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Crystal structure of *catena*-poly[dichlorido-(μ_2 -4-(1*H*-pyrazol-3-yl)-pyridine- κ^2 N,N′)]cadmium(II), $C_{48}H_{42}Cd_3Cl_{16}N_{18}$

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Abstract

$C_{48}H_{42}Cd_3Cl_{16}N_{18}$, monoclinic, $C2/c$ (no. 15), $a = 11.4564(7)$ Å, $b = 21.1547(15)$ Å, $c = 21.3475(13)$ Å, $\beta = 95.192(5)^\circ$, $V = 5152.5(6)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0381$, $wR_{ref}(F^2) = 0.0862$, $T = 293(2)$ K.

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Parts of the title crystal structure are shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $Cd(NO_3)_2 \cdot 2H_2O$ (0.1 mmol, 0.0272 g), 4-(1*H*-pyrazol-3-yl)-pyridine (0.1 mmol, 173.2 mg), HCl (2 mL) and distilled water (8 mL) was heated in a 25 mL stainless steel

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.42 \times 0.32 \times 0.21$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	29.3 cm^{-1}
Diffractometer, scan mode:	Bruker Multiwire, φ and ω
$2\theta_{\max}$, completeness:	51° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14107, 4780, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1412
$N(\text{param})_{\text{refined}}$:	340
Programs:	Bruker programs [1], SHELX [2]

reactor with a teflon liner at 443 K for 38 h, followed by slow cooling to room temperature. Colourless crystals of the compound were formed.

Experimental details

All H atoms were positioned geometrically ($N-H = 0.86$ Å and $C-H = 0.93$ Å) and refined using a riding model, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C, N)$.

Comment

Framework materials based on self assembly of organic ligands and coordinated metal ions are the subject of intense research activity and have found applications in the fields of gas storage [3], catalysis [4], magnetism [5] and luminescence [6]. Many efforts have been devoted to use of N- and O-donor organic ligands as co-ligands to bridge metal ions to form infinite network structures, such as one-dimensional (1D) chain structures and 2- or 3-D networks [7, 8]. However, the design of predictable frameworks with desired properties remains a considerable challenge.

The data, collected at room temperature, indicate the presence of whole-molecule disorder, with each of the three pyrazol rings contained in the asymmetric unit disordered about the approximate, molecular (non-crystallographic) two-fold rotation axes of the pyridine rings. Disorder could not be satisfactorily modelled and an ordered model is presented here.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cd1	0.0000	0.12501(4)	0.7500	0.0312(2)
Cd2	0.33342(5)	0.12499(3)	0.74998(3)	0.03094(16)
Cl1	0.5000	0.03602(13)	0.7500	0.0328(6)
Cl2	0.5000	0.21384(13)	0.7500	0.0343(7)
Cl3	0.16720(16)	0.03600(8)	0.75010(9)	0.0319(4)
Cl4	0.16681(15)	0.21399(8)	0.75000(9)	0.0321(4)
N1	−0.0185(5)	0.1245(3)	0.6409(3)	0.0322(16)
N2	−0.0270(6)	0.1772(4)	0.4038(4)	0.075(3)
N3	−0.0517(8)	0.1529(8)	0.3435(4)	0.131(6)
H3	−0.0467	0.1736	0.3091	0.157*
N4	0.2830(8)	0.1539(7)	0.3459(5)	0.123(5)
H4	0.2920	0.1753	0.3124	0.148*
N5	0.3047(6)	0.1764(5)	0.4064(4)	0.076(3)
N6	0.3163(5)	0.1258(3)	0.6418(2)	0.0308(16)
N7	0.3520(5)	0.1247(3)	0.8582(3)	0.0298(15)
N8	0.3631(6)	0.1774(4)	1.0954(4)	0.079(3)
N9	0.3843(9)	0.1527(8)	1.1553(5)	0.135(6)
H9	0.3763	0.1728	1.1896	0.162*
C1	0.4186(7)	0.0740(5)	1.0949(5)	0.061(3)
H1	0.4369	0.0340	1.0805	0.074*
C2	0.3848(6)	0.1260(4)	1.0577(3)	0.0333(19)
C3	0.4201(9)	0.0909(8)	1.1514(6)	0.088(5)
H3A	0.4423	0.0653	1.1858	0.106*
C4	0.3741(6)	0.1246(4)	0.9900(3)	0.036(2)
C5	0.3961(6)	0.0710(4)	0.9546(3)	0.0379(19)
H5	0.4189	0.0333	0.9746	0.045*
C6	0.3840(6)	0.0746(4)	0.8907(3)	0.038(2)
H6	0.3998	0.0383	0.8684	0.045*
C7	0.3300(6)	0.1778(4)	0.8910(3)	0.043(2)
H7	0.3075	0.2145	0.8692	0.051*
C8	0.3402(6)	0.1785(4)	0.9555(3)	0.037(2)
H8	0.3242	0.2155	0.9766	0.044*
C9	0.3377(6)	0.1771(4)	0.6074(3)	0.039(2)
H9A	0.3617	0.2136	0.6291	0.046*
C10	0.3274(6)	0.1803(4)	0.5429(3)	0.037(2)
H10	0.3438	0.2176	0.5224	0.044*
C11	0.2917(6)	0.1263(4)	0.5088(3)	0.0305(18)
C12	0.2710(5)	0.0711(4)	0.5439(3)	0.036(2)
H12	0.2500	0.0334	0.5233	0.043*
C13	0.2822(6)	0.0736(4)	0.6077(4)	0.037(2)
H13	0.2654	0.0372	0.6296	0.044*
C14	0.2816(6)	0.1234(5)	0.4402(3)	0.038(2)
C15	0.2441(8)	0.0909(7)	0.3467(6)	0.090(5)
H15	0.2210	0.0662	0.3118	0.108*
C16	0.2462(7)	0.0738(5)	0.4045(5)	0.055(3)
H16	0.2267	0.0340	0.4190	0.066*
C17	0.0026(6)	0.1761(4)	0.6096(4)	0.041(2)
H17	0.0248	0.2125	0.6322	0.049*
C18	−0.0065(6)	0.1789(4)	0.5453(3)	0.041(2)
H18	0.0083	0.2167	0.5251	0.049*
C19	−0.0379(5)	0.1251(4)	0.5100(3)	0.033(2)
C20	−0.0630(6)	0.0714(4)	0.5443(4)	0.046(2)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H20	−0.0877	0.0346	0.5233	0.056*
C21	−0.0515(6)	0.0727(4)	0.6077(4)	0.040(2)
H21	−0.0673	0.0360	0.6294	0.048*
C22	−0.0511(7)	0.1236(5)	0.4389(4)	0.047(2)
C23	−0.0859(10)	0.0899(7)	0.3472(5)	0.088(5)
H23	−0.1051	0.0633	0.3131	0.106*
C24	−0.0866(6)	0.0746(5)	0.4046(4)	0.050(3)
H24	−0.1085	0.0355	0.4197	0.059*

The asymmetric unit of the title structure contains one and a half Cd(II) cation three chlorine anions distributed over four sites and three 4-(1H-pyrazol-3-yl)-pyridine molecules as bridging ligands to construct a new coordination polymer. The cadmium cation is six-coordinated by four chlorido ligands and two pyridine ligands. The Cd1–N bond lengths is 2.320(5) Å. The Cd1–Cl bond lengths are 2.6859(18) Å and 2.6824(18) Å, respectively. The bond angles of Cl–Cd1–Cl are in the range of 89.08(5)° to 179.93(7)°. In addition, there are intermolecular hydrogen bonds d(N(9)–H(9)···Cl(4)#3 = 2.78 Å, d(N(4)–H(4)···Cl(4)#4 = 2.76 Å, d(N(3)–H(3)···Cl(2)#4 = 2.77 Å. Symmetry codes: #3 $-x + 1/2, -y + 1/2, -z + 2$; #4 $-x + 1/2, -y + 1/2, -z + 1$. Overall, the hydrogen bonds give rise to a 3D network.

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