metal-organic papers

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Nonaaquaneodymium(III) trichloride bis(1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane tetrahydrate

The crystal structure of the title compound, [Nd(H$_2$O)$_9$]Cl$_3$·2C$_6$H$_{12}$N$_4$·4H$_2$O, is the first neodymium chloride complex with a cage adamanzane without any chloride ion in the lanthanide coordination sphere. The Nd—O distances range from 2.4425 (17) to 2.5635 (18) Å, and the neodymium ion has the coordination geometry of a capped square antiprism distorted toward a tricapped trigonal prism. The cations, [Nd(H$_2$O)$_9$]$^{3+}$, are connected *via* hydrogen bonds to hexamethylenetetramine molecules, water molecules and chloride ions.

Comment

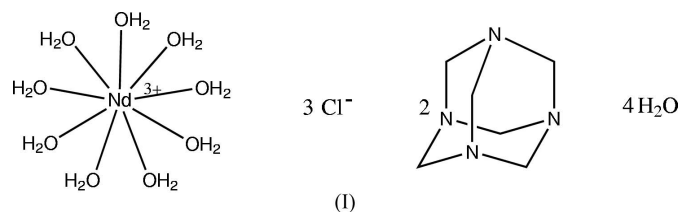The 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane known as hexamethylenetetramine (hmt) is the smallest member of the tricyclic tetramines, so-called cage adamanzanes (Springborg, 2003). It can act as a monofunctional (Ganesh, Radha *et al.*, 1990; Zhang *et al.*, 1999; Banerjee *et al.*, 2003; Zhu *et al.*, 2003), bifunctional (Batten *et al.*, 1998; Tong *et al.*, 2000*a*; Zhang *et al.*, 2000), trifunctional (Hill *et al.*, 1993; Bertelli *et al.*, 1997; Zheng *et al.*, 2003) and tetrafunctional ligand (Hill *et al.*, 1993; Bertelli *et al.*, 1997; Tong *et al.*, 2000*b*). However, in complexes containing water of crystallization, hmt usually does not form bonds with the central metal. These complexes exhibit interesting stereochemical properties depending on the ligand concentration and temperature.

(I)

We present here the crystal structure of [Nd(H$_2$O)$_9$]Cl$_3$·2C$_6$H$_{12}$N$_4$·4H$_2$O, in which hmt is not coordinated to Nd (Fig. 1). One chloride ion (Cl3/Cl4) and one water molecule (indicated by O3′ and O4′) are disordered over two sites.

Each hexamethylenetetramine molecule is linked to four different [Nd(H$_2$O)$_9$]$^{3+}$ cations and each [Nd(H$_2$O)$_9$]$^{3+}$ unit is linked to seven hmt molecules through O—H···N hydrogen bonds (Table 2). Moreover, the independent water molecules (not coordinated to the central atom) and the chloride anions form a number of O—H···O and O—H···Cl hydrogen bonds (Table 2) (Desiraju & Steiner, 1999). The Nd—O distances range from 2.4425 (17) to 2.5635 (18) Å and lie in the normal range of lanthanide–oxygen bond lengths (2.387–2.686 Å) in nine-coordinated neodymium compounds. The trivalent neodymium ion has the coordination geometry of a capped
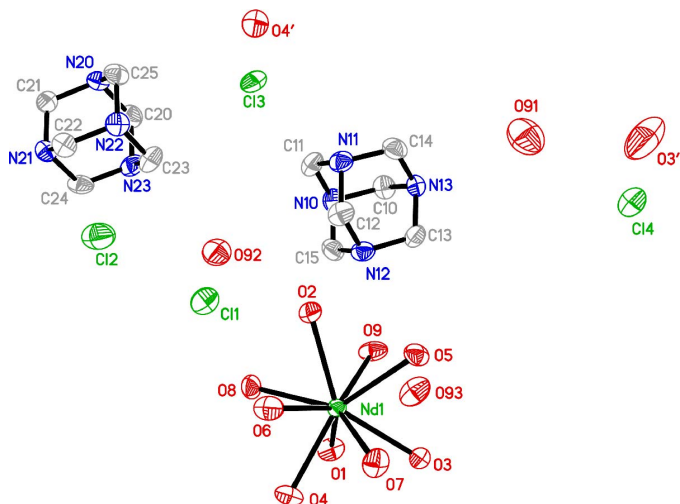
Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. The H atoms have been omitted for clarity.
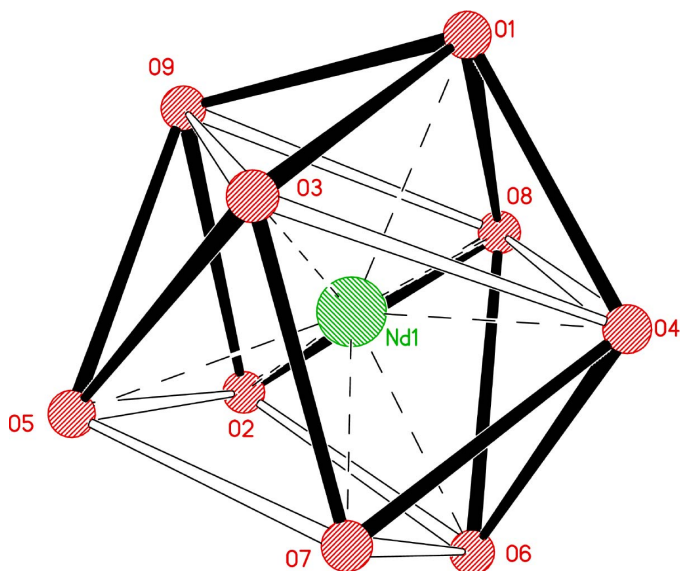

Figure 2
The coordination polyhedron around the central Nd atom.

square antiprism (Fig. 2), slightly distorted toward a tricapped trigonal prism. The C—N bond lengths in the hmt molecules lie in the range 1.461 (3)–1.481 (4) Å; the average C—N—C and N—C—N angles are 108.2 (3) and 111.9 (3)°, respectively, which is in good agreement with those found by Terpstra & Craven (1993).

The description of the coordination sphere was confirmed by a bond-valence sum calculation (Brown, 2002). A total valence of 2.93 v.u. for neodymium was obtained using the calculated bond-valence parameter of 2.086 Å (Trzesowska et al., 2004). According to Palenik (2003), the difference between the observed and expected values larger than 0.25–0.30 v.u. is a reasonable guide to those structural studies that should be examined in more detail because of possible errors.

The structure of (I) is novel in the following respect: the title compound is the first example of a neodymium complex with adamanzane without any chloride ion bonded directly to the lanthanide ion. There are only three lanthanide (Ln) structures with chloride anions and N-donor ligands in the outer coordination sphere [4,4'-bipyridyl (Bukowska-Strzyżewska & Tosik, 1982), o-phenanthroline (Xianglin & Jialie, 1984) and 2,2':6',2''-terpyridine (Kepert et al., 1994)] in the Cambridge Structural Database (Version 5.26 of 2004; Allen, 2002). The most numerous group are the lanthanide structures, which usually do not include polar solvents and which have chloride ions bonded only to the Ln cation. Compound (I) is similar to the previously published isostructural hydrated metal chloride complex compounds of cobalt(II) (Ganesh, Seshasayee et al., 1990), magnesium(II) (Kovacs & Mazzarella, 1966) and nickel(II) (Kokunov et al., 2002). Owing to the smaller ionic radii, all the central atoms are six-coordinate. The number of water molecules in the outer coordination sphere is constant in previously published compounds and in the present lanthanide complex.

Experimental

The title compound was obtained by reaction of hydrated neodymium chloride (2.15 g, 1 mmol) with hexamethylenetetraamine (2.8 g, 2 mmol) in water. The solution was stirred at room temperature and left to crystallize at 278 K. The pale-violet crystals of (I) obtained after several days were removed from the solution, sealed in glass capillaries and used for data collection. Because the crystals tended to decompose, we tried to record a data set at lower temperature, but upon cooling the crystals always broke.

Crystal data

$[Nd(H_2O)_9]Cl_3 \cdot 2C_6H_{12}N_4 \cdot 4H_2O$	$Z = 2$
$M_r = 765.19$	$D_x = 1.638$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.8155$ (6) Å	Cell parameters from 99
$b = 11.7230$ (9) Å	reflections
$c = 14.0699$ (12) Å	$\theta = 2$–25°
$\alpha = 85.964$ (6)°	$\mu = 2.00$ mm^{-1}
$\beta = 76.178$ (6)°	$T = 293$ (2) K
$\gamma = 80.879$ (6)°	Prism, pale violet
$V = 1551.3$ (2) Å^3	$0.56 \times 0.28 \times 0.24$ mm

Data collection

Kuma KM-4 diffractometer	$R_{int} = 0.021$
ω–2θ scans	$\theta_{max} = 27.6°$
Absorption correction: numerical	$h = -12 \rightarrow 0$
(X-RED; Stoe & Cie (1999)	$k = -15 \rightarrow 15$
$T_{min} = 0.381$, $T_{max} = 0.683$	$l = -18 \rightarrow 17$
7597 measured reflections	3 standard reflections
7179 independent reflections	every 100 reflections
6791 reflections with $I > 2\sigma(I)$	intensity decay: 43.7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$+ 1.1931P]$
$wR(F^2) = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.002$
7179 reflections	$\Delta\rho_{max} = 1.77$ e Å^{-3}
354 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
H-atom parameters constrained	Extinction correction: none

Table 1
Selected geometric parameters (Å, °).

Nd1—O4	2.4425 (17)	Nd1—O7	2.5285 (18)
Nd1—O8	2.4442 (18)	Nd1—O5	2.5428 (18)
Nd1—O9	2.4624 (18)	Nd1—O6	2.5542 (18)
Nd1—O3	2.4887 (18)	Nd1—O1	2.5635 (18)
Nd1—O2	2.5069 (18)		
O4—Nd1—O8	76.98 (6)	O3—Nd1—O5	74.30 (6)
O4—Nd1—O9	135.64 (7)	O2—Nd1—O5	67.44 (6)
O8—Nd1—O9	84.62 (7)	O7—Nd1—O5	69.88 (6)
O4—Nd1—O3	88.06 (7)	O4—Nd1—O6	71.35 (7)
O8—Nd1—O3	137.46 (7)	O8—Nd1—O6	76.79 (7)
O9—Nd1—O3	78.84 (6)	O9—Nd1—O6	142.38 (6)
O4—Nd1—O2	133.31 (7)	O3—Nd1—O6	135.52 (6)
O8—Nd1—O2	71.32 (7)	O2—Nd1—O6	68.69 (7)
O9—Nd1—O2	74.48 (7)	O7—Nd1—O6	67.54 (7)
O3—Nd1—O2	138.05 (6)	O5—Nd1—O6	98.57 (7)
O4—Nd1—O7	73.24 (7)	O4—Nd1—O1	68.03 (7)
O8—Nd1—O7	139.09 (7)	O8—Nd1—O1	70.10 (7)
O9—Nd1—O7	136.20 (7)	O9—Nd1—O1	67.80 (7)
O3—Nd1—O7	68.89 (7)	O3—Nd1—O1	67.37 (6)
O2—Nd1—O7	111.25 (7)	O2—Nd1—O1	127.53 (7)
O4—Nd1—O5	142.78 (6)	O7—Nd1—O1	121.22 (7)
O8—Nd1—O5	137.04 (6)	O5—Nd1—O1	129.38 (7)
O9—Nd1—O5	73.48 (7)	O6—Nd1—O1	131.95 (7)

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1A⋯Cl3[i]	0.85	2.63	3.333 (3)	141
O1—H1A⋯O3′[vii]	0.85	2.09	2.835 (11)	146
O1—H1B⋯N10[i]	0.87	2.05	2.910 (3)	170
O2—H2A⋯O92[iii]	0.85	2.08	2.818 (3)	144
O2—H2A⋯O5	0.85	2.39	2.803 (3)	111
O2—H2B⋯O92	0.85	1.98	2.811 (3)	165
O3—H3A⋯N21[iv]	0.85	1.97	2.762 (3)	154
O3—H3B⋯Cl3[v]	0.83	2.35	3.155 (3)	163
O3—H3B⋯Cl4[vi]	0.83	2.64	3.192 (3)	126
O4—H4A⋯O91[ii]	0.88	1.92	2.781 (3)	167
O4—H4B⋯N20[v]	1.04	1.80	2.771 (3)	155
O5—H5A⋯Cl2[iii]	0.88	2.46	3.326 (2)	165
O5—H5B⋯N22[iii]	0.88	1.97	2.846 (3)	174
O6—H6A⋯Cl2[vii]	0.92	2.34	3.248 (2)	172
O6—H6B⋯N11[iii]	0.87	2.08	2.932 (3)	166
O7—H7A⋯O4[iii]	0.87	1.94	2.817 (6)	175
O7—H7B⋯O4′[v]	0.90	2.16	3.060 (6)	174
O7—H7A⋯Cl4[viii]	0.87	2.35	3.198 (3)	162
O7—H7B⋯Cl4[vi]	0.90	2.16	3.019 (3)	159
O8—H8A⋯N13[viii]	0.91	1.86	2.758 (3)	168
O8—H8B⋯Cl1	0.91	2.24	3.118 (2)	162
O9—H9A⋯N12	0.85	2.11	2.806 (3)	139
O9—H9B⋯O93	0.90	1.87	2.774 (3)	173
O91—H91A⋯Cl1[iii]	0.83	2.37	3.190 (3)	174
O91—H91B⋯Cl3[ix]	0.92	2.35	3.252 (4)	164
O91—H91B⋯O3′	0.92	2.05	2.950 (10)	163
O92—H92A⋯Cl2	0.73	2.34	3.061 (3)	170
O92—H92B⋯Cl1	0.68	2.42	3.104 (2)	174
O93—H93A⋯Cl1[i]	0.80	2.35	3.150 (3)	173
O93—H93B⋯N23[i]	0.86	2.15	2.968 (3)	160
C20—H20A⋯Cl3	0.96	2.82	3.731 (4)	158
C21—H21B⋯Cl2[x]	0.96	2.80	3.673 (3)	151

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

All C-bound H atoms were placed in calculated positions (C—H = 0.96 Å) and were refined using a riding model, with U_{iso}(H) values equal to 1.5U_{eq}(C). The H atoms bonded to the ordered O atoms were found in a difference Fourier synthesis and were also refined using a riding model, with U_{iso}(H) values equal to 1.5U_{eq}(O). Because of the small occupation factors of the disordered water molecule, its H atoms cannot be reliably located. At the end of the refinement, the highest peak in the difference Fourier synthesis is at $x = 0.204$, $y = 0.755$, $z = 0.224$. The next peak is distinctly smaller (0.97 e Å^{-3}). In addition, around the above-mentioned position exists a solvent-accessible area. Thus, it can be stated that there exists one partially occupied (by about 0.2 water molecules) site. Because it is both crystallographically and chemically meaningless, this molecule was not included in the refinement.

Data collection: *KM-4 Software* (Kuma, 1993); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990b) *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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