Tris(2,2′-bi-1H-imidazole)cadmium(II) carbonate

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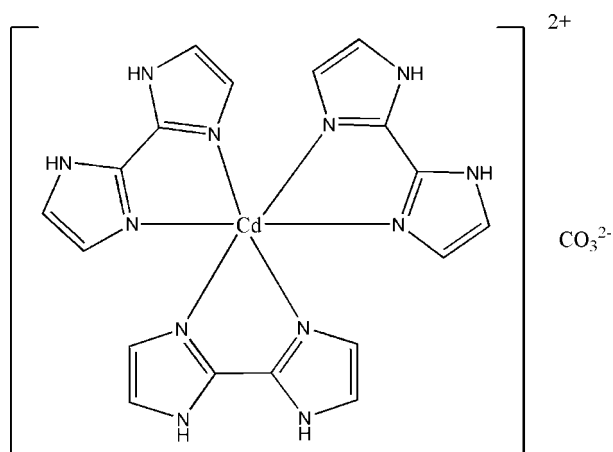
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The title compound, $[Cd(C_6H_6N_4)_3]CO_3$, is composed of discrete cations and anions, which are each located on a twofold rotation axis. The central Cd^{II} ion exhibits a distorted octahedral geometry and is coordinated by six N atoms from three 2,2′-biimidazole molecules. The crystal packing is stabilized by N—H···O hydrogen bonds.

Related literature

For related literature, see: Kamar *et al.* (2004); Xia *et al.* (2006); Xiao & Shreeve (2005).

Experimental

Crystal data

$[Cd(C_6H_6N_4)_3]CO_3$	$Z = 4$
$M_r = 574.85$	Mo $K\alpha$ radiation
Tetragonal, $I4_1$	$\mu = 1.02$ mm^{-1}
$a = 12.3477$ (8) Å	$T = 300$ (2) K
$c = 14.7379$ (10) Å	$0.30 \times 0.20 \times 0.20$ mm
$V = 2247.0$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	6885 measured reflections
	1936 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	1761 reflections with $I > 2\sigma(I)$
$T_{min} = 0.749$, $T_{max} = 0.822$	$R_{int} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.132$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
$S = 1.17$	$\Delta\rho_{min} = -0.45$ e Å^{-3}
1936 reflections	Absolute structure: Flack (1983), 654 Friedel pairs
160 parameters	Flack parameter: -0.15 (6)
1 restraint	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1^i	0.86	1.90	2.737 (9)	163
N1—H1···O2^{ii}	0.86	1.92	2.753 (8)	163
N6—H6A···O1^{iii}	0.86	1.80	2.644 (9)	169

Symmetry codes: (i) $-y + \frac{1}{2}, x, z + \frac{3}{4}$; (ii) $y - \frac{1}{2}, -x + 1, z + \frac{3}{4}$; (iii) $-x + 1, -y + 1, z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

Tris(2,2'-bi-1*H*-imidazole)cadmium(II) carbonate

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Comment

There has been increasing interest in the recent years for the coordinating ability of 2,2'-biimidazole (H_2biim) (Xia *et al.*, 2006; Kamar *et al.*, 2004). It is a bidentate chelating ligand with multiple proton-donor sites which can coordinate to a transition metal in its neutral (H_2biim), singly-deprotonated (Hbiim$^−$) and doubly-deprotonated (biim$^{2−}$) forms. Furthermore, the uncoordinated N atoms, which may be protonated or not, can participate in various patterns of hydrogen bonds with other components of the structure, leading to a broad variety of crystalline structures.

Here, we report the synthesis and crystal structure of the title compound, consisting of $[Cd(H_2biim)_3]^{2+}$ complex cations with $CO_3^{2−}$ acting as counter anions. The central Cd^{II} ion of the title compound exhibits a distorted octahedral geometry. It is coordinated to six N atoms from three 2,2'-biimidazole ligands.

The crystal packing is stabilized by N—H···O hydrogen bonds.

Experimental

2,2'-biimidazole was synthesized according to the literature procedure (Xiao & Shreeve, 2005). A mixture of $Cd(CO_3)_2$, 2,2'-biimidazole in 1:1 molar ratio with 10 ml water was sealed into a Teflon-lined pressure vessel and heated at 433 K for 72 h. After the mixture cooled to room temperature, yellow crystals were formed, coolected by filtration, washed in deionized water, and finally dried in air.

Refinement

After having located them in a difference map, all H-atoms were fixed geometrically at ideal positions. They were allowed to ride on their parent atoms with C–H=0.93 Å and N–H=0.86 Å with $U_{iso}(H)=1.2U_{eq}(C,N)$.
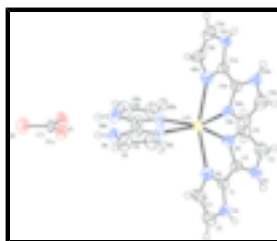
Figures

Fig. 1. View of the molecular structure of the title compound, showing 50% probability displacement ellipsoids for the non-hydrogen atoms. [Symmetry codes:(*a*) $1 − x$, $1 − y$, z;(*b*) $1 − x$, $1 − y$, z]
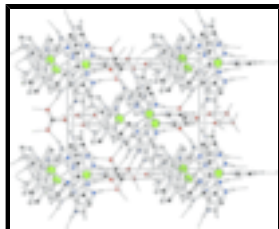
supplementary materials

Fig. 2. Packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

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Crystal data

$[Cd(C_6H_6N_4)_3]CO_3$	$Z = 4$
$M_r = 574.85$	$F_{000} = 1152$
Tetragonal, $I4_1$	$D_x = 1.699$ Mg m^{-3}
Hall symbol: I 4bw	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 12.3477$ (8) Å	Cell parameters from 3277 reflections
$b = 12.3477$ (8) Å	$\theta = 3.3–26.2°$
$c = 14.7379$ (10) Å	$\mu = 1.02$ mm^{-1}
$\alpha = 90°$	$T = 300$ (2) K
$\beta = 90°$	Block, yellow
$\gamma = 90°$	$0.30 \times 0.20 \times 0.20$ mm
$V = 2247.0$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	1936 independent reflections
Radiation source: fine-focus sealed tube	1761 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.071$
$T = 300(2)$ K	$\theta_{max} = 27.0°$
phi and ω scans	$\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -15 \rightarrow 15$
$T_{min} = 0.749$, $T_{max} = 0.822$	$k = -15 \rightarrow 15$
6885 measured reflections	$l = -18 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 13.566P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.17$	$\Delta\rho_{max} = 0.47$ e Å^{-3}

1936 reflections	$\Delta\rho_{min} = -0.45$ e Å^{-3}
160 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 654 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.15 (6)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.5000	0.5000	0.62805 (5)	0.0349 (2)
C1	0.2725 (6)	0.5529 (6)	0.7110 (6)	0.0338 (16)
C2	0.1821 (8)	0.6941 (7)	0.6645 (7)	0.048 (2)
H2	0.1273	0.7445	0.6548	0.058*
C3	0.2828 (6)	0.6956 (7)	0.6299 (8)	0.051 (2)
H3	0.3099	0.7496	0.5923	0.061*
C4	0.3048 (5)	0.4522 (6)	0.7546 (5)	0.0307 (15)
C5	0.3097 (8)	0.3090 (8)	0.8389 (8)	0.050 (2)
H5	0.2936	0.2568	0.8824	0.060*
C6	0.3972 (8)	0.3106 (7)	0.7806 (7)	0.045 (2)
H6	0.4508	0.2578	0.7779	0.054*
C7	0.5318 (8)	0.7177 (7)	0.4728 (7)	0.052 (2)
H7	0.5419	0.7752	0.5126	0.062*
C8	0.5272 (7)	0.7257 (6)	0.3827 (8)	0.047 (2)
H8	0.5331	0.7891	0.3491	0.057*
C9	0.5070 (6)	0.5591 (6)	0.4221 (6)	0.0349 (17)
N1	0.1769 (5)	0.6027 (5)	0.7172 (5)	0.0363 (15)
H1	0.1221	0.5814	0.7485	0.044*
N2	0.3394 (5)	0.6073 (5)	0.6574 (5)	0.0402 (16)
N3	0.2529 (5)	0.3988 (5)	0.8194 (5)	0.0376 (15)
H3A	0.1932	0.4182	0.8446	0.045*
N4	0.3932 (5)	0.4014 (5)	0.7273 (5)	0.0378 (15)
N5	0.5194 (6)	0.6120 (6)	0.4973 (5)	0.0393 (16)
N6	0.5124 (6)	0.6240 (6)	0.3486 (5)	0.0420 (16)
H6A	0.5076	0.6054	0.2925	0.050*
C11	0.5000	0.5000	0.1353 (17)	0.030 (3)
O1	0.4868 (5)	0.4101 (4)	0.1714 (4)	0.0392 (12)

O2	0.5000	0.5000	0.0415 (6)	0.047 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0302 (5)	0.0455 (6)	0.0290 (4)	−0.0016 (5)	0.000	0.000
C1	0.027 (4)	0.044 (4)	0.030 (4)	−0.001 (3)	−0.001 (3)	−0.001 (3)
C2	0.055 (5)	0.045 (5)	0.045 (5)	0.007 (4)	−0.008 (4)	0.013 (4)
C3	0.041 (4)	0.058 (5)	0.054 (6)	0.007 (4)	−0.004 (5)	0.028 (5)
C4	0.025 (3)	0.037 (4)	0.030 (4)	−0.004 (3)	0.002 (3)	0.001 (3)
C5	0.050 (5)	0.049 (5)	0.051 (6)	0.001 (4)	0.000 (4)	0.019 (4)
C6	0.048 (5)	0.039 (4)	0.048 (6)	0.011 (4)	−0.005 (4)	0.009 (4)
C7	0.067 (6)	0.041 (5)	0.048 (6)	−0.012 (4)	−0.006 (5)	−0.011 (4)
C8	0.065 (5)	0.026 (3)	0.051 (6)	−0.004 (3)	0.016 (5)	0.004 (4)
C9	0.034 (4)	0.036 (4)	0.035 (4)	−0.003 (3)	−0.005 (3)	0.004 (3)
N1	0.030 (3)	0.046 (4)	0.033 (4)	0.004 (3)	0.008 (3)	0.005 (3)
N2	0.043 (4)	0.038 (3)	0.040 (4)	0.001 (3)	0.008 (3)	0.011 (3)
N3	0.033 (3)	0.040 (4)	0.040 (4)	0.004 (3)	0.001 (3)	0.011 (3)
N4	0.026 (3)	0.045 (4)	0.043 (4)	0.003 (3)	−0.004 (3)	0.006 (3)
N5	0.048 (4)	0.042 (4)	0.028 (4)	−0.007 (3)	0.011 (3)	−0.005 (3)
N6	0.053 (4)	0.041 (4)	0.031 (4)	−0.004 (3)	−0.002 (3)	0.004 (3)
C11	0.036 (6)	0.038 (7)	0.016 (8)	−0.002 (6)	0.000	0.000
O1	0.052 (3)	0.033 (3)	0.033 (3)	−0.002 (2)	−0.002 (3)	0.005 (2)
O2	0.071 (6)	0.032 (4)	0.037 (5)	0.009 (4)	0.000	0.000

Geometric parameters (Å, °)

Cd1—N4	2.315 (7)	C5—H5	0.9300
Cd1—N4^i	2.315 (7)	C6—N4	1.370 (11)
Cd1—N5^i	2.383 (7)	C6—H6	0.9300
Cd1—N5	2.383 (7)	C7—C8	1.333 (14)
Cd1—N2	2.424 (7)	C7—N5	1.364 (11)
Cd1—N2^i	2.424 (7)	C7—H7	0.9300
C1—N2	1.326 (10)	C8—N6	1.364 (11)
C1—N1	1.334 (10)	C8—H8	0.9300
C1—C4	1.455 (11)	C9—N5	1.296 (11)
C2—C3	1.344 (13)	C9—N6	1.349 (11)
C2—N1	1.372 (11)	C9—C9^i	1.469 (16)
C2—H2	0.9300	N1—H1	0.8600
C3—N2	1.357 (10)	N3—H3A	0.8600
C3—H3	0.9300	N6—H6A	0.8600
C4—N4	1.323 (10)	C11—O1^i	1.242 (12)
C4—N3	1.326 (10)	C11—O1	1.242 (12)
C5—N3	1.343 (11)	C11—O2	1.38 (3)
C5—C6	1.380 (14)		
N4—Cd1—N4^i	101.6 (4)	C5—C6—H6	125.0
N4—Cd1—N5^i	98.5 (2)	C8—C7—N5	109.3 (8)

N4^i—Cd1—N5^i	150.8 (2)	C8—C7—H7	125.4
N4—Cd1—N5	150.8 (2)	N5—C7—H7	125.4
N4^i—Cd1—N5	98.5 (2)	C7—C8—N6	107.7 (8)
N5^i—Cd1—N5	72.1 (3)	C7—C8—H8	126.1
N4—Cd1—N2	73.1 (2)	N6—C8—H8	126.1
N4^i—Cd1—N2	93.8 (2)	N5—C9—N6	112.5 (7)
N5^i—Cd1—N2	112.3 (2)	N5—C9—C9^i	120.9 (5)
N5—Cd1—N2	84.8 (2)	N6—C9—C9^i	126.6 (5)
N4—Cd1—N2^i	93.8 (2)	C1—N1—C2	107.4 (7)
N4^i—Cd1—N2^i	73.1 (2)	C1—N1—H1	126.3
N5^i—Cd1—N2^i	84.8 (2)	C2—N1—H1	126.3
N5—Cd1—N2^i	112.3 (2)	C1—N2—C3	105.3 (7)
N2—Cd1—N2^i	159.5 (4)	C1—N2—Cd1	109.8 (5)
N2—C1—N1	111.0 (7)	C3—N2—Cd1	143.8 (6)
N2—C1—C4	121.7 (7)	C4—N3—C5	108.2 (7)
N1—C1—C4	127.3 (7)	C4—N3—H3A	125.9
C3—C2—N1	105.6 (8)	C5—N3—H3A	125.9
C3—C2—H2	127.2	C4—N4—C6	104.1 (7)
N1—C2—H2	127.2	C4—N4—Cd1	114.4 (5)
C2—C3—N2	110.6 (8)	C6—N4—Cd1	140.6 (6)
C2—C3—H3	124.7	C9—N5—C7	105.6 (7)
N2—C3—H3	124.7	C9—N5—Cd1	112.8 (5)
N4—C4—N3	112.4 (7)	C7—N5—Cd1	141.4 (6)
N4—C4—C1	119.9 (7)	C9—N6—C8	104.9 (8)
N3—C4—C1	127.6 (7)	C9—N6—H6A	127.5
N3—C5—C6	105.3 (8)	C8—N6—H6A	127.5
N3—C5—H5	127.3	O1^i—C11—O1	129 (2)
C6—C5—H5	127.3	O1^i—C11—O2	115.4 (11)
N4—C6—C5	109.9 (8)	O1—C11—O2	115.4 (11)
N4—C6—H6	125.0		
N1—C2—C3—N2	1.4 (12)	C1—C4—N4—Cd1	10.2 (9)
N2—C1—C4—N4	−13.9 (12)	C5—C6—N4—C4	0.3 (10)
N1—C1—C4—N4	165.8 (8)	C5—C6—N4—Cd1	167.6 (8)
N2—C1—C4—N3	169.1 (8)	N4^i—Cd1—N4—C4	86.5 (6)
N1—C1—C4—N3	−11.2 (14)	N5^i—Cd1—N4—C4	−114.8 (6)
N3—C5—C6—N4	0.6 (12)	N5—Cd1—N4—C4	−46.3 (9)
N5—C7—C8—N6	−0.4 (11)	N2—Cd1—N4—C4	−4.0 (6)
N2—C1—N1—C2	0.3 (10)	N2^i—Cd1—N4—C4	159.9 (6)
C4—C1—N1—C2	−179.5 (8)	N4^i—Cd1—N4—C6	−80.0 (10)
C3—C2—N1—C1	−1.0 (11)	N5^i—Cd1—N4—C6	78.7 (10)
N1—C1—N2—C3	0.6 (10)	N5—Cd1—N4—C6	147.2 (9)
C4—C1—N2—C3	−179.7 (8)	N2—Cd1—N4—C6	−170.4 (10)
N1—C1—N2—Cd1	−170.7 (5)	N2^i—Cd1—N4—C6	−6.5 (10)
C4—C1—N2—Cd1	9.1 (9)	N6—C9—N5—C7	1.0 (10)
C2—C3—N2—C1	−1.3 (11)	C9^i—C9—N5—C7	179.0 (9)

C2—C3—N2—Cd1	164.7 (8)	N6—C9—N5—Cd1	176.7 (5)
N4—Cd1—N2—C1	−2.7 (5)	C9^i—C9—N5—Cd1	−5.3 (11)
N4^i—Cd1—N2—C1	−103.7 (6)	C8—C7—N5—C9	−0.4 (11)
N5^i—Cd1—N2—C1	89.8 (6)	C8—C7—N5—Cd1	−174.0 (7)
N5—Cd1—N2—C1	158.0 (6)	N4—Cd1—N5—C9	−73.2 (7)
N2^i—Cd1—N2—C1	−54.7 (5)	N4^i—Cd1—N5—C9	153.4 (5)
N4—Cd1—N2—C3	−168.3 (11)	N5^i—Cd1—N5—C9	1.9 (4)
N4^i—Cd1—N2—C3	90.6 (11)	N2—Cd1—N5—C9	−113.6 (6)
N5^i—Cd1—N2—C3	−75.9 (11)	N2^i—Cd1—N5—C9	78.3 (6)
N5—Cd1—N2—C3	−7.6 (11)	N4—Cd1—N5—C7	100.1 (10)
N2^i—Cd1—N2—C3	139.7 (11)	N4^i—Cd1—N5—C7	−33.2 (10)
N4—C4—N3—C5	1.6 (10)	N5^i—Cd1—N5—C7	175.2 (11)
C1—C4—N3—C5	178.8 (8)	N2—Cd1—N5—C7	59.8 (10)
C6—C5—N3—C4	−1.3 (11)	N2^i—Cd1—N5—C7	−108.4 (10)
N3—C4—N4—C6	−1.2 (9)	N5—C9—N6—C8	−1.3 (9)
C1—C4—N4—C6	−178.6 (7)	C9^i—C9—N6—C8	−179.1 (9)
N3—C4—N4—Cd1	−172.4 (5)	C7—C8—N6—C9	1.0 (10)

Symmetry codes: (i) −x+1, −y+1, z.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3A⋯O1^{ii}	0.86	1.90	2.737 (9)	163
N1—H1⋯O2^{iii}	0.86	1.92	2.753 (8)	163
N6—H6A⋯O1^i	0.86	1.80	2.644 (9)	169

Symmetry codes: (ii) −y+1/2, x, z+3/4; (iii) y−1/2, −x+1, z+3/4; (i) −x+1, −y+1, z.

Fig. 1

Fig. 2