Crystal structure of tetraammonium tris(pyridine-2,6-dicarboxylato-*O,N,O'*)cadmate(II) hexahydrate, $(\text{NH}_4)_4[\text{Cd}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot 6\text{H}_2\text{O}$

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Abstract

$\text{C}_{21}\text{H}_{37}\text{CdN}_7\text{O}_{18}$, monoclinic, $C12/c1$ (no. 15), $a = 16.791(2)$ Å, $b = 10.191(2)$ Å, $c = 20.091(3)$ Å, $\beta = 113.394(3)^\circ$, $V = 3155.3$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.034$, $wR_{\text{ref}}(F^2) = 0.090$, $T = 301$ K.

Source of material

$\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) was dissolved in 20 ml distilled water. To this solution was added dropwise at 333 K, 30 ml of an aqueous mixture of pyridine-2,6-dicarboxylic acid (3 mmol) and ammonia (3 mmol) solutions. The mixture was stirred for 4 h and parts of the solvent were evaporated in a rotary vacuum evaporator. The resulting solution was filtered and stayed in air for about 2 weeks. Large colorless block-like crystals of the title compound were obtained.

Elemental analysis: found – C, 31.95 %; H, 4.66 %; N, 12.40 %; calc. for $\text{C}_{21}\text{H}_{37}\text{CdN}_7\text{O}_{18}$ – C, 32.01 %; H, 4.73 %; N, 12.44 %.

Experimental details

H atoms bonded to C atoms were positioned geometrically and treated as riding with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{parent})$. The water H atoms and ammonium H atoms were

located from Fourier difference maps and refined using distance restraints except for the disordered H atoms belonging to the O9 atoms. Those atoms were also fixed at idealized positions. The occupancy ratio for the disordered O9 atoms was determined from the heights of the Fourier difference peaks.

Discussion

Transition metal complexes with 2,6-pyridinedicarboxylic acid (H_2DPC) have attracted much attention due to their important role in coordination chemistry, catalytic reactions and biological system [1–3].

The asymmetric unit of the title structure consists of one $[\text{Cd}(\text{C}_7\text{H}_3\text{NO}_4)_3]^{4-}$ complex anion, four ammonium cations and six hydrate water molecules. The Cd(II) atom is nine-coordinated by three pyridine-2,6-dicarboxylate (DPC^{2-}) ligands [denoted by $L1$, $L2$ and $L3$] via six O atoms and three N atoms. The coordination environment around Cd(II) corresponds to a distorted tricapped trigonal prism. A crystallographic twofold rotation axis passes through the Cd atom and three atoms of ligand $L1$, viz. N1, C4 and its attached H atom H4. In the ninefold coordination, there are three unique Cd—O distances and two unique Cd—N distances $d(\text{Cd1—O1}) = 2.551(3)$ Å, $d(\text{Cd1—O3}) = 2.427(3)$ Å, $d(\text{Cd1—O5}) = 2.567(3)$ Å, $d(\text{Cd1—N1}) = 2.412(5)$ Å and $d(\text{Cd1—N2}) = 2.358(3)$ Å. The Cd—O (average 2.561(4) Å) and Cd—N (average 2.376(3) Å) bond lengths in the title complex are in the normal ranges comparing to similar bond lengths. The three aromatic rings are located far away from each other which decreases steric effects. The cations are pendent and act as a counterions to maintain charge balance. All NH groups of the cation and all OH groups of the hydrate water molecules, together with all O atoms of the pyridine-2,6-dicarboxylate ligands, contribute to the formation of N—H...O and O—H...O bonds, which connect the cations, anions and crystal water molecules into a three-dimensional supramolecular array.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.29 × 0.37 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	7.82 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\text{max}}$:	46.66°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6867, 2278
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1912
$N(\text{param})_{\text{refined}}$:	267
Programs:	SHELXTL [4], SHELXTL-plus [5]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(3)	8f		−0.0214	0.6011	0.8413	0.052
H(4)	4e		0	0.7188	¾	0.052
H(7)	8f		0.3158	−0.0612	0.8409	0.061
H(8)	8f		0.2974	−0.2152	0.7493	0.074
H(9)	8f		0.1631	−0.2316	0.6531	0.061
H(11)	8f		0.344(2)	0.969(4)	−0.025(2)	0.080
H(12)	8f		0.366(3)	0.868(4)	0.029(2)	0.080
H(13)	8f		0.425(2)	0.971(4)	0.036(2)	0.080
H(14)	8f		0.410(3)	0.875(4)	−0.018(2)	0.080
H(15)	8f		0.105(3)	0.885(4)	0.452(1)	0.080
H(16)	8f		0.093(2)	0.865(4)	0.516(2)	0.080

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(17)	8f		0.177(2)	0.879(4)	0.519(2)	0.080
H(18)	8f		0.130(3)	0.765(2)	0.489(2)	0.080
H(19)	8f		0.186(4)	0.347(3)	0.887(2)	0.080
H(20)	8f		0.199(4)	0.477(3)	0.886(2)	0.080
H(21)	8f		0.916(2)	0.896(6)	0.430(3)	0.080
H(22)	8f		0.831(2)	0.872(6)	0.396(2)	0.080
H(23)	8f	0.85	0.8712	0.7485	0.6242	0.080
H(24)	8f	0.85	0.8214	0.8295	0.5701	0.080
H(25)	8f	0.15	0.8242	0.6047	0.6561	0.080
H(26)	8f	0.15	0.7554	0.6846	0.6282	0.080

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cd(1)	4e		0	0.11795(4)	¾	0.0284(3)	0.0327(3)	0.0338(3)	0	0.0128(2)	0
N(1)	4e		0	0.3546(4)	¾	0.027(2)	0.031(3)	0.027(3)	0	0.008(2)	0
N(2)	8f		0.1134(2)	−0.0119(3)	0.7444(2)	0.035(2)	0.031(2)	0.030(2)	0.003(2)	0.018(2)	0.005(2)
N(3)	8f		0.3852(3)	0.9202(4)	0.0043(2)	0.053(2)	0.049(3)	0.042(2)	0.005(2)	0.020(2)	0.000(2)
N(4)	8f		0.1255(3)	0.8468(5)	0.4934(2)	0.064(3)	0.073(3)	0.045(2)	−0.006(2)	0.023(2)	−0.004(2)
O(1)	8f		−0.0392(2)	0.2205(3)	0.8489(2)	0.060(2)	0.033(2)	0.040(2)	−0.002(2)	0.028(2)	−0.001(1)
O(2)	8f		−0.0138(2)	0.3973(3)	0.9192(2)	0.059(2)	0.051(2)	0.035(2)	−0.008(2)	0.027(2)	−0.009(2)
O(3)	8f		0.1386(2)	0.1808(3)	0.8437(2)	0.031(2)	0.040(2)	0.044(2)	0.003(1)	0.012(1)	−0.006(2)
O(4)	8f		0.2698(2)	0.1042(3)	0.9121(2)	0.043(2)	0.053(2)	0.040(2)	0.008(2)	0.004(2)	−0.002(2)
O(5)	8f		−0.0472(2)	−0.0522(3)	0.6374(2)	0.042(2)	0.061(2)	0.049(2)	0.008(2)	0.018(2)	−0.013(2)
O(6)	8f		0.0112(2)	−0.1661(4)	0.5731(2)	0.059(2)	0.082(3)	0.046(2)	0.002(2)	0.021(2)	−0.024(2)
O(7)	8f		0.1996(3)	0.4134(5)	0.9164(2)	0.072(3)	0.085(3)	0.078(3)	0.008(2)	0.020(2)	−0.034(2)
O(8)	8f		0.8731(4)	0.8680(6)	0.4371(3)	0.128(4)	0.103(4)	0.075(3)	0.041(4)	0.052(3)	0.015(3)
C(1)	8f		−0.0227(2)	0.3389(4)	0.8616(2)	0.027(2)	0.039(3)	0.032(2)	0.003(2)	0.013(2)	−0.002(2)
C(2)	8f		−0.0112(2)	0.4211(4)	0.8030(2)	0.029(2)	0.037(3)	0.029(2)	0.003(2)	0.009(2)	−0.002(2)
C(3)	8f		−0.0124(3)	0.5572(4)	0.8042(2)	0.054(3)	0.037(3)	0.036(3)	0.003(2)	0.014(2)	−0.008(2)
C(4)	4e		0	0.6276(6)	¾	0.069(4)	0.023(3)	0.033(3)	0	0.015(3)	0
C(5)	8f		0.2001(3)	0.1031(4)	0.8564(2)	0.030(2)	0.039(3)	0.030(2)	−0.004(2)	0.013(2)	0.004(2)
C(6)	8f		0.1914(3)	0.0006(4)	0.7991(2)	0.037(2)	0.037(2)	0.030(2)	0.004(2)	0.019(2)	0.004(2)
C(7)	8f		0.2621(3)	−0.0722(5)	0.8027(3)	0.041(3)	0.070(3)	0.041(3)	0.013(2)	0.017(2)	0.001(3)
C(8)	8f		0.2513(3)	−0.1628(6)	0.7476(2)	0.047(3)	0.086(4)	0.050(3)	0.030(3)	0.018(3)	−0.008(3)
C(9)	8f		0.1714(3)	−0.1733(5)	0.6909(2)	0.059(3)	0.060(3)	0.038(3)	0.015(3)	0.024(2)	−0.005(2)
C(10)	8f		0.1037(3)	−0.0966(4)	0.6907(2)	0.041(2)	0.035(3)	0.033(2)	0.003(2)	0.022(2)	0.003(2)
C(11)	8f		0.0147(3)	−0.1039(4)	0.6285(2)	0.047(3)	0.035(3)	0.034(2)	−0.001(2)	0.018(2)	0.001(2)
O(9)	8f	0.85	0.8150(3)	0.7394(7)	0.5852(3)	0.061(4)	0.234(9)	0.156(6)	0.010(5)	0.020(4)	−0.140(7)
O(9')	8f	0.15	0.773(1)	0.615(2)	0.650(1)	0.05(1)	0.04(1)	0.07(2)	0.01(1)	0.01(1)	−0.03(1)

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