Crystal structure of *trans-trans-trans*-diaquabis(nicotinamide)-dinitratocadium(II) — nicotinamide (1:2), $Cd(H_2O)_2(C_6H_6N_2O)_2(NO_3)_2 \cdot 2C_6H_6N_2O$

Zhaoxun Lian*, Ning Zhao, Fengxia Yang and Ping Liu

School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, P. R. China

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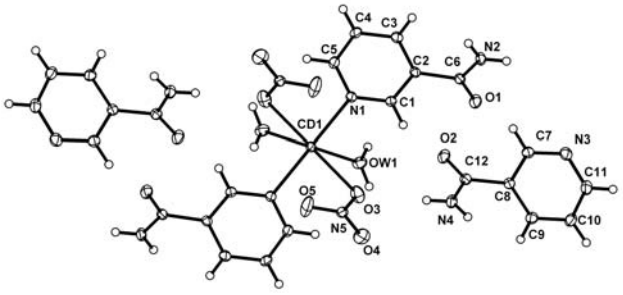

Abstract

$C_{24}H_{28}CdN_{10}O_{12}$, monoclinic, $P12_1/n1$ (no. 14), a = 7.3803(9) Å, b = 22.684(3) Å, c = 9.444(1) Å, β = 108.642(2)°, V = 1498.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.090, T = 298 K.

Source of material

Nicotinamide (0.048 g, 0.4 mmol) was added with constant stirring to 20 mL of an aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.062 g, 0.2 mmol). Colourless crystals of the title complex were collected after 10 days (74 % yield based on Cd). Elemental analysis — found: C, 37.63 %; H, 3.61 %; N, 18.43 %; calculated for $C_{24}H_{28}CdN_{10}O_{12}$: C, 37.88 %; H, 3.71%; N, 18.41 %.

Experimental details

The hydrogen atoms bound to carbon and nitrogen atoms were geometrically placed with d(C—H) = 0.93 Å, d(N—H) = 0.86 Å and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C,N). The O-bound H atoms were located in difference maps and refined as riding in their as-found relative positions with d(O—H) = 0.85 - 0.86 Å and U_{iso}(H) = 1.2 U_{eq}(O).

Discussion

There has been growing interest in recent years in the design and synthesis of hydrogen-bonded networks [1-4]. To target such networks by design, a reasonable choice of ligands is important. Nicotinamides (NA) with the inherent coordination and hydrogen-bonding donor/acceptor functionalities are good ligands for the contruction of supramolecular architectures [1-3,5,6].

The asymmetric unit of the title crystal structure contains an octahedral Cd(II) complex and two nicotinamide molecules, of which one nicotinamide molecule does not coordinate the Cd centre. The coordination of the cadmium ion is similar to that observed in *trans*-tetraaquabis(nicotinamide-*N*)cadmium(II) biphenyl-4,4′-disulfonate [7]. The Cd centre is located on crystallographic inversion center and is hexa-coordinated with two symmetry-related nicotinamide ligands at the apical positions through pyridine nitrogen atoms with d(Cd—N) = 2.282(2) Å, two aqua ligands with d(Cd—O) = 2.329(2) Å at equatorial positions, and two monodentate NO_3^- in the equatorial positions with d(Cd—O) = 2.449(2) Å to complete octahedral environment. The amide substituents are twisted away from the pyridine ring plane with the torsion angle of 25.08(9)° and 25.28(8)°, respectively. The most interesting structural features are the selfcomplementary hydrogen-bonding interactions and the host-guest interactions between the host channels and the guest nicotinamide molecules. The hexa-coordinated Cd complexes are linked via two symmetry related hydrogen bonds formed by the coordinating water molecules and nitrate oxygen atoms (d(OW1—H1A···O5) = 2.992(3) Å to result in an infinite chain of $\{Cd(NO_3)_2(H_2O)_2(NA)_2\}_n$. Adjacent chains are further linked by hydrogen bonds N–H···O (amide-amide) (d(N2–H2B···O1^{i}) = 2.857(3) Å and d(N2–H2A···O4^{ii}) = 2.995(3) Å; symmetry codes i: x–½,–y+½,z–½ ; ii: x+½,–y+½,z–½) formed by the part of N–H proton on the nicotinamide ligands and nitrate oxygen atoms to generate 2D layers. These layers are further connected through hydrogen bonds between the remaining of N–H proton on the nicotinamide ligands and nitrate oxygen atoms to generate a 3D channel structure. Uncoordinated nicotinamide ligands are located in the channels in head-to-tail fashion to form infinite chains through amide-amide hydrogen bonds (d(N4–H4B···O2^{iii}) = 2.943(3) Å; symmetry code iii: x+½,–y+½,z+½), and make contact with the host channels through hydrogen-bonding interactions between the coordinating water molecules and nitrate oxygen atoms, as well as the coordinated water molecules and pyridine nitrogen atoms (d(OW1–H1A···O5) = 2.992(3) Å, d(OW1–H1B···N3) = 2.878(3) Å).

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.20 × 0.40 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.09 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8663, 3244
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2729
$N(param)_{refined}$:	216
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

* Correspondence author (e-mail: zhxalian@yahoo.com.cn)

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	0.8951	0.0438	0.6288	0.07
H(1B)	4*e*	0.8137	0.0545	0.7415	0.07
H(2A)	4*e*	0.5238	0.3038	0.1844	0.048
H(2B)	4*e*	0.4010	0.2588	0.0834	0.048
H(4A)	4*e*	0.4668	0.1833	0.6650	0.048
H(4B)	4*e*	0.5546	0.2371	0.7497	0.048
H(1)	4*e*	0.5702	0.1362	0.4372	0.038
H(3)	4*e*	0.4040	0.1709	–0.0008	0.046
H(4)	4*e*	0.3428	0.0706	–0.0440	0.054
H(5)	4*e*	0.3904	0.0075	0.1524	0.048
H(7)	4*e*	0.3242	0.3357	0.3550	0.044
H(9)	4*e*	0.4885	0.3267	0.8007	0.044
H(10)	4*e*	0.4899	0.4290	0.8060	0.051
H(11)	4*e*	0.4087	0.4805	0.5861	0.053

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	2*c*	½	0	½	0.0429(2)	0.0254(1)	0.0250(2)	–0.00226(8)	0.0081(1)	0.00271(8)
O(1)	4*e*	0.6868(3)	0.23625(8)	0.3863(2)	0.050(1)	0.043(1)	0.0329(9)	–0.0103(8)	–0.0033(7)	–0.0003(8)
O(2)	4*e*	0.2694(2)	0.23347(7)	0.4401(2)	0.0477(9)	0.0410(9)	0.0347(9)	–0.0065(7)	–0.0031(7)	–0.0043(8)
O(3)	4*e*	0.4109(3)	0.08203(9)	0.6328(3)	0.046(1)	0.050(1)	0.091(2)	0.0021(9)	0.034(1)	0.007(1)
O(4)	4*e*	0.1779(3)	0.11408(9)	0.7015(3)	0.088(2)	0.050(1)	0.083(2)	0.026(1)	0.049(1)	–0.000(1)
O(5)	4*e*	0.1590(3)	0.0313(1)	0.5948(3)	0.079(2)	0.058(2)	0.118(2)	–0.024(1)	0.029(2)	–0.040(2)
OW(1)	4*e*	0.7824(2)	0.04378(9)	0.6481(2)	0.0362(9)	0.066(1)	0.039(1)	–0.0098(8)	0.0129(7)	–0.0118(9)
N(1)	4*e*	0.4805(3)	0.06602(8)	0.3134(2)	0.042(1)	0.0292(9)	0.0253(9)	–0.0037(8)	0.0071(8)	0.0024(8)
N(3)	4*e*	0.3606(3)	0.41342(9)	0.4486(2)	0.048(1)	0.038(1)	0.036(1)	0.0003(9)	0.0071(9)	0.0075(9)
N(2)	4*e*	0.4871(3)	0.26781(8)	0.1662(2)	0.051(1)	0.029(1)	0.032(1)	–0.0094(8)	0.0022(9)	0.0040(8)
N(4)	4*e*	0.4787(3)	0.22103(9)	0.6704(2)	0.047(1)	0.031(1)	0.032(1)	–0.0022(8)	–0.0003(8)	0.0016(8)
N(5)	4*e*	0.2480(3)	0.07624(8)	0.6420(2)	0.040(1)	0.0298(9)	0.029(1)	0.0043(8)	0.0115(8)	0.0014(8)
C(1)	4*e*	0.5224(3)	0.1232(1)	0.3388(2)	0.038(1)	0.032(1)	0.024(1)	–0.0034(9)	0.0075(8)	–0.0001(9)
C(2)	4*e*	0.4978(3)	0.16407(9)	0.2248(2)	0.028(1)	0.029(1)	0.026(1)	–0.0019(8)	0.0060(8)	0.0030(8)
C(3)	4*e*	0.4260(3)	0.1446(1)	0.0785(3)	0.048(1)	0.037(1)	0.026(1)	–0.004(1)	0.0059(9)	0.0055(9)
C(4)	4*e*	0.3878(4)	0.0850(1)	0.0532(3)	0.070(2)	0.039(1)	0.022(1)	–0.009(1)	0.008(1)	–0.005(1)
C(5)	4*e*	0.4163(4)	0.0474(1)	0.1712(3)	0.055(1)	0.030(1)	0.031(1)	–0.008(1)	0.009(1)	–0.003(1)
C(6)	4*e*	0.5630(3)	0.2263(1)	0.2655(2)	0.032(1)	0.034(1)	0.028(1)	–0.0055(9)	0.0080(8)	0.0016(9)
C(7)	4*e*	0.3580(3)	0.3546(1)	0.4472(3)	0.040(1)	0.040(1)	0.029(1)	–0.0022(9)	0.0072(9)	0.001(1)
C(8)	4*e*	0.4024(3)	0.31990(9)	0.5744(2)	0.028(1)	0.032(1)	0.028(1)	–0.0008(8)	0.0048(8)	0.0014(9)
C(9)	4*e*	0.4551(3)	0.3483(1)	0.7124(3)	0.039(1)	0.038(1)	0.029(1)	0.0004(9)	0.0045(9)	0.001(1)
C(10)	4*e*	0.4566(4)	0.4089(1)	0.7154(3)	0.049(1)	0.037(1)	0.037(1)	–0.003(1)	0.006(1)	–0.006(1)
C(11)	4*e*	0.4082(4)	0.4396(1)	0.5825(3)	0.047(1)	0.032(1)	0.048(2)	–0.003(1)	0.008(1)	0.001(1)
C(12)	4*e*	0.3800(3)	0.2544(1)	0.5563(2)	0.030(1)	0.035(1)	0.030(1)	–0.0015(8)	0.0066(9)	0.0003(9)

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