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catena-Poly[[[diididocadmium(II)]-μ-3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl-κ^2N:N'] methanol solvate]

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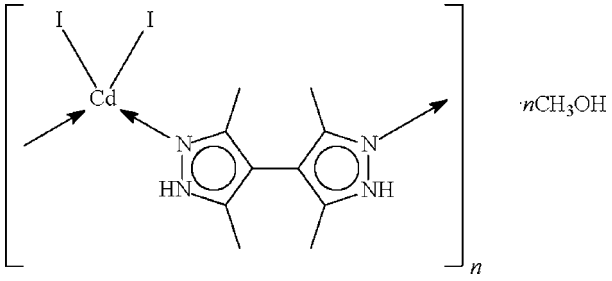
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.031; wR factor = 0.090; data-to-parameter ratio = 17.3.

The substituted bipyrazole heterocycle in the title compound, $\{[CdI_2(C_{10}H_{12}N_4)]\cdot CH_4O\}_n$, links CdI_2 units into a helical chain which runs parallel to the b axis of the monoclinic unit cell. One of the two –NH sites forms a hydrogen bond with a solvent methanol molecule. The Cd^{II} atom is in a slightly distorted tetrahedral coordination environment.

Related literature

For the synthesis of 3,3′,5,5′-tetramethyl-4,4′-bipyrazole, see: Mosby (1957). For literature on other metal derivatives of 3,3′,5,5′-tetramethyl-4,4′-bipyrazole, see: Boldog *et al.* (2001); Boldog, Rusanov *et al.* (2003); Boldog, Sieler *et al.* (2003); He *et al.* (2006); Ponomarova *et al.* (2002); Zhang *et al.* (2007).



Experimental

Crystal data

$[CdI_2(C_{10}H_{12}N_4)]\cdot CH_4O$
M_r = 588.49
Monoclinic, $P2_1/n$
a = 11.1294 (6) Å
b = 12.2109 (7) Å
c = 13.2924 (7) Å
β = 101.008 (1)°
V = 1773.2 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.71 mm^{-1}
T = 293 (2) K
0.35 × 0.30 × 0.11 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.255, T_{max} = 0.625
8299 measured reflections
3077 independent reflections
2813 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.090
S = 1.11
3077 reflections
178 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—Cd1	2.7154 (5)	Cd1—N1	2.277 (4)
I2—Cd1	2.7008 (5)	Cd1—N3^{i}	2.263(4)
I1—Cd1—I2	118.43 (2)	I2—Cd1—N1	102.0 (1)
I1—Cd1—N1	112.6 (1)	I2—Cd1—N3^{i}	114.6 (1)
I1—Cd1—N3^{i}	112.9 (1)	N1—Cd1—N3^{i}	92.7 (1)

Symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O1	0.86	1.92	2.762 (6)	168

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2414).

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supplementary materials

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catena-Poly[[[diididocadmium(II)]-μ-3,3',5,5'-tetramethyl-4,4'-bipyrazolyl-κ^2N:N'] methanol solvate]

D.-Q. Li, L. Hou and S. W. Ng

Comment

3,3',5,5'-Tetramethyl-4,4'-bipyrazolyl in its doubly-deprotonated form is capable of connecting to four metal sites (Boldog *et al.*, 2001; Boldog, Rusanov *et al.*, 2003; Boldog, Sieler *et al.*, 2003; He *et al.*, 2006; Ponomarova *et al.*, 2002). The disilver(I) derivative exemplifies such a feature; the framework is porous (Zhang *et al.*, 2007). The attempted synthesis of the cadmium derivative yielded an adduct, the neutral heterocycle binding to cadmium diiodide in a 1:1 molar stoichiometry. The compound crystallizes with a molecule of methanol. The title compound exists as helical chain that runs along the *b*-axis of the unit cell; the methanol molecules are linked to the chain by hydrogen bonds, with the –NH group serving as donor.

Experimental

3,3',5,5'-Tetramethyl-4,4'-bipyrazolyl was synthesized by using a reported procedure (Mosby, 1957). The ligand (0.02 g, 0.1 mmol), cadmium iodide (0.07 g, 0.2 mmol), potassium iodide (0.03 g, 0.2 mmol), methanol (5 ml) and water (5 ml) were mixed in a 15-ml Telfon-lined, stainless-steel Parr bomb. The bomb was heated at 423 K for 72 h and then cooled to room temperature at a rate of 5 K h-1. The resulting solution was left for two days to give colorless block-shaped crystals in about 70% yield.

Refinement

All H atoms were generated geometrically (O—H 0.82, N—H 0.86 Å and C—H 0.96 Å), and were included in the refinement in the riding model approximation, with U(H) set to 1.2 or 1.5U_{eq}(C,*N*,*O*).

Figures

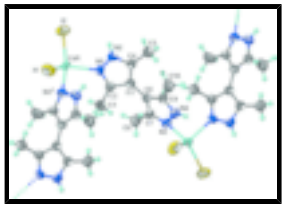

Fig. 1. Thermal ellipsoid plot of a portion of the chain structure of $[(C_{10}H_{12}N_4)I_2Cd{\cdot}CH_4O]_n$; displacement ellipsoids are drawn at the 70% probability level, and H atoms as spheres of arbitrary radius. The lattice methanol is not shown. [Symmetry code (i): 1/2 − *x*, *y* − 1/2, 1/2 − *z*].

catena-Poly[[[diididocadmium(II)]-μ-3,3',5,5'-tetramethyl-4,4'- bipyrazolyl-κ^2*N*:*N*'] methanol solvate]

Crystal data

$[CdI_2(C_{10}H_{12}N_4)]{\cdot}CH_4O$	F_{000} = 1096
M_r = 588.49	D_x = 2.204 Mg m^{-3}

Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 4773 reflections
$a = 11.1294$ (6) Å	$\theta = 2.2$–27.2°
$b = 12.2109$ (7) Å	$\mu = 4.71$ mm^{-1}
$c = 13.2924$ (7) Å	$T = 293$ (2) K
$\beta = 101.008$ (1)°	Block, colourless
$V = 1773.2$ (2) Å^3	0.35 × 0.30 × 0.11 mm
$Z = 4$	

Data collection

Bruker APEX area-detector diffractometer	3077 independent reflections
Radiation source: fine-focus sealed tube	2813 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
$T = 293(2)$ K	$\theta_{max} = 25.0^\circ$
φ and ω scans	$\theta_{min} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13 \rightarrow 13$
$T_{min} = 0.255$, $T_{max} = 0.625$	$k = -13 \rightarrow 14$
8299 measured reflections	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 2.2498P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
3077 reflections	$\Delta\rho_{max} = 0.93$ e Å^{-3}
178 parameters	$\Delta\rho_{min} = -0.90$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. High-angle reflections were omitted as their inclusion led to somewhat large peaks and deep holes near the iodine atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.70846 (4)	0.50859 (4)	0.42967 (3)	0.06227 (15)
I2	0.72925 (4)	0.63673 (4)	0.10377 (3)	0.06328 (16)
Cd1	0.59541 (3)	0.59870 (3)	0.24959 (3)	0.03701 (13)

O1	0.1126 (6)	1.2458 (4)	0.5060 (4)	0.0839 (15)
H1	0.1723	1.2865	0.5149	0.126*
N1	0.5170 (3)	0.7677 (3)	0.2704 (3)	0.0374 (9)
N2	0.5426 (4)	0.8568 (3)	0.2178 (3)	0.0406 (10)
H2	0.6002	0.8594	0.1830	0.049*
N3	0.0920 (3)	1.0264 (3)	0.3095 (3)	0.0373 (9)
N4	0.1727 (4)	1.0898 (3)	0.3735 (3)	0.0384 (9)
H4	0.1519	1.1447	0.4069	0.046*
C1	0.3664 (5)	0.7180 (4)	0.3772 (4)	0.0488 (13)
H1A	0.3066	0.6737	0.3338	0.073*
H1B	0.3277	0.7579	0.4245	0.073*
H1C	0.4293	0.6718	0.4145	0.073*
C2	0.4215 (4)	0.7964 (4)	0.3133 (4)	0.0354 (10)
C3	0.3872 (4)	0.9052 (4)	0.2869 (4)	0.0352 (10)
C4	0.4669 (4)	0.9408 (4)	0.2266 (4)	0.0368 (10)
C5	0.4749 (5)	1.0490 (4)	0.1743 (5)	0.0514 (14)
H5A	0.5112	1.1024	0.2240	0.077*
H5B	0.3943	1.0726	0.1427	0.077*
H5C	0.5244	1.0412	0.1230	0.077*
C6	0.1046 (5)	0.8661 (4)	0.1984 (5)	0.0523 (14)
H6A	0.0299	0.8405	0.2164	0.078*
H6B	0.1606	0.8060	0.2003	0.078*
H6C	0.0873	0.8965	0.1306	0.078*
C7	0.1599 (4)	0.9514 (4)	0.2722 (4)	0.0353 (10)
C8	0.2850 (4)	0.9679 (4)	0.3138 (4)	0.0334 (10)
C9	0.2887 (4)	1.0570 (4)	0.3788 (4)	0.0362 (10)
C10	0.3915 (5)	1.1113 (4)	0.4491 (5)	0.0499 (13)
H10A	0.3749	1.1882	0.4526	0.075*
H10B	0.4660	1.1009	0.4240	0.075*
H10C	0.3999	1.0798	0.5163	0.075*
C11	0.1035 (11)	1.1962 (7)	0.5970 (7)	0.110 (3)
H11A	0.1789	1.1593	0.6243	0.165*
H11B	0.0378	1.1440	0.5855	0.165*
H11C	0.0876	1.2506	0.6450	0.165*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0510 (2)	0.0729 (3)	0.0595 (3)	−0.00489 (18)	0.00184 (19)	0.0232 (2)
I2	0.0582 (3)	0.0767 (3)	0.0645 (3)	−0.00017 (19)	0.0359 (2)	0.0071 (2)
Cd1	0.02859 (19)	0.0373 (2)	0.0473 (2)	0.00236 (13)	0.01280 (16)	0.00152 (15)
O1	0.108 (4)	0.060 (3)	0.090 (4)	−0.007 (3)	0.036 (3)	−0.023 (3)
N1	0.034 (2)	0.033 (2)	0.047 (2)	0.0043 (16)	0.0137 (18)	−0.0008 (17)
N2	0.034 (2)	0.041 (2)	0.051 (3)	−0.0006 (17)	0.0182 (19)	0.0022 (19)
N3	0.0305 (19)	0.040 (2)	0.043 (2)	0.0010 (17)	0.0102 (18)	−0.0054 (18)
N4	0.036 (2)	0.038 (2)	0.041 (2)	0.0054 (17)	0.0073 (18)	−0.0076 (17)
C1	0.053 (3)	0.041 (3)	0.058 (3)	0.004 (2)	0.025 (3)	0.006 (2)
C2	0.036 (2)	0.035 (2)	0.037 (3)	0.0016 (19)	0.011 (2)	−0.0009 (19)

C3	0.029 (2)	0.036 (2)	0.041 (3)	−0.0002 (19)	0.006 (2)	−0.001 (2)
C4	0.030 (2)	0.035 (2)	0.045 (3)	0.0005 (19)	0.008 (2)	−0.001 (2)
C5	0.044 (3)	0.048 (3)	0.065 (4)	0.004 (2)	0.017 (3)	0.013 (3)
C6	0.042 (3)	0.050 (3)	0.065 (4)	0.004 (2)	0.010 (3)	−0.020 (3)
C7	0.035 (2)	0.033 (2)	0.040 (3)	0.0041 (19)	0.013 (2)	−0.001 (2)
C8	0.033 (2)	0.032 (2)	0.036 (3)	0.0047 (19)	0.0096 (19)	0.0036 (19)
C9	0.034 (2)	0.033 (2)	0.041 (3)	0.0053 (19)	0.006 (2)	0.004 (2)
C10	0.047 (3)	0.042 (3)	0.056 (4)	0.005 (2)	−0.003 (3)	−0.005 (2)
C11	0.190 (11)	0.061 (4)	0.091 (6)	0.000 (5)	0.058 (7)	−0.010 (4)

Geometric parameters (Å, °)

I1—Cd1	2.7154 (5)	C3—C4	1.375 (7)
I2—Cd1	2.7008 (5)	C3—C8	1.470 (6)
Cd1—N1	2.277 (4)	C4—C5	1.503 (7)
Cd1—N3^{i}	2.263 (4)	C5—H5A	0.9600
O1—C11	1.374 (10)	C5—H5B	0.9600
O1—H1	0.8200	C5—H5C	0.9600
N1—C2	1.345 (6)	C6—C7	1.482 (7)
N1—N2	1.353 (5)	C6—H6A	0.9600
N2—C4	1.347 (6)	C6—H6B	0.9600
N2—H2	0.8600	C6—H6C	0.9600
N3—C7	1.341 (6)	C7—C8	1.411 (6)
N3—N4	1.356 (6)	C8—C9	1.386 (7)
N3—Cd1^{ii}	2.263 (4)	C9—C10	1.488 (7)
N4—C9	1.341 (6)	C10—H10A	0.9600
N4—H4	0.8600	C10—H10B	0.9600
C1—C2	1.488 (7)	C10—H10C	0.9600
C1—H1A	0.9600	C11—H11A	0.9600
C1—H1B	0.9600	C11—H11B	0.9600
C1—H1C	0.9600	C11—H11C	0.9600
C2—C3	1.409 (6)		
I1—Cd1—I2	118.43 (2)	C4—C5—H5A	109.5
I1—Cd1—N1	112.6 (1)	C4—C5—H5B	109.5
I1—Cd1—N3^{i}	112.9 (1)	H5A—C5—H5B	109.5
I2—Cd1—N1	102.0 (1)	C4—C5—H5C	109.5
I2—Cd1—N3^{i}	114.6 (1)	H5A—C5—H5C	109.5
N1—Cd1—N3^{i}	92.7 (1)	H5B—C5—H5C	109.5
C11—O1—H1	109.5	C7—C6—H6A	109.5
C2—N1—N2	105.7 (4)	C7—C6—H6B	109.5
C2—N1—Cd1	129.7 (3)	H6A—C6—H6B	109.5
N2—N1—Cd1	122.9 (3)	C7—C6—H6C	109.5
C4—N2—N1	111.8 (4)	H6A—C6—H6C	109.5
C4—N2—H2	124.1	H6B—C6—H6C	109.5
N1—N2—H2	124.1	N3—C7—C8	110.0 (4)
C7—N3—N4	105.6 (4)	N3—C7—C6	122.2 (4)
C7—N3—Cd1^{ii}	133.2 (3)	C8—C7—C6	127.9 (4)

N4—N3—Cd1^{ii}	116.8 (3)	C9—C8—C7	105.4 (4)
C9—N4—N3	112.2 (4)	C9—C8—C3	128.9 (4)
C9—N4—H4	123.9	C7—C8—C3	125.6 (4)
N3—N4—H4	123.9	N4—C9—C8	106.7 (4)
C2—C1—H1A	109.5	N4—C9—C10	121.1 (4)
C2—C1—H1B	109.5	C8—C9—C10	132.1 (4)
H1A—C1—H1B	109.5	C9—C10—H10A	109.5
C2—C1—H1C	109.5	C9—C10—H10B	109.5
H1A—C1—H1C	109.5	H10A—C10—H10B	109.5
H1B—C1—H1C	109.5	C9—C10—H10C	109.5
N1—C2—C3	109.8 (4)	H10A—C10—H10C	109.5
N1—C2—C1	121.3 (4)	H10B—C10—H10C	109.5
C3—C2—C1	128.9 (4)	O1—C11—H11A	109.5
C4—C3—C2	105.6 (4)	O1—C11—H11B	109.5
C4—C3—C8	126.3 (4)	H11A—C11—H11B	109.5
C2—C3—C8	128.0 (4)	O1—C11—H11C	109.5
N2—C4—C3	107.1 (4)	H11A—C11—H11C	109.5
N2—C4—C5	122.4 (4)	H11B—C11—H11C	109.5
C3—C4—C5	130.5 (4)		
N3^{i}—Cd1—N1—C2	46.2 (4)	C8—C3—C4—N2	−177.3 (5)
I2—Cd1—N1—C2	162.0 (4)	C2—C3—C4—C5	179.1 (5)
I1—Cd1—N1—C2	−70.0 (4)	C8—C3—C4—C5	1.2 (9)
N3^{i}—Cd1—N1—N2	−116.9 (4)	N4—N3—C7—C8	0.2 (5)
I2—Cd1—N1—N2	−1.1 (4)	Cd1^{ii}—N3—C7—C8	155.2 (3)
I1—Cd1—N1—N2	126.9 (3)	N4—N3—C7—C6	−179.9 (5)
C2—N1—N2—C4	0.3 (5)	Cd1^{ii}—N3—C7—C6	−24.8 (7)
Cd1—N1—N2—C4	166.9 (3)	N3—C7—C8—C9	0.2 (5)
C7—N3—N4—C9	−0.6 (5)	C6—C7—C8—C9	−179.7 (5)
Cd1^{ii}—N3—N4—C9	−160.4 (3)	N3—C7—C8—C3	−176.7 (4)
N2—N1—C2—C3	0.0 (5)	C6—C7—C8—C3	3.4 (8)
Cd1—N1—C2—C3	−165.3 (3)	C4—C3—C8—C9	−71.1 (7)
N2—N1—C2—C1	179.5 (5)	C2—C3—C8—C9	111.5 (6)
Cd1—N1—C2—C1	14.1 (7)	C4—C3—C8—C7	105.1 (6)
N1—C2—C3—C4	−0.3 (6)	C2—C3—C8—C7	−72.3 (7)
C1—C2—C3—C4	−179.7 (5)	N3—N4—C9—C8	0.8 (5)
N1—C2—C3—C8	177.5 (5)	N3—N4—C9—C10	−176.5 (4)
C1—C2—C3—C8	−1.9 (8)	C7—C8—C9—N4	−0.6 (5)
N1—N2—C4—C3	−0.6 (6)	C3—C8—C9—N4	176.2 (5)
N1—N2—C4—C5	−179.3 (5)	C7—C8—C9—C10	176.2 (5)
C2—C3—C4—N2	0.5 (5)	C3—C8—C9—C10	−7.0 (9)

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O1	0.86	1.92	2.762 (6)	168

Fig. 1