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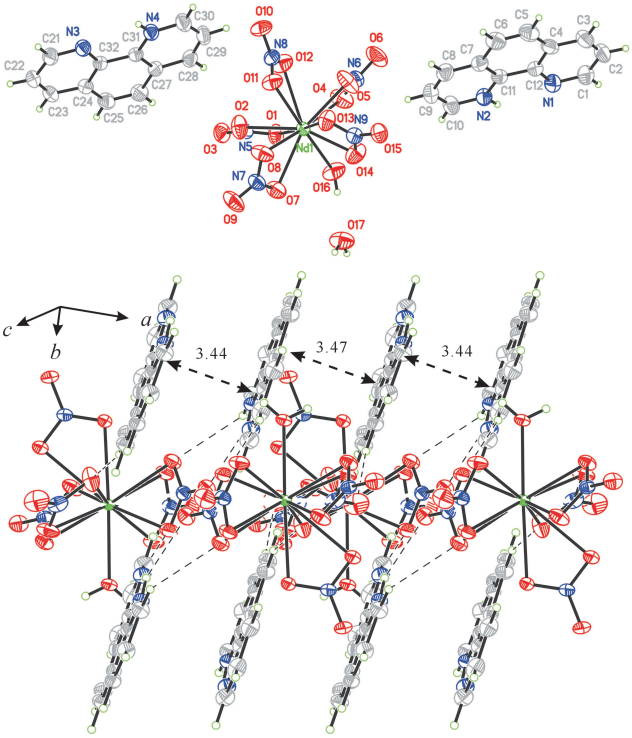
# Crystal structures of bis(1,10-phenanthrolin-1-ium) aquapentakis(nitrato-κ²*O*,*O*′)neodym(III) monohydrate, $C_{24}H_{22}N_9NdO_{17}$

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## Abstract

$C_{24}H_{22}N_9NdO_{17}$, triclinic, $P\bar{1}$ (no. 2), $a = 7.6445(15)$ Å, $b = 7.9378(16)$ Å, $c = 25.741(5)$ Å, $\alpha = 94.51(3)°$, $\beta = 91.76(3)°$, $\gamma = 97.34(3)°$, $V = 1543.1(5)$ Å$^3$, $Z = 2$, $R_{gt}(F) = 0.0274$, $wR_{ref}(F^2) = 0.0686$, $T = 290(2)$ K.

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

| | |
|---|---|
| Crystal: | Colorless, block, size 0.15×0.16×0.22 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 17.78 cm$^{-1}$ |
| Diffractometer, scan mode: | Rigaku R-AXIS RAPID, $\omega$ scans |
| $2\theta_{max}$: | 49.98° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 12190, 5405 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 5027 |
| $N(param)_{refined}$: | 460 |
| Programs: | SHELX [4, 5] |

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| HN(2) | 2*i* | 0.7206 | −0.2171 | 0.4265 | 0.050 |
| HN(4) | 2*i* | 0.2961 | 1.1934 | 0.0699 | 0.046 |
| H(1) | 2*i* | 0.9106 | −0.3664 | 0.5590 | 0.069 |
| H(2) | 2*i* | 0.9468 | −0.1802 | 0.6330 | 0.074 |
| H(3) | 2*i* | 0.8762 | 0.0907 | 0.6305 | 0.069 |
| H(5) | 2*i* | 0.7614 | 0.3132 | 0.5767 | 0.065 |
| H(6) | 2*i* | 0.6497 | 0.3829 | 0.5004 | 0.063 |
| H(8) | 2*i* | 0.5624 | 0.3004 | 0.4052 | 0.058 |
| H(9) | 2*i* | 0.5403 | 0.1015 | 0.3346 | 0.062 |
| H(10) | 2*i* | 0.6291 | −0.1622 | 0.3442 | 0.059 |
| H(21) | 2*i* | 0.0907 | 1.3406 | −0.0625 | 0.054 |
| H(22) | 2*i* | 0.0459 | 1.1559 | −0.1369 | 0.055 |
| H(23) | 2*i* | 0.1111 | 0.8826 | −0.1350 | 0.053 |
| H(25) | 2*i* | 0.2204 | 0.6562 | −0.0817 | 0.055 |
| H(26) | 2*i* | 0.3354 | 0.5824 | −0.0062 | 0.056 |
| H(28) | 2*i* | 0.4440 | 0.6681 | 0.0878 | 0.052 |
| H(29) | 2*i* | 0.4907 | 0.8741 | 0.1566 | 0.058 |
| H(30) | 2*i* | 0.4065 | 1.1404 | 0.1479 | 0.057 |
| H(16A) | 2*i* | −0.0913 | 0.1128 | 0.2518 | 0.066 |
| H(16B) | 2*i* | 0.0902 | 0.1357 | 0.2490 | 0.066 |
| H(17B) | 2*i* | −0.4015 | −0.0244 | 0.2419 | 0.078 |
| H(17A) | 2*i* | −0.2892 | −0.1440 | 0.2365 | 0.078 |

Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

**Table 3:** Fractional coordinates and atomic displacement parameters (Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Nd(1) | 2*i* | 0.03040(2) | 0.49114(2) | 0.249093(5) | 0.0320(1) | 0.02175(9) | 0.0312(1) | 0.00720(7) | −0.00508(7) | −0.00064(6) |
| N(1) | 2*i* | 0.8165(4) | −0.2166(4) | 0.5117(1) | 0.053(2) | 0.047(2) | 0.049(2) | 0.006(1) | −0.004(1) | 0.008(1) |
| N(2) | 2*i* | 0.6963(4) | −0.1190(3) | 0.4187(1) | 0.049(2) | 0.038(1) | 0.038(1) | 0.007(1) | 0.001(1) | 0.002(1) |
| N(3) | 2*i* | 0.1870(4) | 1.1892(3) | −0.0166(1) | 0.045(2) | 0.035(1) | 0.040(1) | 0.007(1) | −0.003(1) | 0.003(1) |
| N(4) | 2*i* | 0.3213(4) | 1.0932(3) | 0.0749(1) | 0.043(2) | 0.037(1) | 0.034(1) | 0.006(1) | −0.000(1) | 0.002(1) |
| N(5) | 2*i* | 0.1443(4) | 0.4406(3) | 0.1378(1) | 0.044(2) | 0.033(1) | 0.034(1) | 0.001(1) | −0.003(1) | −0.001(1) |
| N(6) | 2*i* | 0.3408(4) | 0.4930(4) | 0.3217(1) | 0.051(2) | 0.051(2) | 0.052(2) | 0.001(1) | −0.023(1) | 0.014(1) |
| N(7) | 2*i* | −0.3107(4) | 0.4824(3) | 0.1882(1) | 0.038(2) | 0.040(2) | 0.046(2) | 0.009(1) | −0.009(1) | −0.002(1) |
| N(8) | 2*i* | 0.2390(4) | 0.8406(3) | 0.2415(1) | 0.045(2) | 0.028(1) | 0.043(1) | 0.006(1) | −0.000(1) | 0.004(1) |
| N(9) | 2*i* | −0.1417(4) | 0.5359(3) | 0.3514(1) | 0.039(2) | 0.038(1) | 0.039(1) | 0.006(1) | 0.002(1) | 0.002(1) |
| C(1) | 2*i* | 0.8799(5) | −0.2574(5) | 0.5571(2) | 0.056(2) | 0.058(2) | 0.061(2) | 0.008(2) | −0.008(2) | 0.019(2) |
| C(2) | 2*i* | 0.9028(5) | −0.1449(6) | 0.6021(2) | 0.051(2) | 0.083(3) | 0.049(2) | −0.002(2) | −0.013(2) | 0.017(2) |
| C(3) | 2*i* | 0.8609(5) | 0.0151(5) | 0.6008(1) | 0.055(2) | 0.070(3) | 0.042(2) | −0.004(2) | −0.008(2) | 0.001(2) |
| C(4) | 2*i* | 0.7939(5) | 0.0658(4) | 0.5537(1) | 0.039(2) | 0.052(2) | 0.041(2) | −0.005(2) | −0.000(2) | −0.004(2) |
| C(5) | 2*i* | 0.7468(5) | 0.2325(5) | 0.5482(2) | 0.059(2) | 0.049(2) | 0.052(2) | 0.003(2) | −0.001(2) | −0.012(2) |
| C(6) | 2*i* | 0.6821(5) | 0.2746(4) | 0.5027(2) | 0.055(2) | 0.039(2) | 0.063(2) | 0.010(2) | −0.002(2) | −0.006(2) |
| C(7) | 2*i* | 0.6620(4) | 0.1554(4) | 0.4574(1) | 0.039(2) | 0.038(2) | 0.047(2) | 0.004(1) | 0.002(2) | 0.003(1) |
| C(8) | 2*i* | 0.5970(5) | 0.1937(4) | 0.4089(1) | 0.046(2) | 0.045(2) | 0.057(2) | 0.008(2) | 0.001(2) | 0.012(2) |
| C(9) | 2*i* | 0.5839(5) | 0.0758(5) | 0.3668(1) | 0.057(2) | 0.059(2) | 0.042(2) | 0.011(2) | −0.001(2) | 0.011(2) |
| C(10) | 2*i* | 0.6361(5) | −0.0816(5) | 0.3727(1) | 0.056(2) | 0.054(2) | 0.038(2) | 0.008(2) | −0.001(2) | 0.000(2) |
| C(11) | 2*i* | 0.7097(4) | −0.0063(4) | 0.4619(1) | 0.034(2) | 0.037(2) | 0.039(2) | 0.002(1) | 0.003(1) | 0.000(1) |
| C(12) | 2*i* | 0.7761(4) | −0.0559(4) | 0.5106(1) | 0.035(2) | 0.040(2) | 0.040(2) | −0.000(1) | 0.001(1) | 0.005(1) |
| C(21) | 2*i* | 0.1201(5) | 1.2309(4) | −0.0612(1) | 0.050(2) | 0.038(2) | 0.048(2) | 0.009(2) | −0.006(2) | 0.009(1) |
| C(22) | 2*i* | 0.0911(5) | 1.1194(4) | −0.1064(1) | 0.046(2) | 0.051(2) | 0.041(2) | 0.004(2) | −0.011(2) | 0.011(2) |
| C(23) | 2*i* | 0.1296(5) | 0.9580(4) | −0.1053(1) | 0.049(2) | 0.047(2) | 0.035(2) | 0.001(2) | −0.008(2) | −0.002(1) |
| C(24) | 2*i* | 0.1979(4) | 0.9049(4) | −0.0586(1) | 0.038(2) | 0.038(2) | 0.037(2) | 0.001(1) | −0.001(1) | 0.002(1) |
| C(25) | 2*i* | 0.2402(5) | 0.7371(4) | −0.0533(1) | 0.058(2) | 0.036(2) | 0.041(2) | 0.003(2) | −0.005(2) | −0.006(1) |
| C(26) | 2*i* | 0.3081(5) | 0.6925(4) | −0.0084(1) | 0.052(2) | 0.032(2) | 0.056(2) | 0.009(2) | −0.006(2) | 0.002(1) |
| C(27) | 2*i* | 0.3387(4) | 0.8140(4) | 0.0363(1) | 0.035(2) | 0.037(2) | 0.039(2) | 0.002(1) | −0.000(1) | 0.007(1) |
| C(28) | 2*i* | 0.4130(5) | 0.7763(4) | 0.0841(1) | 0.040(2) | 0.045(2) | 0.048(2) | 0.008(2) | −0.001(2) | 0.016(2) |
| C(29) | 2*i* | 0.4397(5) | 0.8984(5) | 0.1252(1) | 0.047(2) | 0.065(2) | 0.035(2) | 0.008(2) | −0.002(2) | 0.014(2) |
| C(30) | 2*i* | 0.3907(5) | 1.0578(5) | 0.1199(1) | 0.049(2) | 0.058(2) | 0.034(2) | 0.006(2) | −0.002(2) | 0.002(2) |
| C(31) | 2*i* | 0.2956(4) | 0.9780(4) | 0.0322(1) | 0.030(2) | 0.036(2) | 0.035(2) | 0.002(1) | 0.002(1) | 0.004(1) |
| C(32) | 2*i* | 0.2226(4) | 1.0277(4) | −0.0156(1) | 0.031(2) | 0.034(1) | 0.035(2) | 0.002(1) | −0.000(1) | 0.005(1) |
| O(1) | 2*i* | 0.1809(4) | 0.3461(3) | 0.17192(8) | 0.063(2) | 0.045(1) | 0.037(1) | 0.022(1) | 0.005(1) | 0.0032(9) |
| O(2) | 2*i* | 0.0563(4) | 0.5574(3) | 0.15118(9) | 0.086(2) | 0.051(1) | 0.0380(9) | 0.032(1) | 0.002(1) | 0.007(1) |
| O(3) | 2*i* | 0.1885(4) | 0.4176(3) | 0.09226(9) | 0.073(2) | 0.051(1) | 0.034(1) | 0.005(1) | 0.003(1) | −0.002(1) |
| O(4) | 2*i* | 0.3186(4) | 0.3913(3) | 0.2824(1) | 0.062(2) | 0.039(1) | 0.099(2) | 0.024(1) | −0.036(2) | −0.008(1) |
| O(5) | 2*i* | 0.2227(4) | 0.5900(4) | 0.3296(1) | 0.050(2) | 0.102(2) | 0.045(1) | 0.017(1) | −0.013(1) | −0.014(1) |
| O(6) | 2*i* | 0.4709(4) | 0.5061(4) | 0.3514(1) | 0.069(2) | 0.084(2) | 0.101(2) | 0.005(2) | −0.053(2) | 0.018(2) |
| O(7) | 2*i* | −0.2463(3) | 0.3470(3) | 0.1954(1) | 0.055(2) | 0.035(1) | 0.073(2) | 0.006(1) | −0.029(1) | −0.004(1) |
| O(8) | 2*i* | −0.2398(3) | 0.6145(3) | 0.2148(1) | 0.039(1) | 0.038(1) | 0.082(2) | 0.016(1) | −0.019(1) | −0.015(1) |
| O(9) | 2*i* | −0.4301(4) | 0.4855(4) | 0.1561(1) | 0.058(2) | 0.075(2) | 0.072(2) | 0.021(2) | −0.035(2) | −0.004(2) |
| O(10) | 2*i* | 0.3185(4) | 0.9876(3) | 0.2430(1) | 0.056(2) | 0.028(1) | 0.077(2) | −0.004(1) | 0.005(1) | 0.001(1) |
| O(11) | 2*i* | 0.0765(3) | 0.8163(3) | 0.2470(1) | 0.039(1) | 0.0269(8) | 0.075(2) | 0.008(1) | 0.007(1) | 0.005(1) |
| O(12) | 2*i* | 0.3183(3) | 0.7128(3) | 0.2338(1) | 0.043(1) | 0.032(1) | 0.086(2) | 0.0089(9) | 0.011(1) | 0.010(1) |
| O(13) | 2*i* | −0.1207(4) | 0.6593(3) | 0.32379(9) | 0.063(2) | 0.042(1) | 0.048(1) | 0.021(1) | 0.015(1) | 0.005(1) |
| O(14) | 2*i* | −0.1242(4) | 0.3920(3) | 0.3296(1) | 0.080(2) | 0.036(1) | 0.057(1) | 0.009(1) | 0.026(1) | 0.004(1) |
| O(15) | 2*i* | −0.1750(3) | 0.5544(3) | 0.39773(9) | 0.057(2) | 0.056(1) | 0.040(1) | 0.012(1) | 0.001(1) | 0.001(1) |
| O(16) | 2*i* | −0.0004(4) | 0.1801(3) | 0.2520(1) | 0.049(2) | 0.025(1) | 0.092(2) | 0.012(1) | 0.012(1) | 0.006(1) |
| O(17) | 2*i* | −0.2994(4) | −0.0444(3) | 0.2454(1) | 0.050(2) | 0.042(1) | 0.101(2) | 0.010(1) | −0.007(2) | −0.009(1) |

## Source of material

$Nd_2O_3$ (0.02103 g, 0.025 mmol) was dissolved in appropriate amount of nitric acid, and the phenanthroline monohydrate (phen · $H_2O$, 0.0991 g, 0.10 mmol) and 2-bromobenzoic acid (0.1005 g, 0.10 mmol), $CH_3OH/H_2O$ (v/v = 1:2, 15 mL), were stirred for 2.0 h. Subsequently, the resulting suspension was

heated in a 23 mL Teflon-lined stainless steel autoclave at 433 K for 7 days. After the autoclave was cooled to room temperature within 12 h, the solid was filtered off. The resulting filtrate was allowed to stand at room temperature, and slow evaporation for 3 months afforded colorless block crystals.

## Experimental details

The hydrogen atoms were idealized and refined using a riding model (AFIX 43 or AFIX 3 option of the SHELX- program [5]).

## Discussion

The crystal structure of the title compound is similar to the structure of bis(1,10-phenanthrolinium) diaqua pentakis (nitrato-*O*,*O*′)cerium(III) monohydrate $[Ce(NO_3)_5(H_2O)_2](Hphen)_2 \cdot H_2O$ [1]. There are at least two structurally related complexes: (2,2′-bipyridyl)tetrakis(nitrato-*O*,*O*′)gadolinium [2], tris(2,2′-bipyridinium) nitratehexanitratothorium(IV) [3].

The $Nd^{III}$ atom is coordinated by eleven O atoms from five nitrate ligands and one water molecules in an irregular polyhedron $NdO_{11}$ environment (upper part of the figure). All nitrato ligands are bidentate, the Nd—O16($H_2O$) bond length is 2.457(2) Å, and is shorter than the other Nd—O bond lengths. Two phen molecules and one water molecule are not involved in coordination, both $Hphen^+$ cations are protonated at one of the two N atoms. The $Hphen^+$ cations exhibit nearly perfect coplanarity (r.m.s. deviation = 0.017 Å). In the crystal, strong N—H···N, N—H···O, O—H···O hydrogen bonds and weak C—H···O hydrogen bonds and π—π stacking interactions [mean interplanar distance of 3.44(2) and 3.47(0) Å between adjacent phen molecules (lower part of the figure)] link the $Hphen^+$ cations and $[Nd(H_2O)(NO_3)_5]^{2-}$ anions into a three-dimensional structure.

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