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1,4-Diazoniabicyclo[2.2.2]octane triaquatrichloronickelate(II) chloride monohydrate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.075
Data-to-parameter ratio = 21.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_6H_{14}N_2)[NiCl_3(H_2O)_3]Cl\cdot H_2O$, contains doubly protonated 1,4-diazoniabicyclo[2.2.2]octane (dabconium) $(C_6H_{14}N_2)^{2+}$ cations, *mer*-$[Ni^{II}(H_2O)_3Cl_3]^-$ octahedra, [mean Ni—O = 2.054 (2) Å and mean Ni—Cl = 2.4272 (6) Å] and additional (non-coordinated) chloride ions and water molecules. These species interact by way of numerous O—H···O, O—H···Cl and N—H···Cl hydrogen bonds and possible C—H···Cl interactions [mean H···Cl = 2.75 Å, mean C···Cl = 3.575 (3) Å and mean C—H···Cl = 142°] to result in a structure with a layered character. $(C_6H_{14}N_2)[Ni(H_2O)_3Cl_3]Cl\cdot H_2O$ is isostructural with its manganese(II)-containing congener.

Comment

The title compound, (I) (Fig. 1), arose as a by-product during synthetic investigations of organically templated nickel(II) phosphate networks (Guillou *et al.*, 2001). Compound (I) is isostructural with $(C_6H_{14}N_2)[Mn(H_2O)_3X_3]X\cdot H_2O$ (X = Cl and Br) as described by Feist *et al.* (1997). Related compounds built up from $(C_6H_{14}N_2)^{2+}$ 1,4-diazoniabicyclo[2.2.2]octane (dabconium) cations, metal-chloride/water polyhedra, and 'extra' (non-coordinated) chloride ions include $(C_6H_{14}N_2)$-$[Cu(H_2O)_2Cl_3]Cl\cdot H_2O$ (Wei & Willett, 1996), containing trigonal bipyramidal $[Cu^{II}(H_2O)_2Cl_3]^-$ groupings, and $(C_6H_{14}N_2)[Fe(H_2O)_2Cl_4]Cl$ (James *et al.*, 2001), containing *trans*-$[Fe^{III}(H_2O)_2Cl_4]^-$ octahedra. The structures, spectroscopic properties and thermal behaviour of these types of materials have been reviewed by Bentrup *et al.* (1999).

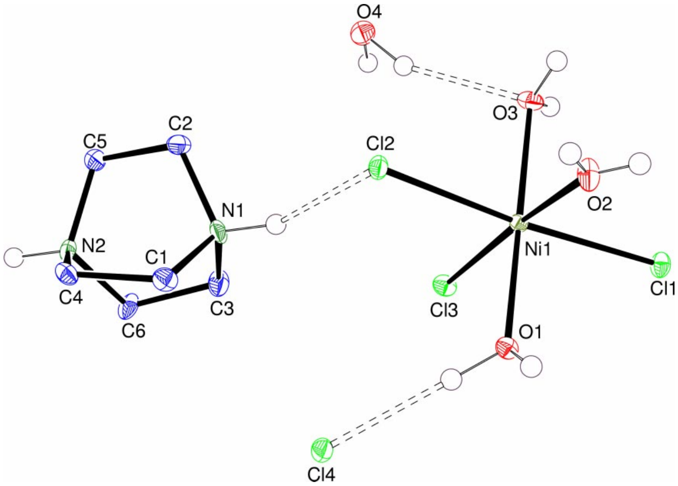
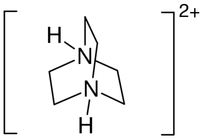


Figure 1
The asymmetric unit of (I) (50% displacement ellipsoids). H atoms are shown as arbitrary spheres and H atoms attached to C atoms have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.



· $[Ni(H_2O)_3Cl_3]$ · Cl · H_2O

(I)

In (I) (Fig. 1 and Table 1), three water molecules [Ni—O = 2.054 (2) Å] and three chloride ions [mean Ni—Cl = 2.4272 (6) Å] surround the nickel(II) cation in meridional (*mer*) conformation [spread of *cis* bond angles is 86.47 (5)–95.36 (5)°]. The dabconium cation has typical (Bremner & Harrison, 2003) geometrical parameters [mean N—C = 1.502 (3) Å, mean C—C = 1.532 (3) Å, mean C—N—C = 109.6 (2)° and mean N—C—C = 108.1 (2)°]. In addition, an uncoordinated water molecule (O4) and chloride ion (Cl4) are present in the structure.

The component species in (I) interact by way of an extensive network of O—H···O, O—H···Cl, N—H···Cl and bifurcated N—H···(Cl,Cl) hydrogen bonds and possible C—H···Cl interactions (Table 2). This results in sheets of stoichiometry $\{[Ni(H_2O)_3Cl_3]Cl{\cdot}H_2O\}^{2-}$ propagating in the (001) plane (Fig. 2). The $[Ni(H_2O)_3Cl_3]^-$ moieties interact in the [100] direction by way of interoctahedral O3—H8···Cl3^{ii} bonds and a pair of unusual O2—H5···Cl4^{ii}···H4^{ii}—O1^{ii} and O2—H6···O4^{iii}—H10^{iii}···O1^{ii} bonds, which connect adjacent octahedra *via* the non-coordinated Cl4 and O4 (water) species, respectively. Crosslinking in the [010] direction is provided by O1—H3···Cl3^{i} O3—H7···Cl4^{iv}, and O4—H9···Cl2 bonds (see Table 2 for the acceptor-atom symmetry codes). Thus, atom Cl4 accepts three conventional O—H···Cl hydrogen bonds [mean H···Cl4 = 2.20 Å, mean O···Cl4 = 3.094 (2) Å and mean O—H···Cl4 = 172°] in very asymmetric, roughly pyramidal, coordination.

The organic species serves to bridge the $\{[Ni(H_2O)_3Cl_3)]Cl{\cdot}H_2O\}^{2-}$ sheets in the [001] direction. One N/H group makes a simple N1—H1···Cl2 link, and one makes a bifurcated N2—H2···Cl1^{v},Cl3^{v} link (mean Cl1^{v}···H2···Cl3^{v} = 87°; see Table 2 for acceptor-atom symmetry codes). The energetics of N—H···Cl—*M* interactions, and their possible role as synthons in supramolecular chemistry are described in detail by Brammer *et al.* (2002).

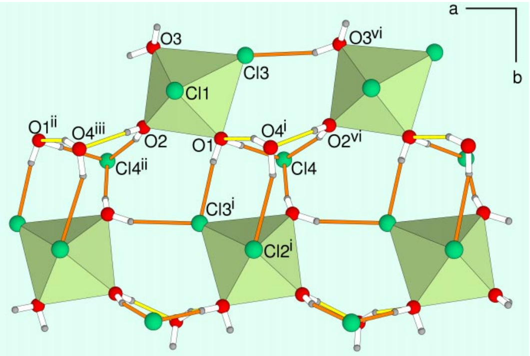


Figure 2
A detail of (I), showing part of an $\{[Ni(H_2O)_3Cl_3]Cl{\cdot}H_2O\}^{2-}$ sheet viewed down [001]. Colour key: $[Ni(H_2O)_3Cl_3)]^-$ octahedra green, Cl atoms green, O atoms red and H atoms grey (all radii arbitrary). The H···*A* portions of the H···O and H···Cl hydrogen bonds are coloured yellow and orange, respectively. Symmetry codes as in Table 2.

A *PLATON* analysis (Spek, 2003) of (I) indicated the presence (Table 2) of a number of C—H···Cl interactions [mean H···Cl = 2.75 Å, mean C···Cl = 3.575 (3) Å and mean C—H···Cl = 142°]. If these are not merely artifacts of the crystal packing, then atom Cl4 accepts no fewer than five of these weak bonds, in addition to the three O—H···Cl4 links, as shown in Fig. 4 (*PLATON* van der Waals radius sum of H and Cl = 2.95 Å; next-nearest Cl4···H contact = 3.23 Å).

Experimental

$NiCl_2$ (10 ml, 1 *M*), H_3PO_4 (10 ml, 1 *M*) and dabco (0.5 g, $C_6H_{12}N_2$) were mixed together in a plastic bottle and heated at 373 K for 24 h, producing a green solution. The solution was cooled to room temperature, and bright-green plate-shaped crystals of (I) grew as water evaporated slowly from the viscous liquors over several weeks.

Crystal data

$(C_6H_{14}N_2)[NiCl_3(H_2O)_3]Cl{\cdot}H_2O$
M_r = 386.77
Orthorhombic, $P2_12_12_1$
a = 6.7019 (1) Å
b = 11.9573 (2) Å
c = 18.0923 (4) Å
V = 1449.86 (5) Å^3
Z = 4
D_x = 1.772 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 6654 reflections
θ = 2.9–27.5°
μ = 2.08 mm^{-1}
T = 120 (2) K
Block, bright green
0.35 × 0.26 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
ω and *φ* scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.517, T_{max} = 0.745
10 211 measured reflections
3303 independent reflections

3224 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 27.5°
h = −8 → 8
k = −15 → 12
l = −23 → 23

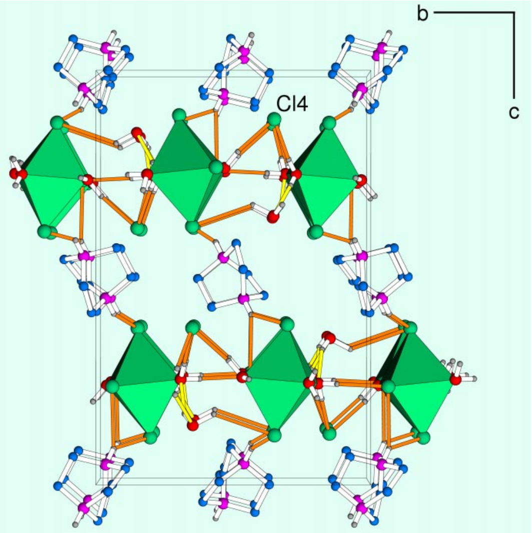


Figure 3
The unit-cell packing in (I), viewed down [100]. Colour key as in Fig. 2; additionally, C atoms blue, N atoms purple. H atoms attached to C atoms have been omitted for clarity.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.3311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$(\Delta/\sigma)_{\rm max} = 0.001$
$wR(F^2) = 0.075$	$\Delta\rho_{\rm max} = 0.44$ e Å^{-3}
$S = 1.15$	$\Delta\rho_{\rm min} = -0.78$ e Å^{-3}
3303 reflections	Absolute structure: Flack (1983), 1395 Friedel pairs
155 parameters	Flack parameter = 0.478 (12)
H-atom parameters constrained	

Table 1
Selected interatomic distances (Å).

Ni1—O1	2.0451 (17)	Ni1—Cl1	2.4127 (6)
Ni1—O2	2.0453 (17)	Ni1—Cl2	2.4178 (6)
Ni1—O3	2.0713 (16)	Ni1—Cl3	2.4512 (6)

Table 2
Hydrogen-bonding and C—H···Cl contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H3···Cl3$^{\rm i}$	0.86	2.26	3.1231 (17)	174
O1—H4···Cl4	0.94	2.14	3.0817 (18)	179
O2—H5···Cl4$^{\rm ii}$	0.82	2.33	3.1392 (18)	168
O2—H6···O4$^{\rm iii}$	0.74	2.08	2.815 (3)	177
O3—H7···Cl4$^{\rm iv}$	0.95	2.12	3.0623 (17)	168
O3—H8···Cl3$^{\rm ii}$	0.91	2.50	3.3833 (17)	163
O4—H9···O3	1.02	2.10	3.036 (2)	152
O4—H9···Cl2	1.02	2.82	3.5791 (18)	132
O4—H10···O1$^{\rm iv}$	0.87	2.01	2.836 (2)	158
N1—H1···Cl2	0.93	2.21	3.056 (2)	151
N2—H2···Cl1$^{\rm v}$	0.93	2.32	3.110 (2)	143
N2—H2···Cl3$^{\rm v}$	0.93	2.75	3.399 (2)	128
C1—H11···Cl4$^{\rm vi}$	0.99	2.70	3.470 (3)	135
C1—H12···Cl4	0.99	2.70	3.510 (2)	140
C2—H22···Cl4$^{\rm vi}$	0.99	2.80	3.693 (3)	150
C3—H32···Cl1$^{\rm iv}$	0.99	2.79	3.682 (3)	151
C4—H41···Cl4$^{\rm vii}$	0.99	2.63	3.537 (3)	153
C6—H62···Cl2$^{\rm viii}$	0.99	2.78	3.544 (3)	135
C4—H42···Cl4$^{\rm vi}$	0.99	2.86	3.591 (3)	131

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

H atoms attached to O atoms were located from difference maps and treated as riding in their as-found locations. H atoms attached to C and N atoms were placed in idealized locations (N—H = 0.93 Å and C—H = 0.99 Å) and treated as riding on their attached atom. The constraint $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom) was applied in all cases. Refinement of the Flack (1983) absolute structure parameter to 0.478 (12) indicated a merohedrally twinned crystal.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *ATOMS* (Shape software, 1999); software used to prepare material for publication: *SHELXL*97.

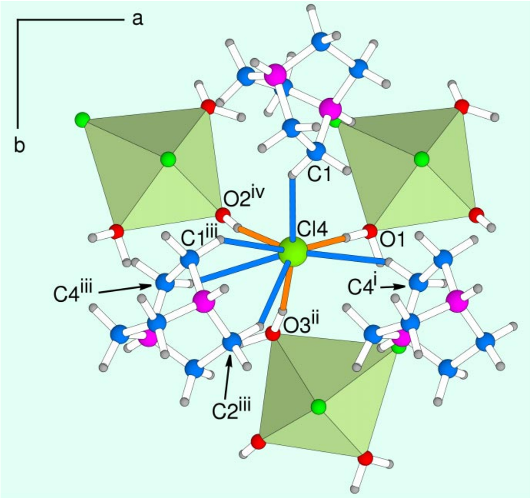


Figure 4
The environment of atom Cl4 in (I), showing the O—H···Cl hydrogen bonds and possible C—H···Cl interactions associated with this species. Colour key as in Fig. 2; additionally, the H···Cl portions of the C—H···Cl contacts are highlighted in blue. [Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iv) $x-1, y, z$.]

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