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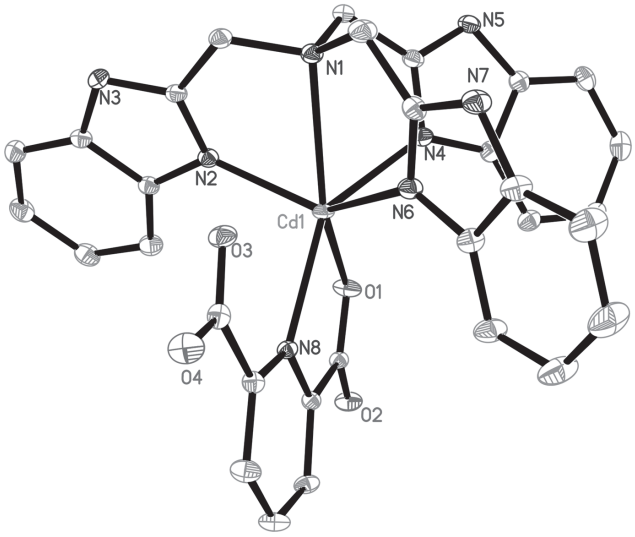
Crystal structure of [tris(2-benzimidazolylmethyl)amine-κ^4*N*,*N′*,*N″*,*N‴*]-[(pyridine-2,6-dicarboxylato-κ^2*O*,*N*)]cadmium(II)–methanol (1:3) $C_{34}H_{36}CdN_8O_7$



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Abstract

$C_{34}H_{36}CdN_8O_7$, monoclinic, $P2_1/n$ (no. 14), $a = 14.863(3)$ Å, $b = 13.184(3)$ Å, $c = 17.202(3)$ Å, $\beta = 91.33(3)°$, $V = 3369.8(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0311$, $wR_{ref}(F^2) = 0.0825$, $T = 113(2)$ K.

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The title complex is shown in the figure. Hydrogen atoms and the solvent molecules are omitted in the figure for clarity. 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

Tris(2-benzimidazolylmethyl)amine (*ntb*) was prepared according to the literature method [1]. To a stirred methanol solution (20 mL) containing cadmium perchlorate hexahydrate (0.066 g, 0.2 mmol) and ntb (0.08 g, 0.2 mmol), a methanol solution (10 mL) of 2,6-pyridinedicarboxylic acid (H_2dipic, 0.033 g, 0.2 mmol) and triethylamine (0.022 g, 0.2 mmol) was added dropwise. After stirring for 3 h, the filtrate of the resulting solution was allowed to stand at room temperature for several weeks to give colorless crystals of the title compound, in a yield of 55%.

Table 1: Crystal collection and handling.

Crystal:	Block, colorless
Size:	0.20 × 0.18 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å)
μ:	0.71 mm^{-1}
Diffractometer, scan mode:	Rigaku Saturn, ω-scans
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	26169, 5942, 0.0418
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5322
$N(param)_{refined}$:	470
Programs:	CrystalClear [1], OLEX2 [2], SHELX [3]

Experimental details

The crystal structure was refined using the SHELX-18/3 package [3, 4]. Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C).

Discussion

Imidazole is a typical heterocyclic ligand as a component of biologically important molecules [5]. Moreover, the derivates of imidazole have long been used in coordination chemistry [6]. For example, tris(2-benzimidazylmethyl)amine (*ntb*) was used in the coordination of transition metals to mimic the active sites of superoxide dismutase by Nie's group [7]. The tetradentate tripodal ligand ntb contains three aromatic N-donors on its arms, which can each rotate freely around an N(apical)-C bond. Thus, multicomponent complexes or coordination polymeric networks can be formed from this ligand with metal ions of low coordination number [8]. Compared to other metal complexes, cadmium complexes of ntb are rarely

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.45533(2)	0.66299(2)	0.19391(2)	0.01846(9)
O1	0.42429(12)	0.83302(12)	0.22599(12)	0.0266(4)
O2	0.48056(12)	0.98530(12)	0.25336(11)	0.0258(4)
O3	0.59558(12)	0.57476(13)	0.12598(11)	0.0266(4)
O4	0.74589(13)	0.57663(14)	0.13254(13)	0.0348(5)
O5	0.51552(18)	0.16590(14)	0.32849(14)	0.0435(6)
H5B	0.509252	0.117700	0.296892	0.065
O6	0.81779(17)	0.45483(17)	0.01979(13)	0.0458(6)
H6A	0.796394	0.493015	0.053805	0.069
O7	0.2559(2)	0.3689(3)	0.3279(2)	0.0882(11)
H7B	0.203286	0.349567	0.316733	0.132
N1	0.37136(14)	0.49860(15)	0.15055(12)	0.0208(5)
N2	0.40522(14)	0.67795(14)	0.06861(12)	0.0191(5)
N3	0.39026(15)	0.60436(17)	−0.04767(13)	0.0229(5)
H3	0.389(2)	0.547(3)	−0.077(2)	0.055(11)
N4	0.32154(15)	0.64542(15)	0.26295(13)	0.0210(5)
N5	0.18698(16)	0.57512(17)	0.27714(13)	0.0230(5)
H5	0.143(2)	0.545(2)	0.2665(17)	0.024(8)
N6	0.50089(14)	0.53459(15)	0.27323(13)	0.0225(5)
N7	0.50273(16)	0.37580(17)	0.31344(14)	0.0269(5)
H7	0.491(2)	0.317(2)	0.3146(19)	0.031(9)
N8	0.58794(14)	0.75823(14)	0.19662(11)	0.0168(4)
C1	0.39067(18)	0.48901(18)	0.06741(15)	0.0222(6)
H1A	0.342963	0.448177	0.041262	0.027
H1B	0.448728	0.453418	0.061278	0.027
C2	0.39515(16)	0.59158(18)	0.03011(15)	0.0199(5)
C3	0.40705(17)	0.75294(18)	0.01157(15)	0.0200(5)
C4	0.41311(19)	0.8586(2)	0.01843(17)	0.0271(6)
H4	0.419353	0.890475	0.067771	0.033
C5	0.40963(19)	0.9145(2)	−0.04952(18)	0.0304(6)
H5A	0.412888	0.986331	−0.046602	0.037
C6	0.4014(2)	0.8679(2)	−0.12273(18)	0.0313(6)
H6	0.399408	0.909062	−0.168079	0.038
C7	0.39622(18)	0.7639(2)	−0.13043(16)	0.0278(6)
H7A	0.391640	0.732307	−0.179979	0.033
C8	0.39803(17)	0.70762(19)	−0.06180(15)	0.0217(5)
C9	0.27525(17)	0.5200(2)	0.16188(15)	0.0226(6)
H9A	0.241771	0.455288	0.165121	0.027
H9B	0.250850	0.558390	0.116637	0.027
C10	0.26185(17)	0.58023(18)	0.23468(15)	0.0209(5)
C11	0.28341(18)	0.68408(19)	0.32997(15)	0.0211(5)
C12	0.31704(19)	0.75318(19)	0.38503(16)	0.0250(6)
H12	0.374197	0.784252	0.379430	0.030
C13	0.2640(2)	0.7746(2)	0.44797(16)	0.0290(6)
H13	0.285503	0.821146	0.486254	0.035
C14	0.1799(2)	0.7300(2)	0.45682(16)	0.0307(7)
H14	0.145698	0.746751	0.500984	0.037
C15	0.1451(2)	0.66212(19)	0.40311(17)	0.0266(6)
H15	0.087758	0.631681	0.409125	0.032
C16	0.19834(18)	0.64034(19)	0.33945(15)	0.0218(5)
C17	0.4044(2)	0.41187(19)	0.19722(17)	0.0289(6)
H17A	0.434023	0.362803	0.162551	0.035
H17B	0.352492	0.377273	0.220624	0.035
C18	0.46970(18)	0.44257(18)	0.26067(15)	0.0220(6)
C19	0.55817(18)	0.5276(2)	0.33790(16)	0.0242(6)
C20	0.6115(2)	0.6014(2)	0.37436(18)	0.0325(7)
H20	0.612150	0.669393	0.355992	0.039
C21	0.6633(2)	0.5722(2)	0.4380(2)	0.0439(8)
H21	0.700546	0.620767	0.463916	0.053
C22	0.6619(2)	0.4721(3)	0.4649(2)	0.0497(9)
H22	0.697595	0.454431	0.509353	0.060
C23	0.6101(2)	0.3984(2)	0.4287(2)	0.0427(8)
H23	0.609767	0.330467	0.447061	0.051
C24	0.55882(19)	0.4278(2)	0.36453(17)	0.0274(6)
C25	0.48851(16)	0.89342(17)	0.23674(14)	0.0177(5)
C26	0.58303(17)	0.85247(17)	0.22608(14)	0.0172(5)
C27	0.65886(17)	0.90985(19)	0.24322(15)	0.0222(6)
H27	0.653895	0.975977	0.264632	0.027
C28	0.74233(19)	0.8681(2)	0.22826(18)	0.0292(6)
H28	0.795747	0.905176	0.239970	0.035
C29	0.74734(18)	0.7722(2)	0.19622(17)	0.0272(6)
H29	0.804070	0.743264	0.184873	0.033
C30	0.66892(17)	0.71907(18)	0.18091(14)	0.0189(5)
C31	0.67039(18)	0.61376(18)	0.14363(15)	0.0215(6)
C32	0.5106(3)	0.1287(3)	0.4049(2)	0.0645(11)
H32A	0.566413	0.092662	0.418728	0.097
H32B	0.459545	0.081974	0.408404	0.097
H32C	0.502434	0.185396	0.440883	0.097
C33	0.8446(3)	0.3624(3)	0.0542(2)	0.0490(9)
H33A	0.902175	0.371695	0.082254	0.073
H33B	0.851382	0.310845	0.013742	0.073
H33C	0.798868	0.340247	0.090719	0.073
C34	0.2974(3)	0.2989(4)	0.3697(3)	0.0702(13)
H34A	0.341050	0.331236	0.405364	0.105
H34B	0.328805	0.252312	0.335231	0.105
H34C	0.253237	0.261142	0.399652	0.105

reported [9, 10]. On the other hand cadmium(II) complexes of ntb using 2,6-pyridinedicarboxylate as coligand have never been reported. In this article, we report the structures of a new 2,6-pyridinedicarboxylate-containing cadmium(II) complex of ntb, which exhibits hydrogen-bonding forming a chain structure.

The title compound consists of one [Cd(ntb)(dipic)] complex, and three methanol molecules. The Cd(II) ion is octahedrally coordinated by four N atoms of ntb, one carboxylate oxygen and pyridine nitrogen of the 2,6-pyridinedicarboxylate ligand. The equatorial plane is defined by three benzimidazoles N(1), N(2), N(6) of ntb and one carboxylate oxygen atom O(1). Equatorial bond angles are ranging from 69.7° to 139.8°. The bond distance of Cd(1)—N(1) = 2.602(2) Å, lies *trans*-to O(1) atom, is significantly longer than Cd(1)—N(2) = 2.272(2) Å, Cd(1)—N(6) = 2.268(2) Å, and Cd(1)—O(1) = 2.3571(19) Å. The axial positions are occupied by N(4) and N(8) with N(4)—Cd(1)—N(8) angle of 139.91°. The bond length of Cd(1)—N(4) is 2.352(3) Å and the distance of Cd(1)—N(8) is 2.336(2) Å.

The bond distance Cd(1)—N(1) and the angle N(4)—Cd(1)—N(8) reflect the distortions of the coordination octahedron. Other significant distortions are observed in the angles, N(1)—Cd(1)—O(1) = 139.82°, N(2)—Cd(1)—N(6) = 136.32°. In addition, intermolecular H-bond of type N—H···O [N(3)H(3)···O(3) = 2.72 Å N(3)H(3)···O(3) 168°] between the NH group of ntb and the uncoordinated carboxylate oxygen atom of pyridinedicarboxylate anion bridges adjacent molecules to form a dimeric unit. These dimers are further connected *via* two hydrogen bonds: one between the NH group of ntb and methanol oxygen N—H···O [N(7)—H(7 A)···O(5) = 2.775 Å N(7)—H(7 A)···O(5) 152.94°] and the other between OH of methanol and the uncoordinated carboxylate oxygen of the picolinato ligand O—H···O [O(5)—H(5 A)···O(2) = 2.752 Å O(5)—H(5 A)···O(2) 161.23°] to form two antiparallel chains. Geometric parameters of the ligands and coordination modes are in perfect accord with the literature [11].

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