# metal-organic compounds

## Tetrakis(μ-3-azaniumylbenzoato)-κ³O:O,O′;κ³O,O′:O;κ⁴O:O′-bis-[tetraaquaneodymium(III)] hexachloride tetrahydrate

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The structure of the title compound, $[Nd_2(C_7H_7NO_2)_4(H_2O)_8]Cl_6 \cdot 4H_2O$, consists of dimeric cationic units related by an inversion centre. The two $Nd^{III}$ atoms are linked by two bridging bidentate carboxylate groups and two bidentate chelating bridging carboxylate groups, with an $Nd\cdots Nd$ separation of 4.1259 (4) Å. Each $Nd^{III}$ atom is nine-coordinated by five O atoms from the carboxylate groups of the zwitterionic azaniumylbenzoate ligands and four from water molecules. They adopt a distorted tricapped trigonal–prismatic arrangement. The dihedral angle between the mean planes of the benzene ring and the carboxlate groups are 7.7 (6) and 24.4 (5)°. The two carboxylate groups are almost perpendicular to one another with a dihedral angle of 84.0 (7)°, while the two benzene rings are inclined to one another by 81.8 (2)°. The molecular packing is stabilized by $O-H_{water}\cdots Cl$, $O-H_{water}\cdots N$, $N-H\cdots Cl$, $N-H\cdots O$, and $O-H_{water}\cdots O$ hydrogen bonds and $\pi-\pi$ stacking interactions [centroid–centroid distance = 3.500 (3) Å] between symmetry-related benzene rings. All of the $Cl^-$ anions and the uncoordinated water molecules are disordered over two sets of sites with different occupancy ratios.

## Related literature

For applications of lanthanide complexes, see: Yan *et al.* (1997); Scott & Horrocks (1992). For lanthanide complexes with aromatic carboxylic acids, see: Ma *et al.* (1994). For similar complexes, see: Qin *et al.* (2005, 2006); Sun *et al.* (2002); Benslimane *et al.* (2011).
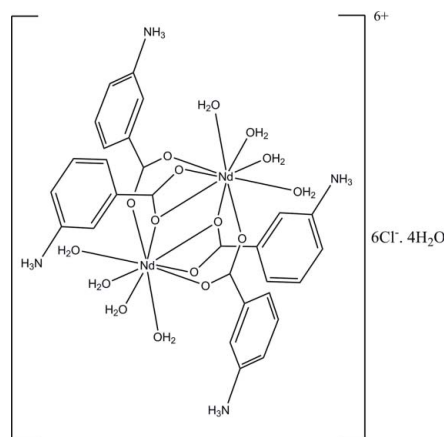


## Experimental

### Crystal data

$[Nd_2(C_7H_7NO_2)_4(H_2O)_8]Cl_6 \cdot 4H_2O$
$M_r = 1265.92$
Monoclinic, $P2_1/c$
$a = 12.1717$ (1) Å
$b = 19.8544$ (1) Å
$c = 10.5170$ (1) Å
$\beta = 112.018$ (1)°

$V = 2356.19$ (4) Å$^3$
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.59$ mm$^{-1}$
$T = 293$ K
$0.30 \times 0.24 \times 0.16$ mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: multi-scan (Blessing, 1997)
$T_{min} = 0.410$, $T_{max} = 0.444$
7192 measured reflections

6852 independent reflections
4724 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
2 standard reflections every 60 min intensity decay: 3%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.096$
$S = 1.02$
6852 reflections

300 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.81$ e Å$^{-3}$
$\Delta\rho_{min} = -1.15$ e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| N1—H1A⋯O6WA | 0.89 | 2.16 | 3.007 (12) | 160 |
| N1—H1B⋯Cl1 | 0.89 | 2.30 | 3.174 (5) | 168 |
| N1—H1C⋯O6WA[i] | 0.89 | 1.98 | 2.828 (12) | 159 |
| N2—H2A⋯O4[ii] | 0.89 | 2.22 | 2.967 (6) | 141 |
| N2—H2B⋯Cl2[iii] | 0.89 | 2.31 | 3.166 (5) | 161 |
| N2—H2C⋯Cl3A[iv] | 0.89 | 2.26 | 3.129 (5) | 167 |
| O1W—H11⋯Cl2[v] | 0.97 | 2.21 | 3.170 (4) | 172 |
| O2W—H12⋯O5W | 1.04 | 2.28 | 2.960 (7) | 121 |
| O2W—H12⋯Cl2[v] | 1.04 | 2.65 | 3.443 (5) | 132 |
| O3W—H13⋯Cl2 | 0.95 | 2.26 | 3.190 (5) | 169 |
| O4W—H14⋯Cl3A[vi] | 0.86 | 2.58 | 3.240 (5) | 134 |
| O5W—H15W⋯Cl1[vii] | 0.85 | 2.68 | 3.208 (7) | 122 |
| O1W—H21⋯Cl1[iv] | 0.78 | 2.52 | 3.215 (4) | 148 |
| O2W—H22⋯Cl2 | 0.90 | 2.26 | 3.104 (4) | 156 |
| O3W—H23⋯Cl3A | 0.80 | 2.56 | 3.244 (4) | 144 |
| O4W—H24⋯Cl1[viii] | 0.93 | 2.23 | 3.134 (5) | 163 |
| O5W—H25W⋯N1[iii] | 0.85 | 2.52 | 3.247 (8) | 144 |
| C10—H01⋯Cl1[iv] | 0.93 | 2.81 | 3.724 (6) | 169 |
| C14—H04⋯O2W[iii] | 0.93 | 2.59 | 3.504 (7) | 170 |

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x+2, -y+1, -z+1$; (vi) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (vii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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**supplementary materials**

# Tetrakis($\mu$-3-azaniumylbenzoato)-$\kappa^3 O{:}O,O'$;$\kappa^3 O,O'{:}O$;$\kappa^4 O{:}O'$-bis[tetraaquaneodymium(III)] hexachloride tetrahydrate

## M. Benslimane, H. Merazig and J.-C. Daran

## Comment

In recent years, much research has been done on lanthanide coordination compounds with some organic ligands, which have chelated structures and exhibit photophysical properties for the application in luminescence probes for chemical or biological macromolecules and the active center for molecular based luminescent materials (Yan *et al.*, 1997; Scott *et al.*, 1992). Especially lanthanide complexes with aromatic carboxylic acids show higher thermal and luminescent stability for practical applications than other lanthanide complexes because they readily form dimer or infinite chain polymeric structures (Ma *et al.*, 1994).We report herein on the preparation and crystal structure of the title compound.

The molecular structure of the title compound consists of dimeric units related by an inversion centre (Fig. 1). The two Nd$^{III}$ atoms are linked by two bridging bidentate carboxylate groups and two bidentate chelating bridging carboxylate groups. Each Nd$^{III}$ atom is nine-coordinated by five O atoms from carboxylate groups of the 3-ammoniumbenzoate, and four O atoms from the water molecules. They adopt a distorted tricapped trigonal-prismatic arrangement. A similar coordination environment was observed previously for lanthanoid(III) complexes, such as [(pyridine-3,4-dicarboxylate)$_2$(NO$_3$)$_2$(H$_2$O)$_3$] (Qin *et al.*, 2006) and [Ln$_2$(imidazole-4,5-dicarboxylate)$_2$(H$_2$O)$_3$]1.5H$_2$O (Ln = Sm and Eu; Qin *et al.*, 2005). The Nd-O distances involving the carboxylate groups range from 2.394 (3) Å to 2.458 (4) Å and those of the Nd-O$_{water}$ bonds from 2.506 (4)Å to 2.525 (4) Å. The Nd1-O1-Nd1$^i$ (Symmetry codes: (i) -x+1, -y+1, -z+1) angle is 101.96 (13)°, the resulting Nd⋯Nd intradimer separation is 4.1259 (4) Å indicates that the metal⋯metal distances are primarily governed by the nature and mode of the coordination of the bridging groups (Sun *et al.*, 2002). The carboxylate group shows a distortion from the molecular plane; the dihedral angle between the mean-planes of the benzene ring (C2-C7; plane 1) and the carboxlate group (O2/C1/O3$^i$) is 7.7 (6)°, and that between the mean-planes of benzene ring (C9-C14; plane 2) and the O1/C8/O4 carboxlate group is 24.4 (5)°. The two carboxylate groups are almost perpendicular to one another with a dihedral angle of 84.0 (7) °, and planes 1 and 2 are inclined to one another by 81.8 (2) ° compared with the corresponding value found in the complex [La$_2$(C$_7$H$_7$NO$_2$)$_4$Cl$_2$(H$_2$O)$_6$]Cl$_4$.2H$_2$O [(Benslimane *et al.*, 2011) 80.0 (2)].

In the crystal hydrogen bonds involving the free and the coordinated water molecules, the ammonium group NH$_3$ and the Cl atoms build up a three dimensionnal network (Fig. 2, Table 1). There is also slipped π -π stacking interactions between the symetry related C9—C14 phenyl ring (Table 2). Both hydrogen-bonding and π-π interactions combine to stabilize the three-dimensional network.

## Experimental

NdCl$_3$(0.25 g, 1mmol) was dissolved in an aqueous solution of NaOH (0.5 M, 25 ml) with constant stirring. 3-aminobenzoic acid (0.14 g, 1 mmol) was added to the mixture and the pH was adjusted to ca. 3 using 4M HCl. The mixture was refluxed

# supplementary materials

at 353K for about 1 h and then cooled to room temperature. Slow evaporation of the solvent at room temperature lead to the formation of prismatic purple crystals of the title compound.

### Refinement

The chloride anion Cl3 is disordered over three sites, Cl3A, Cl3B and Cl3C, which were refined with occupancies of 0.75, 0.15 and 0.10, respectively. The water molecule O6W is also disordered over two positions (O6WA and O6WB), which were refined with occupancy factors 0.72/0.28, so no H-atoms could be reliably defined. All H atoms attached to C and N atoms were fixed geometrically and treated as riding with C—H = 0.93 Å and N—H = 0.89 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(N)$. The H-atoms of the coordinated water molecules were initially refined using distance restraints [O—H = 0.85 (2) Å, and H···H = 1.40 (2) Å] with $U_{iso}(H) = 1.5U_{eq}(O)$. However, in the last cycles of refinement, they were treated as riding on their parent O atoms.

### Figures
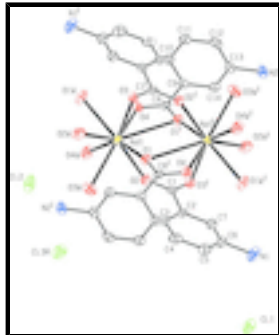


Fig. 1. The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [Symmetry code: (i) -x + 1, -y + 1, -z + 1; Hydrogen atoms have been omitted for clarity].
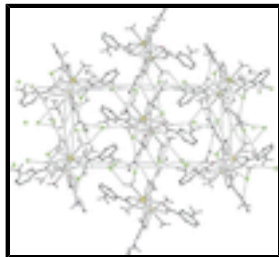


Fig. 2. The crystal packing of the title compound, viewed approximately down the *a* axis. Hydrogen bonds are shown as dashed lines [see Table 1 for details; hydrogen atoms not involved in hydrogen bonding have been omitted for clarity].

## Tetrakis(μ-3-azaniumylbenzoato)-κ$^3$O:O,O'; κ$^3$O,O':O;κ$^4$O:O'- bis[tetraaquaneodymium(III)] hexachloride tetrahydrate

*Crystal data*

| | |
|---|---|
| $[Nd_2(C_7H_7NO_2)_4(H_2O)_8]Cl_6 \cdot 4H_2O$ | $F(000) = 1260$ |
| $M_r = 1265.92$ | $D_x = 1.784$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 7192 reflections |
| $a = 12.1717$ (1) Å | $\theta = 1.0$–$30.0°$ |
| $b = 19.8544$ (1) Å | $\mu = 2.59$ mm$^{-1}$ |
| $c = 10.5170$ (1) Å | $T = 293$ K |

$\beta = 112.018\ (1)°$

$V = 2356.19\ (4)$ Å$^3$

$Z = 2$

Prism, violet

$0.30 \times 0.24 \times 0.16$ mm

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.031$ |
| graphite | $\theta_{max} = 30.0°$, $\theta_{min} = 1.8°$ |
| non–profiled ω/2τ scans | $h = -15 \rightarrow 17$ |
| Absorption correction: multi-scan (Blessing, 1997) | $k = -27 \rightarrow 0$ |
| $T_{min} = 0.410$, $T_{max} = 0.444$ | $l = -14 \rightarrow 0$ |
| 7192 measured reflections | 2 standard reflections every 60 min |
| 6852 independent reflections | intensity decay: 3% |
| 4724 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.096$ | H-atom parameters constrained |
| $S = 1.02$ | $w = 1/[\sigma^2(F_o^2) + (0.0201P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 6852 reflections | $(\Delta/\sigma)_{max} = 0.002$ |
| 300 parameters | $\Delta\rho_{max} = 0.81$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -1.15$ e Å$^{-3}$ |

*Special details*

**Geometry**. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Nd1 | 0.67791 (2) | 0.47629 (1) | 0.58312 (3) | 0.0236 (1) | |
| O1 | 0.5246 (3) | 0.48149 (15) | 0.3573 (4) | 0.0328 (10) | |
| O1W | 0.8553 (3) | 0.53988 (16) | 0.7384 (4) | 0.0470 (13) | |

| O2 | 0.5576 (2) | 0.38174 (14) | 0.5941 (4) | 0.0338 (12) | |
| O2W | 0.7992 (3) | 0.51554 (18) | 0.4499 (5) | 0.0522 (14) | |
| O3 | 0.6299 (3) | 0.59263 (14) | 0.5323 (4) | 0.0318 (10) | |
| O3W | 0.7348 (3) | 0.37860 (16) | 0.4667 (5) | 0.0516 (16) | |
| O4 | 0.6548 (3) | 0.50923 (15) | 0.7970 (4) | 0.0336 (13) | |
| O4W | 0.8127 (3) | 0.40099 (16) | 0.7663 (5) | 0.0518 (16) | |
| N1 | 0.1193 (4) | 0.2246 (2) | 0.5525 (7) | 0.063 (2) | |
| N2 | 0.2428 (3) | 0.5776 (2) | 0.9569 (5) | 0.0432 (16) | |
| C1 | 0.4479 (4) | 0.36950 (19) | 0.5480 (5) | 0.0264 (14) | |
| C2 | 0.4066 (4) | 0.30648 (19) | 0.5946 (5) | 0.0265 (14) | |
| C3 | 0.4840 (4) | 0.2636 (2) | 0.6904 (6) | 0.0334 (16) | |
| C4 | 0.4435 (5) | 0.2104 (2) | 0.7436 (6) | 0.0422 (18) | |
| C5 | 0.3240 (5) | 0.1978 (2) | 0.7016 (7) | 0.0450 (19) | |
| C6 | 0.2491 (4) | 0.2391 (2) | 0.6034 (7) | 0.0410 (18) | |
| C7 | 0.2861 (4) | 0.2928 (2) | 0.5493 (6) | 0.0354 (16) | |
| C8 | 0.5479 (4) | 0.5265 (2) | 0.7622 (5) | 0.0258 (14) | |
| C9 | 0.5114 (4) | 0.5576 (2) | 0.8680 (5) | 0.0266 (14) | |
| C10 | 0.5955 (4) | 0.5888 (2) | 0.9817 (6) | 0.0315 (14) | |
| C11 | 0.5631 (4) | 0.6181 (2) | 1.0799 (6) | 0.0391 (19) | |
| C12 | 0.4470 (4) | 0.6159 (2) | 1.0698 (6) | 0.0410 (19) | |
| C13 | 0.3648 (4) | 0.5835 (2) | 0.9597 (6) | 0.0332 (14) | |
| C14 | 0.3941 (4) | 0.5556 (2) | 0.8575 (6) | 0.0300 (14) | |
| O5W | 0.9028 (5) | 0.6248 (3) | 0.3390 (7) | 0.126 (3) | |
| Cl1 | 0.08111 (11) | 0.07403 (8) | 0.44309 (19) | 0.0593 (6) | |
| Cl2 | 0.93715 (13) | 0.40966 (10) | 0.3509 (2) | 0.0708 (7) | |
| Cl3A | 0.8142 (3) | 0.22254 (14) | 0.4682 (4) | 0.0718 (12) | 0.750 |
| O6WA | 0.0280 (8) | 0.2247 (5) | 0.7815 (11) | 0.081 (4) | 0.720 |
| Cl3B | 0.7983 (15) | 0.2369 (6) | 0.5423 (16) | 0.068 (5) | 0.150 |
| Cl3C | 0.8035 (14) | 0.2679 (7) | 0.731 (3) | 0.076 (8) | 0.100 |
| O6WB | 0.042 (2) | 0.2654 (13) | 0.750 (3) | 0.101 (11) | 0.280 |
| H01 | 0.67440 | 0.58980 | 0.99080 | 0.0380* | |
| H1A | 0.09130 | 0.23580 | 0.61660 | 0.0940* | |
| H1B | 0.10720 | 0.18090 | 0.53370 | 0.0940* | |
| H1C | 0.08210 | 0.24840 | 0.47680 | 0.0940* | |
| H2 | 0.61980 | 0.63960 | 1.15420 | 0.0470* | |
| H02 | 0.42470 | 0.63590 | 1.13640 | 0.0490* | |
| H2A | 0.23900 | 0.54320 | 1.00940 | 0.0650* | |
| H2B | 0.19280 | 0.57050 | 0.87110 | 0.0650* | |
| H2C | 0.22310 | 0.61540 | 0.98840 | 0.0650* | |
| H3 | 0.56510 | 0.27100 | 0.71920 | 0.0400* | |
| H04 | 0.33630 | 0.53550 | 0.78210 | 0.0360* | |
| H4 | 0.49720 | 0.18260 | 0.80860 | 0.0500* | |
| H5 | 0.29540 | 0.16250 | 0.73860 | 0.0540* | |
| H7 | 0.23170 | 0.31980 | 0.48320 | 0.0420* | |
| H11 | 0.92430 | 0.55420 | 0.72050 | 0.0700* | |
| H12 | 0.84330 | 0.56120 | 0.48200 | 0.0790* | |
| H13 | 0.78720 | 0.38670 | 0.42090 | 0.0770* | |
| H14 | 0.79880 | 0.35900 | 0.77100 | 0.0500* | |
| H21 | 0.87730 | 0.53200 | 0.81700 | 0.0700* | |

| | | | | |
|---|---|---|---|---|
| H22 | 0.83660 | 0.47750 | 0.44180 | 0.0790* |
| H23 | 0.74080 | 0.34060 | 0.49470 | 0.0770* |
| H24 | 0.88800 | 0.41770 | 0.81750 | 0.0500* |
| H15W | 0.94470 | 0.63530 | 0.29310 | 0.1890* |
| H25W | 0.86390 | 0.65960 | 0.34420 | 0.1890* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Nd1 | 0.0204 (1) | 0.0285 (1) | 0.0211 (2) | −0.0019 (1) | 0.0066 (1) | −0.0007 (1) |
| O1 | 0.0360 (16) | 0.0417 (17) | 0.019 (2) | −0.0037 (14) | 0.0085 (16) | −0.0053 (16) |
| O1W | 0.0292 (16) | 0.069 (2) | 0.037 (3) | −0.0175 (15) | 0.0057 (18) | −0.0001 (19) |
| O2 | 0.0273 (15) | 0.0316 (16) | 0.040 (3) | −0.0036 (12) | 0.0097 (16) | 0.0021 (15) |
| O2W | 0.064 (2) | 0.054 (2) | 0.052 (3) | −0.0250 (18) | 0.037 (2) | −0.020 (2) |
| O3 | 0.0314 (15) | 0.0278 (15) | 0.031 (2) | −0.0023 (12) | 0.0057 (16) | −0.0001 (14) |
| O3W | 0.073 (2) | 0.0372 (19) | 0.064 (4) | 0.0064 (17) | 0.048 (3) | 0.0026 (19) |
| O4 | 0.0321 (16) | 0.0421 (18) | 0.028 (3) | 0.0005 (13) | 0.0129 (17) | −0.0040 (15) |
| O4W | 0.0349 (17) | 0.047 (2) | 0.056 (4) | 0.0004 (15) | −0.003 (2) | 0.007 (2) |
| N1 | 0.047 (3) | 0.061 (3) | 0.082 (6) | −0.023 (2) | 0.026 (3) | 0.004 (3) |
| N2 | 0.041 (2) | 0.055 (3) | 0.041 (3) | 0.0043 (19) | 0.024 (2) | −0.002 (2) |
| C1 | 0.035 (2) | 0.0224 (19) | 0.025 (3) | −0.0056 (16) | 0.015 (2) | −0.0054 (18) |
| C2 | 0.031 (2) | 0.025 (2) | 0.024 (3) | −0.0044 (16) | 0.011 (2) | −0.0034 (18) |
| C3 | 0.037 (2) | 0.028 (2) | 0.031 (4) | −0.0027 (17) | 0.008 (2) | −0.007 (2) |
| C4 | 0.059 (3) | 0.028 (2) | 0.034 (4) | 0.000 (2) | 0.011 (3) | 0.003 (2) |
| C5 | 0.059 (3) | 0.035 (3) | 0.045 (4) | −0.010 (2) | 0.024 (3) | 0.006 (2) |
| C6 | 0.037 (2) | 0.041 (3) | 0.050 (4) | −0.012 (2) | 0.022 (3) | −0.008 (3) |
| C7 | 0.032 (2) | 0.032 (2) | 0.040 (4) | −0.0040 (18) | 0.011 (2) | 0.000 (2) |
| C8 | 0.032 (2) | 0.0269 (19) | 0.019 (3) | −0.0076 (18) | 0.010 (2) | −0.005 (2) |
| C9 | 0.036 (2) | 0.026 (2) | 0.017 (3) | 0.0001 (17) | 0.009 (2) | 0.0003 (18) |
| C10 | 0.032 (2) | 0.037 (2) | 0.025 (3) | 0.0012 (18) | 0.010 (2) | −0.004 (2) |
| C11 | 0.045 (3) | 0.045 (3) | 0.026 (4) | −0.006 (2) | 0.012 (3) | −0.016 (2) |
| C12 | 0.051 (3) | 0.045 (3) | 0.028 (4) | 0.007 (2) | 0.016 (3) | −0.010 (2) |
| C13 | 0.034 (2) | 0.037 (2) | 0.031 (3) | 0.0070 (19) | 0.015 (2) | 0.003 (2) |
| C14 | 0.034 (2) | 0.033 (2) | 0.021 (3) | −0.0010 (18) | 0.008 (2) | −0.001 (2) |
| O5W | 0.140 (5) | 0.124 (5) | 0.118 (7) | 0.037 (4) | 0.052 (5) | 0.024 (5) |
| Cl1 | 0.0401 (7) | 0.0667 (9) | 0.0549 (13) | −0.0080 (6) | −0.0009 (8) | 0.0083 (8) |
| Cl2 | 0.0441 (8) | 0.1218 (14) | 0.0541 (14) | −0.0135 (8) | 0.0270 (9) | −0.0161 (11) |
| Cl3A | 0.0611 (13) | 0.0457 (14) | 0.099 (3) | −0.0090 (11) | 0.0190 (19) | 0.0111 (15) |
| O6WA | 0.058 (4) | 0.129 (8) | 0.060 (7) | 0.000 (5) | 0.027 (5) | −0.006 (6) |
| Cl3B | 0.093 (10) | 0.023 (5) | 0.056 (11) | 0.000 (5) | −0.008 (9) | 0.007 (5) |
| Cl3C | 0.071 (10) | 0.042 (8) | 0.12 (2) | 0.013 (7) | 0.042 (12) | 0.001 (9) |
| O6WB | 0.086 (15) | 0.15 (2) | 0.07 (2) | 0.007 (16) | 0.034 (14) | 0.029 (18) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Nd1—O1 | 2.411 (4) | N1—H1A | 0.8900 |
| Nd1—O1W | 2.506 (4) | N2—H2A | 0.8900 |
| Nd1—O2 | 2.410 (3) | N2—H2B | 0.8900 |
| Nd1—O2W | 2.510 (4) | N2—H2C | 0.8900 |

| | | | |
|---|---|---|---|
| Nd1—O3 | 2.394 (3) | C1—C2 | 1.498 (6) |
| Nd1—O3W | 2.525 (4) | C2—C3 | 1.384 (7) |
| Nd1—O4 | 2.458 (4) | C2—C7 | 1.389 (7) |
| Nd1—O4W | 2.504 (4) | C3—C4 | 1.371 (7) |
| Nd1—O1<sup>i</sup> | 2.886 (4) | C4—C5 | 1.375 (9) |
| O1—C8<sup>i</sup> | 1.246 (6) | C5—C6 | 1.365 (8) |
| O2—C1 | 1.262 (6) | C6—C7 | 1.362 (7) |
| O3—C1<sup>i</sup> | 1.255 (6) | C8—C9 | 1.479 (7) |
| O4—C8 | 1.260 (6) | C9—C14 | 1.391 (8) |
| O1W—H11 | 0.9700 | C9—C10 | 1.394 (7) |
| O1W—H21 | 0.7800 | C10—C11 | 1.366 (8) |
| O2W—H12 | 1.0400 | C11—C12 | 1.378 (8) |
| O2W—H22 | 0.9000 | C12—C13 | 1.374 (8) |
| O3W—H23 | 0.8000 | C13—C14 | 1.370 (8) |
| O3W—H13 | 0.9500 | C3—H3 | 0.9300 |
| O4W—H14 | 0.8600 | C4—H4 | 0.9300 |
| O4W—H24 | 0.9300 | C5—H5 | 0.9300 |
| O5W—H25W | 0.8500 | C7—H7 | 0.9300 |
| O5W—H15W | 0.8500 | C10—H01 | 0.9300 |
| N1—C6 | 1.494 (8) | C11—H2 | 0.9300 |
| N2—C13 | 1.479 (7) | C12—H02 | 0.9300 |
| N1—H1C | 0.8900 | C14—H04 | 0.9300 |
| N1—H1B | 0.8900 | | |
| O1—Nd1—O1W | 141.27 (11) | C6—N1—H1C | 109.00 |
| O1—Nd1—O2 | 79.67 (12) | C6—N1—H1A | 110.00 |
| O1—Nd1—O2W | 80.61 (14) | C6—N1—H1B | 109.00 |
| O1—Nd1—O3 | 72.82 (12) | H1A—N1—H1B | 109.00 |
| O1—Nd1—O3W | 78.87 (13) | H1B—N1—H1C | 109.00 |
| O1—Nd1—O4 | 125.33 (13) | H1A—N1—H1C | 110.00 |
| O1—Nd1—O4W | 145.66 (11) | H2B—N2—H2C | 110.00 |
| O1—Nd1—O1<sup>i</sup> | 78.04 (12) | H2A—N2—H2B | 109.00 |
| O1W—Nd1—O2 | 138.75 (12) | C13—N2—H2A | 109.00 |
| O1W—Nd1—O2W | 70.36 (14) | C13—N2—H2B | 109.00 |
| O1W—Nd1—O3 | 74.80 (12) | H2A—N2—H2C | 109.00 |
| O1W—Nd1—O3W | 112.16 (13) | C13—N2—H2C | 110.00 |
| O1W—Nd1—O4 | 68.64 (13) | O2—C1—C2 | 118.2 (4) |
| O1W—Nd1—O4W | 69.11 (12) | O2—C1—O3<sup>i</sup> | 124.5 (4) |
| O1<sup>i</sup>—Nd1—O1W | 108.03 (11) | O3<sup>i</sup>—C1—C2 | 117.4 (4) |
| O2—Nd1—O2W | 139.79 (12) | C3—C2—C7 | 118.2 (4) |
| O2—Nd1—O3 | 131.34 (12) | C1—C2—C3 | 122.1 (5) |
| O2—Nd1—O3W | 72.96 (12) | C1—C2—C7 | 119.5 (4) |
| O2—Nd1—O4 | 83.30 (12) | C2—C3—C4 | 121.4 (5) |
| O2—Nd1—O4W | 74.50 (12) | C3—C4—C5 | 120.5 (5) |
| O1<sup>i</sup>—Nd1—O2 | 68.41 (9) | C4—C5—C6 | 117.4 (5) |
| O2W—Nd1—O3 | 73.81 (13) | N1—C6—C5 | 118.2 (5) |
| O2W—Nd1—O3W | 69.04 (12) | N1—C6—C7 | 118.2 (5) |
| O2W—Nd1—O4 | 136.16 (13) | C5—C6—C7 | 123.7 (5) |

| | | | |
|---|---|---|---|
| O2W—Nd1—O4W | 105.19 (14) | C2—C7—C6 | 118.8 (5) |
| O1$^i$—Nd1—O2W | 139.46 (11) | O1$^i$—C8—O4 | 121.5 (5) |
| O3—Nd1—O3W | 136.17 (14) | O1$^i$—C8—C9 | 120.9 (5) |
| O3—Nd1—O4 | 81.11 (12) | O4—C8—C9 | 117.6 (4) |
| O3—Nd1—O4W | 141.52 (13) | C10—C9—C14 | 118.9 (5) |
| O1$^i$—Nd1—O3 | 67.12 (11) | C8—C9—C14 | 121.2 (4) |
| O3W—Nd1—O4 | 142.60 (12) | C8—C9—C10 | 120.0 (5) |
| O3W—Nd1—O4W | 72.23 (14) | C9—C10—C11 | 120.7 (5) |
| O1$^i$—Nd1—O3W | 137.75 (11) | C10—C11—C12 | 120.5 (5) |
| O4—Nd1—O4W | 73.83 (13) | C11—C12—C13 | 118.8 (5) |
| O1$^i$—Nd1—O4 | 47.46 (12) | N2—C13—C14 | 120.5 (5) |
| O1$^i$—Nd1—O4W | 111.90 (12) | C12—C13—C14 | 122.0 (5) |
| Nd1—O1—Nd1$^i$ | 101.96 (13) | N2—C13—C12 | 117.6 (5) |
| Nd1—O1—C8$^i$ | 169.3 (3) | C9—C14—C13 | 119.2 (5) |
| Nd1$^i$—O1—C8$^i$ | 85.2 (3) | C2—C3—H3 | 119.00 |
| Nd1—O2—C1 | 134.9 (3) | C4—C3—H3 | 119.00 |
| Nd1—O3—C1$^i$ | 142.0 (3) | C5—C4—H4 | 120.00 |
| Nd1—O4—C8 | 105.5 (3) | C3—C4—H4 | 120.00 |
| H11—O1W—H21 | 107.00 | C4—C5—H5 | 121.00 |
| Nd1—O1W—H11 | 128.00 | C6—C5—H5 | 121.00 |
| Nd1—O1W—H21 | 117.00 | C6—C7—H7 | 121.00 |
| H12—O2W—H22 | 123.00 | C2—C7—H7 | 121.00 |
| Nd1—O2W—H22 | 102.00 | C9—C10—H01 | 120.00 |
| Nd1—O2W—H12 | 115.00 | C11—C10—H01 | 120.00 |
| Nd1—O3W—H23 | 123.00 | C12—C11—H2 | 120.00 |
| H13—O3W—H23 | 111.00 | C10—C11—H2 | 120.00 |
| Nd1—O3W—H13 | 118.00 | C11—C12—H02 | 121.00 |
| Nd1—O4W—H24 | 117.00 | C13—C12—H02 | 121.00 |
| H14—O4W—H24 | 119.00 | C9—C14—H04 | 120.00 |
| Nd1—O4W—H14 | 123.00 | C13—C14—H04 | 120.00 |
| H15W—O5W—H25W | 108.00 | | |
| O1W—Nd1—O1—Nd1$^i$ | −103.98 (19) | O4W—Nd1—O4—C8 | −146.0 (3) |
| O2—Nd1—O1—Nd1$^i$ | 69.90 (11) | O1$^i$—Nd1—O4—C8 | −3.6 (2) |
| O2W—Nd1—O1—Nd1$^i$ | −145.32 (12) | Nd1—O1$^i$—C8—C9 | 173.3 (4) |
| O3—Nd1—O1—Nd1$^i$ | −69.49 (12) | Nd1—O1$^i$—C8—O4 | −5.9 (4) |
| O3W—Nd1—O1—Nd1$^i$ | 144.37 (13) | Nd1—O2—C1—O3$^i$ | 6.6 (8) |
| O4—Nd1—O1—Nd1$^i$ | −4.17 (16) | Nd1—O2—C1—C2 | −171.7 (3) |
| O4W—Nd1—O1—Nd1$^i$ | 111.5 (2) | Nd1$^i$—O3$^i$—C1—C2 | 142.4 (4) |
| O1$^i$—Nd1—O1—Nd1$^i$ | 0.00 (9) | Nd1$^i$—O3$^i$—C1—O2 | −35.9 (9) |
| O1$^i$—Nd1$^i$—O1—Nd1 | 0.00 (11) | Nd1—O4—C8—O1$^i$ | 7.1 (5) |
| O1W$^i$—Nd1$^i$—O1—Nd1 | −140.33 (11) | Nd1—O4—C8—C9 | −172.1 (3) |
| O2$^i$—Nd1$^i$—O1—Nd1 | 83.50 (13) | O3$^i$—C1—C2—C7 | −0.6 (7) |
| O2W$^i$—Nd1$^i$—O1—Nd1 | −59.7 (2) | O2—C1—C2—C7 | 177.8 (5) |
| O3$^i$—Nd1$^i$—O1—Nd1 | −76.21 (13) | O2—C1—C2—C3 | 3.0 (7) |

| | | | |
|---|---|---|---|
| O3W$^i$—Nd1$^i$—O1—Nd1 | 58.2 (2) | O3$^i$—C1—C2—C3 | −175.4 (5) |
| O4$^i$—Nd1$^i$—O1—Nd1 | −175.39 (17) | C1—C2—C3—C4 | 172.4 (5) |
| O4W$^i$—Nd1$^i$—O1—Nd1 | 145.54 (12) | C1—C2—C7—C6 | −173.3 (5) |
| O1—Nd1—O2—C1 | −36.4 (4) | C7—C2—C3—C4 | −2.4 (8) |
| O1W—Nd1—O2—C1 | 137.8 (4) | C3—C2—C7—C6 | 1.7 (7) |
| O2W—Nd1—O2—C1 | −98.2 (5) | C2—C3—C4—C5 | 0.7 (8) |
| O3—Nd1—O2—C1 | 19.5 (5) | C3—C4—C5—C6 | 1.6 (8) |
| O3W—Nd1—O2—C1 | −117.8 (5) | C4—C5—C6—N1 | 177.7 (5) |
| O4—Nd1—O2—C1 | 91.4 (4) | C4—C5—C6—C7 | −2.4 (9) |
| O4W—Nd1—O2—C1 | 166.5 (5) | C5—C6—C7—C2 | 0.7 (9) |
| O1$^i$—Nd1—O2—C1 | 44.7 (4) | N1—C6—C7—C2 | −179.3 (5) |
| O1—Nd1—O3—C1$^i$ | 15.9 (5) | O4—C8—C9—C10 | 23.0 (6) |
| O1W—Nd1—O3—C1$^i$ | 174.4 (6) | O1$^i$—C8—C9—C14 | 24.7 (6) |
| O2—Nd1—O3—C1$^i$ | −42.6 (6) | O4—C8—C9—C14 | −156.1 (4) |
| O2W—Nd1—O3—C1$^i$ | 100.9 (6) | O1$^i$—C8—C9—C10 | −156.2 (4) |
| O3W—Nd1—O3—C1$^i$ | 68.0 (6) | C8—C9—C10—C11 | 179.6 (4) |
| O4—Nd1—O3—C1$^i$ | −115.5 (6) | C14—C9—C10—C11 | −1.3 (7) |
| O4W—Nd1—O3—C1$^i$ | −165.0 (5) | C8—C9—C14—C13 | 178.3 (4) |
| O1$^i$—Nd1—O3—C1$^i$ | −68.1 (6) | C10—C9—C14—C13 | −0.8 (6) |
| O1—Nd1—O4—C8 | 2.0 (3) | C9—C10—C11—C12 | 1.5 (7) |
| O1W—Nd1—O4—C8 | 140.5 (3) | C10—C11—C12—C13 | 0.3 (7) |
| O2—Nd1—O4—C8 | −70.3 (3) | C11—C12—C13—N2 | 175.6 (4) |
| O2W—Nd1—O4—C8 | 118.7 (3) | C11—C12—C13—C14 | −2.5 (7) |
| O3—Nd1—O4—C8 | 63.5 (3) | N2—C13—C14—C9 | −175.3 (4) |
| O3W—Nd1—O4—C8 | −120.5 (3) | C12—C13—C14—C9 | 2.7 (7) |

Symmetry codes: (i) −x+1, −y+1, −z+1.

*Hydrogen-bond geometry (Å, °)*

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| N1—H1A⋯O6WA | 0.89 | 2.16 | 3.007 (12) | 160 |
| N1—H1B⋯Cl1 | 0.89 | 2.30 | 3.174 (5) | 168 |
| N1—H1C⋯O6WA$^{ii}$ | 0.89 | 1.98 | 2.828 (12) | 159 |
| N2—H2A⋯O4$^{iii}$ | 0.89 | 2.22 | 2.967 (6) | 141 |
| N2—H2B⋯Cl2$^i$ | 0.89 | 2.31 | 3.166 (5) | 161 |
| N2—H2C⋯Cl3A$^{iv}$ | 0.89 | 2.26 | 3.129 (5) | 167 |
| O1W—H11⋯Cl2$^v$ | 0.97 | 2.21 | 3.170 (4) | 172 |
| O2W—H12⋯O5W | 1.04 | 2.28 | 2.960 (7) | 121 |
| O2W—H12⋯Cl2$^v$ | 1.04 | 2.65 | 3.443 (5) | 132 |
| O3W—H13⋯Cl2 | 0.95 | 2.26 | 3.190 (5) | 169 |
| O4W—H14⋯Cl3A$^{vi}$ | 0.86 | 2.58 | 3.240 (5) | 134 |
| O5W—H15W⋯Cl1$^{vii}$ | 0.85 | 2.68 | 3.208 (7) | 122 |
| O1W—H21⋯Cl1$^{iv}$ | 0.78 | 2.52 | 3.215 (4) | 148 |
| O2W—H22⋯Cl2 | 0.90 | 2.26 | 3.104 (4) | 156 |
| O3W—H23⋯Cl3A | 0.80 | 2.56 | 3.244 (4) | 144 |

| | | | | |
|---|---|---|---|---|
| O4W—H24···Cl1<sup>viii</sup> | 0.93 | 2.23 | 3.134 (5) | 163 |
| O5W—H25W···N1<sup>i</sup> | 0.85 | 2.52 | 3.247 (8) | 144 |
| C10—H01···Cl1<sup>iv</sup> | 0.93 | 2.81 | 3.724 (6) | 169 |
| C14—H04···O2W<sup>i</sup> | 0.93 | 2.59 | 3.504 (7) | 170 |

Symmetry codes: (ii) $x$, $-y+1/2$, $z-1/2$; (iii) $-x+1$, $-y+1$, $-z+2$; (i) $-x+1$, $-y+1$, $-z+1$; (iv) $-x+1$, $y+1/2$, $-z+3/2$; (v) $-x+2$, $-y+1$, $-z+1$; (vi) $x$, $-y+1/2$, $z+1/2$; (vii) $-x+1$, $y+1/2$, $-z+1/2$; (viii) $x+1$, $-y+1/2$, $z+1/2$.

*Table 2*
*Table 2 π-π stacking interactions (Å)*

Cg1 is the centroid of the C9—C14 ring.

| CgI | CgJ | CgI···CgJ<sup>a</sup> | CgI···P(J)<sup>b</sup> | CgJ···P(I)<sup>c</sup> | Slippage |
|---|---|---|---|---|---|
| Cg1 | Cg1<sup>ii</sup> | 3.499 (2) | 3.2720 (18) | 3.2721 (18) | 1.240 |

Symmetry code: (ii) 1-x,1-y,2-z. Notes: (a) Distance between centroids; (b) Perpendicular distance of CgI on ring plan J; (c) Perpendicular distance of CgJ on ring plan I. Slippage = vertical displacement between ring centroids.
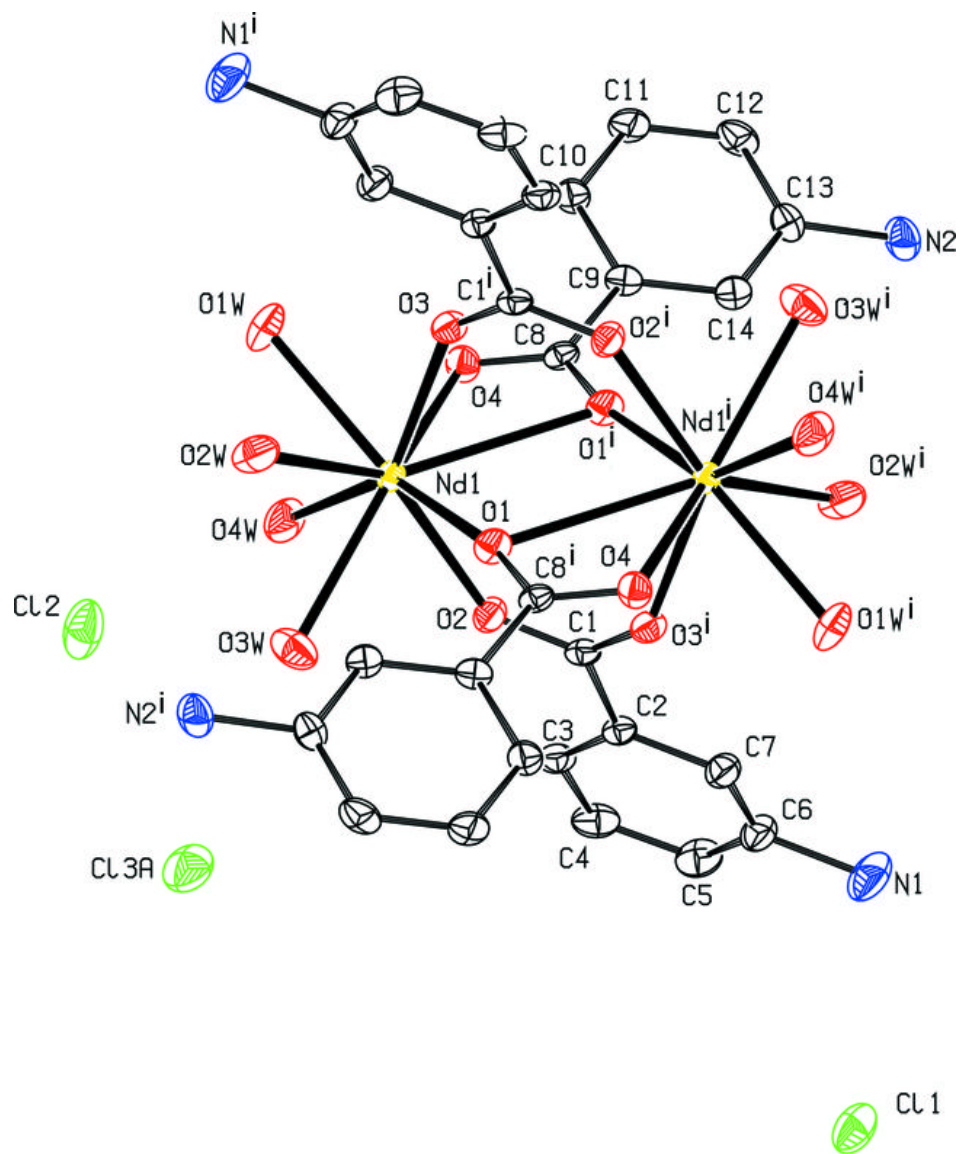
**Fig. 1**

**Fig. 2**