# Crystal structure of 4-hydroxypyridinium triaqua-bis(4-hydroxypyridine-2,6-dicarboxylato)neodymium(III) dihydrate, $[C_5H_6NO][Nd(C_7H_3NO_5)_2(H_2O)_3] \cdot 2H_2O$

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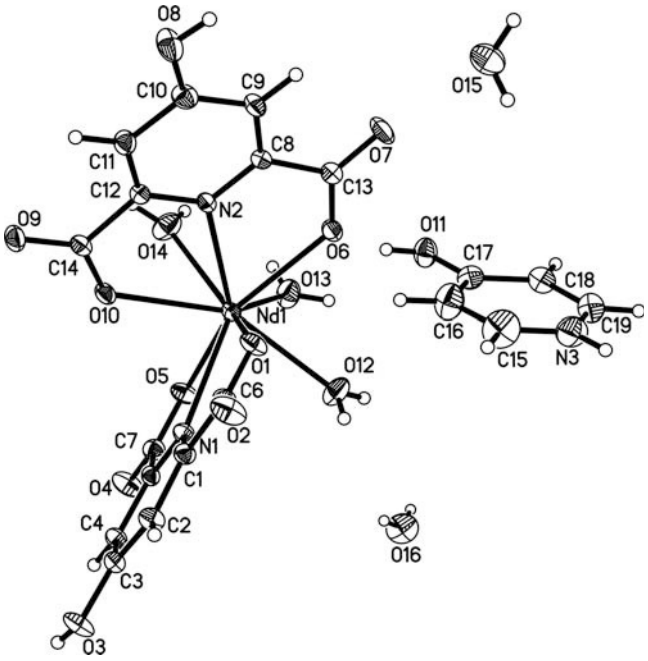


**Abstract**

$C_{19}H_{22}N_3NdO_{16}$, monoclinic, $P12_1/c1$ (no. 14), $a$ = 11.347(2) Å, $b$ = 10.857(2) Å, $c$ = 19.514(3) Å, $\beta$ = 92.927(2)°, $V$ = 2400.9 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.022, $wR_{ref}(F^2)$ = 0.053, $T$ = 296 K.

**Source of material**

The mixture of $Nd(NO_3)_3 \cdot 6H_2O$ (0.088 g, 0.2 mmol) and 4-hydroxypyridine-2,6-dicarboxylic acid ($H_2CAM$, 0.074 g, 0.4 mmol), was stirred into 15 ml aqueous solution. Then the pH value was adjusted to approx. 6 with 1.5 M solution of ammonia. And then 5 ml ethanol solution of 4-hydroxypyridine (4-Hpy, 0.025 g, 0.2 mmol) was added. The reaction mixture was heated on a water bath for 10 h at 70 °C, then filtered. The resulting clear solution was diffused with diethyl ether vapor at room temperature for two weeks, block-shaped pink crystals were obtained, the products are insoluble in water (yield 0.049 g, 36 %). Elemental analysis — found: C, 32.61 %; H, 3.18 %; N, 6.14 %; calculated for $C_{19}H_{22}N_3NdO_{16}$: C, 32.95 %; H, 3.20 %; N, 6.06 %. IR data are available in the CIF.

**Discussion**

The study of metal-organic supramolecule has gained great recognition as an important interface between synthetic chemistry and materials science and provides a solid foundation for understanding how molecules can be organized and how functions can be achieved [1-3]. The current attention is focus on the construction of metal-organic frameworks (MOFs) with novel topology, and on the crystal engineering of molecular architectures organized by coordination bonds and supramolecular contacts (such as hydrogen bonding, $\pi$-$\pi$ stacking interactions, etc.) [4,5]. In this work, $H_2CAM$ was employed as the major ligand because the unit has unique a coordination geometry, which can potentially provide more coordination motifs [6].

The title crystal structure is composited of one neodymium(III) ion, two $CAM^{2-}$ ligands, three coordinated water molecules, and two lattice water molecules as well as a free 4-hydroxypyridinium cation. Nd(III) is nine-coordinated with a tricapped trigonal prism configuration. The Nd atom is coordinated by two CAM molecules using four oxygen atoms of chaleated deprotonated carboxylate group and two nitrogen atoms of the pyridine ring, and three oxygen atoms from the water molucules, with $d$(Nd—O) rang from 2.480(2) to 2.560(2) Å, and $d$(Nd—N) rang from 2.567(2) to 2.581(2) Å, which are within normal ranges [6,7]. The angles of the CAM to the central ion range from 61.72(7)° to 123.62(7)°. The dihedral angle between the two pyridyl rings attached to the central ion is 60.21°, and the dihedral angle between pyridyl rings attached to the central ion and the pyridyl ring of free 4-Hpy ligand vary from 63.59° to 68.18°. In both CAM ligands the dicarboxylate groups are almost coplanar, and the atoms in the pyridine deviate from the mean plane defined by the pyridine ring by less than 0.100 Å. Deviation from the mean plane defined by the pyridine ring are observed for both of carboxylate groups with values ranging from O4 –0.0641 to O2 +0.0893 Å. This implies that the CAM is a fairly rigid ligand and retains its integrity on metal chelation. This coordination mode can also be observed in analogous lanthanide complexes [7,8]. In the IR spectra, the vibrations of $\nu_{as}(CO^{2-})$ and $\nu_{as}(CO^{2-})$ are at 1638.3 cm$^{-1}$ and 1396.7 cm$^{-1}$, respectively. The absence of the characteristic bands at around 1700 cm$^{-1}$ in the title complex indicates the complete deprotonation of dicarboxylate groups in $H_2CAM$ upon reaction with the rare earth ions [9].

There exist two kinds of hydrogen bond interactions between the oxygen atoms of the 2-carboxylate groups and the oxygen of the 4-Hpy, the strong ones is O11–H11···O6 [2.593 Å, 171.8°], the weak one is revealed as O14–H5W···O11 [3.029(3) Å , 111.1°] [10]. The neighbor $Nd(CAM)_2 \cdot 3H_2O$ units were linked into a

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dimer unit *via* the hydrogen bonds with the Nd···Nd spearation of 9.537 Å, and the two lattice water molecules are located on the two sides of the free 4-Hpy ring, respectively. Then these dimer units were further grafted onto a chain along [001] by the hydrogen bond interaction O14–H6W···O9 [2.983(3) Å, 167.4 ]. In addition, there are obvious several hydrogen bond interactions between the adjacent units mentioned above involving to the oxygeon atoms of coordinated waters, uncoordinated waters, the free 4-Hpy as follows: O8–H8···O1 [2.585(3) Å, 149.7°]; O3–H3···O10 [2.610(3) Å, 164.0°]; O16–H9W···O2 [2.751(3) Å, 173.8°]; O15–H8W···O4 [2.754(3) Å, 149.8°]. These chains were connected by the hydrogen bonds, resulting in the infinite 3D porous framework.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | pink block, size 0.11 × 0.18 × 0.19 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 22.51 $cm^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART CCD, $\varphi/\omega$ |
| $2\theta_{max}$: | 51° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 17222, 4468 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 3862 |
| $N(param)_{refined}$: | 355 |
| Programs: | SHELXS-97 [11], SHELXL-97 [12], SHELXTL [13] |

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

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(3) | 4*e* | –0.2399 | 0.9317 | 1.0364 | 0.044 |
| H(8) | 4*e* | 0.7235 | 0.5278 | 1.0516 | 0.056 |
| H(11) | 4*e* | 0.3435 | 0.5377 | 0.7364 | 0.049 |
| H(1W) | 4*e* | 0.0749 | 0.6097 | 0.8167 | 0.054 |
| H(2W) | 4*e* | 0.0966 | 0.6498 | 0.7521 | 0.054 |
| H(3W) | 4*e* | 0.2590 | 0.7950 | 0.6957 | 0.055 |
| H(4W) | 4*e* | 0.3249 | 0.8965 | 0.7145 | 0.055 |
| H(5W) | 4*e* | 0.4353 | 0.9830 | 0.7942 | 0.056 |
| H(6W) | 4*e* | 0.4537 | 0.9997 | 0.8633 | 0.056 |
| H(7W) | 4*e* | 0.7049 | 0.1691 | 0.8817 | 0.061 |
| H(8W) | 4*e* | 0.8244 | 0.1526 | 0.8809 | 0.061 |
| H(9W) | 4*e* | 0.0599 | 0.5438 | 0.1154 | 0.086 |
| H(10W) | 4*e* | 0.0505 | 0.5325 | 0.1941 | 0.086 |
| H(3A) | 4*e* | 0.1687 | 0.0910 | 0.7501 | 0.049 |
| H(2) | 4*e* | –0.0580 | 0.6922 | 1.0471 | 0.027 |
| H(4) | 4*e* | –0.1447 | 0.9994 | 0.9411 | 0.024 |
| H(9) | 4*e* | 0.6387 | 0.5150 | 0.9402 | 0.027 |
| H(11A) | 4*e* | 0.5630 | 0.7756 | 1.0784 | 0.029 |
| H(15) | 4*e* | 0.1897 | 0.2221 | 0.8362 | 0.060 |
| H(16) | 4*e* | 0.2655 | 0.4136 | 0.8170 | 0.052 |
| H(18) | 4*e* | 0.2976 | 0.3182 | 0.6195 | 0.037 |
| H(19) | 4*e* | 0.2155 | 0.1311 | 0.6433 | 0.046 |

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

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Nd(1) | 4*e* | 0.26186(1) | 0.79677(1) | 0.853501(8) | 0.01636(9) | 0.01844(9) | 0.01692(9) | 0.00270(6) | 0.00187(5) | –0.00049(6) |
| O(1) | 4*e* | 0.2185(2) | 0.6300(2) | 0.9372(1) | 0.024(1) | 0.022(1) | 0.032(1) | 0.0079(9) | 0.0099(9) | 0.0041(9) |
| O(2) | 4*e* | 0.1296(2) | 0.5566(2) | 1.0280(1) | 0.035(1) | 0.029(1) | 0.041(1) | 0.011(1) | 0.013(1) | 0.016(1) |
| O(3) | 4*e* | –0.2054(2) | 0.8671(2) | 1.0456(1) | 0.029(1) | 0.028(1) | 0.033(1) | 0.0121(9) | 0.017(1) | 0.008(1) |
| O(4) | 4*e* | –0.0359(2) | 1.0820(2) | 0.8359(1) | 0.035(1) | 0.036(1) | 0.030(1) | 0.018(1) | 0.009(1) | 0.014(1) |
| O(5) | 4*e* | 0.1200(2) | 0.9634(2) | 0.8195(1) | 0.024(1) | 0.029(1) | 0.026(1) | 0.0065(9) | 0.0093(9) | 0.0084(9) |
| O(6) | 4*e* | 0.3867(2) | 0.6295(2) | 0.8088(1) | 0.023(1) | 0.029(1) | 0.026(1) | 0.0074(9) | –0.0033(9) | –0.0091(9) |
| O(7) | 4*e* | 0.5458(2) | 0.5093(2) | 0.8127(1) | 0.035(1) | 0.043(1) | 0.033(1) | 0.021(1) | –0.001(1) | –0.016(1) |
| O(8) | 4*e* | 0.6894(2) | 0.5875(2) | 1.0670(1) | 0.049(2) | 0.035(1) | 0.028(1) | 0.024(1) | –0.012(1) | –0.006(1) |
| O(9) | 4*e* | 0.4121(2) | 0.9544(2) | 1.0576(1) | 0.031(1) | 0.031(1) | 0.020(1) | 0.0060(9) | –0.0006(9) | –0.008(1) |
| O(10) | 4*e* | 0.3099(2) | 0.9188(2) | 0.9587(1) | 0.022(1) | 0.023(1) | 0.022(1) | 0.0088(8) | –0.0005(8) | –0.0033(8) |
| O(11) | 4*e* | 0.3330(2) | 0.4974(2) | 0.7010(1) | 0.043(1) | 0.031(1) | 0.024(1) | –0.005(1) | 0.005(1) | –0.003(1) |
| O(12) | 4*e* | 0.1159(2) | 0.6553(2) | 0.7936(1) | 0.037(1) | 0.045(1) | 0.026(1) | –0.017(1) | –0.001(1) | –0.003(1) |
| O(13) | 4*e* | 0.2765(2) | 0.8453(2) | 0.7267(1) | 0.045(1) | 0.040(1) | 0.026(1) | –0.013(1) | 0.009(1) | –0.005(1) |
| O(14) | 4*e* | 0.4109(2) | 0.9680(2) | 0.8325(1) | 0.036(1) | 0.047(1) | 0.028(1) | –0.015(1) | 0.001(1) | 0.004(1) |
| O(15) | 4*e* | 0.7701(2) | 0.2040(2) | 0.8813(1) | 0.041(1) | 0.040(1) | 0.042(1) | 0.010(1) | 0.005(1) | 0.007(1) |
| O(16) | 4*e* | 0.0272(2) | 0.5307(3) | 0.1519(1) | 0.065(2) | 0.065(2) | 0.044(2) | –0.009(2) | 0.014(1) | 0.015(1) |
| N(1) | 4*e* | 0.0723(2) | 0.8144(2) | 0.9206(1) | 0.018(1) | 0.018(1) | 0.019(1) | 0.0030(9) | 0.0017(9) | 0.002(1) |
| N(2) | 4*e* | 0.4481(2) | 0.7354(2) | 0.9257(1) | 0.018(1) | 0.019(1) | 0.018(1) | 0.0025(9) | 0.0024(9) | –0.003(1) |
| N(3) | 4*e* | 0.1975(3) | 0.1624(3) | 0.7418(2) | 0.040(2) | 0.032(2) | 0.052(2) | –0.005(1) | 0.009(2) | 0.008(2) |
| C(1) | 4*e* | 0.0501(2) | 0.7360(3) | 0.9719(2) | 0.019(1) | 0.017(1) | 0.023(2) | 0.002(1) | 0.002(1) | 0.001(1) |
| C(2) | 4*e* | –0.0440(2) | 0.7497(3) | 1.0132(2) | 0.024(2) | 0.023(1) | 0.022(2) | 0.002(1) | 0.005(1) | 0.006(1) |
| C(3) | 4*e* | –0.1179(2) | 0.8513(3) | 1.0029(2) | 0.020(2) | 0.021(2) | 0.021(2) | 0.002(1) | 0.003(1) | –0.002(1) |
| C(4) | 4*e* | –0.0961(2) | 0.9317(3) | 0.9497(2) | 0.020(2) | 0.018(1) | 0.024(2) | 0.006(1) | 0.001(1) | 0.001(1) |
| C(5) | 4*e* | –0.0017(2) | 0.9101(2) | 0.9096(1) | 0.018(1) | 0.019(1) | 0.016(1) | 0.002(1) | –0.001(1) | –0.002(1) |
| C(6) | 4*e* | 0.1380(2) | 0.6321(3) | 0.9816(2) | 0.021(2) | 0.021(2) | 0.026(2) | 0.002(1) | 0.003(1) | 0.000(1) |
| C(7) | 4*e* | 0.0287(3) | 0.9923(3) | 0.8507(2) | 0.022(2) | 0.024(2) | 0.023(2) | 0.001(1) | –0.000(1) | 0.001(1) |
| C(8) | 4*e* | 0.5115(2) | 0.6369(3) | 0.9094(1) | 0.017(1) | 0.021(2) | 0.021(2) | 0.001(1) | 0.003(1) | –0.002(1) |
| C(9) | 4*e* | 0.5958(2) | 0.5830(3) | 0.9536(2) | 0.023(2) | 0.019(2) | 0.026(2) | 0.005(1) | 0.003(1) | –0.002(1) |
| C(10) | 4*e* | 0.6144(3) | 0.6337(3) | 1.0187(2) | 0.026(2) | 0.025(2) | 0.026(2) | 0.006(1) | –0.001(1) | 0.003(1) |
| C(11) | 4*e* | 0.5506(3) | 0.7383(3) | 1.0358(2) | 0.026(2) | 0.025(2) | 0.020(2) | 0.004(1) | –0.002(1) | –0.003(1) |
| C(12) | 4*e* | 0.4688(2) | 0.7851(2) | 0.9881(2) | 0.017(1) | 0.019(1) | 0.021(2) | 0.001(1) | 0.002(1) | –0.002(1) |
| C(13) | 4*e* | 0.4817(3) | 0.5863(3) | 0.8381(2) | 0.022(2) | 0.024(2) | 0.025(2) | 0.002(1) | 0.002(1) | –0.003(1) |
| C(14) | 4*e* | 0.3928(2) | 0.8955(3) | 1.0040(2) | 0.020(2) | 0.020(1) | 0.021(2) | 0.002(1) | 0.006(1) | –0.000(1) |
| C(15) | 4*e* | 0.2112(4) | 0.2434(4) | 0.7924(2) | 0.062(3) | 0.058(3) | 0.029(2) | –0.008(2) | 0.007(2) | 0.013(2) |
| C(16) | 4*e* | 0.2563(3) | 0.3572(3) | 0.7812(2) | 0.060(2) | 0.045(2) | 0.026(2) | –0.010(2) | 0.005(2) | –0.000(2) |
| C(17) | 4*e* | 0.2885(3) | 0.3881(3) | 0.7159(2) | 0.026(2) | 0.031(2) | 0.025(2) | 0.000(1) | –0.001(1) | 0.004(1) |
| C(18) | 4*e* | 0.2747(3) | 0.3005(3) | 0.6636(2) | 0.033(2) | 0.033(2) | 0.026(2) | 0.003(1) | 0.003(1) | 0.004(1) |
| C(19) | 4*e* | 0.2273(3) | 0.1892(3) | 0.6780(2) | 0.039(2) | 0.034(2) | 0.043(2) | 0.000(2) | 0.004(2) | –0.004(2) |

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