaert, Y. Garcia, Synthesis (2008) 149;
- (b) R.K. Bartlett, I.R. Humphrey, J. Chem. Soc. C (1967) 1664.
- [23] I. Boldog, K.V. Domasevitch, Personal Communications, 2008.
 [24] G. Sheldrick, Program sadabs, Area-Detector Absorption Correction, University
- of Göttingen, Germany, 1996.
- [25] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.

- [26] K. Brandenburg, DIAMOND, Version 3.2d, Crystal and Molecular Structure Visualization, Crystal Impact – K, Brandenburg and H. Putz Gbr, Bonn, Germany, 2009.
- [27] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7; A.L. Spek, PLATON – A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2008.; L.J. Farrugia, Windows Implementation, Version 40608, University of Glasgow, Scotland, 2008.
- [28] W. Zhang, X. Tang, H. Ma, W. Sun, C. Janiak, Eur. J. Inorg. Chem. 2008 (2008) 2830
- [29] F. Neve, A. Crispini, Cryst. Growth Des. 1 (2001) 287.
- [30] C. Janiak, T. Scharmann, Polyhedron 22 (2003) 1123.
- [31] (a) G.R. Desiraju, T. Steiner, The weak hydrogen bond, in: IUCr Monograph on Crystallography, vol. 9, Oxford Science, Oxford, 1999.;
 (b) G.R. Desiraju, Acc. Chem. Res. 35 (2002) 565;
- (c) M. Mascal, Chem. Commun. (1998) 303.
- [32] H.D. Flack, Helv. Chim. Acta 86 (2003) 905.
- [33] (a) H. Flack, G. Bernardinelli, Chirality 20 (2008) 681;
 (b) H.D. Flack, G. Bernardinelli, Acta Crystallogr., Sect. A 55 (1999) 908;
 (c) H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.
- [34] (a) B. Gil-Hernández, H.A. Höppe, J.K. Vieth, J. Sanchiz, C. Janiak, Chem. Commun. 46 (2010) 8270;
 (b) B. Gil-Hernández, P. Gili, J.K. Vieth, C. Janiak, J. Sanchiz, Inorg. Chem. 49
 - (2010) 7478; (c) C. Janiak, A.-C. Chamayou, A.K.M.R. Uddin, M. Uddin, K.S. Hagen, M.
 - Enamullah, Dalton Trans. (2009) 3698; (d) M. Enamullah, A. Sharmin, M. Hasegawa, T. Hoshi, A.-C. Chamayou, C.
 - Janiak, Eur. J. Inorg. Chem. (2006) 2146.