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trans-Aquachloro[(1*R*,4*R*,8*S*,11*S*)-6,13-diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^{1,4,8,11}$]nickel(II) trichloride trihydrate

Neil F. Curtis,[a]* Rebekah Pawley[b] and Ward T. Robinson[b]

[a]School of Chemical and Physical Sciences, Victoria University of Wellington, Box 600, Wellington, New Zealand, and [b]Chemistry Department, University of Canterbury, Christchurch, New Zealand
Correspondence e-mail: neil.curtis@vuw.ac.nz

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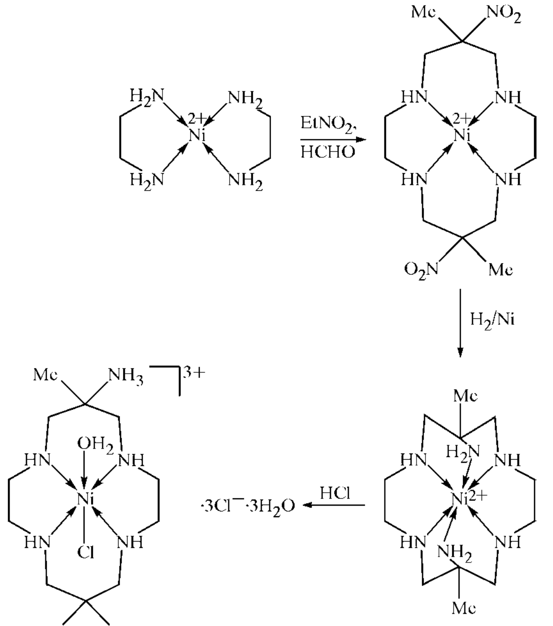
The title compound, $[NiCl(C_{12}H_{32}N_6)(H_2O)]Cl_3\cdot 3H_2O$, has the bis(diamine)-substituted cyclic tetraamine in a planar coordination to triplet ground-state Ni^{II} [average Ni—N = 2.068 (3) Å], with a chloride ion [Ni—Cl = 2.4520 (5) Å] and a water molecule [Ni—O = 2.177 (2) Å] coordinated in the axial sites. The amine substituents are protonated and equatorially oriented. The amine groups, ammonium groups, water molecules and chloride ions are linked by an extensive hydrogen-bonding network.

Comment

The structures of a variety of compounds of *trans*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane, or diam (Comba *et al.*, 1986), with Ni^{II} have been described. Structures have been reported by Curtis *et al.* (1993) for octahedral triplet ground-state Ni^{II} compounds with six-coordinate diam (diam-N_6) in the 1*RS*,4*RS*,8*SR*,11*SR* configuration (labelled as β) for β-$[Ni(diam\text{-}N_6)](ClO_4)_2\cdot H_2O$, β-$[Ni(diam\text{-}N_6)]Cl_2$ and β-$[Ni(diam\text{-}N_6)][ZnCl_4]\cdot 1.5H_2O$, and with four-coordinate diam (diam-N_4) for *trans*-β-$[Ni(diam\text{-}N_4)(NCS)_2]$. The compound α-$[NiCl(diamH\text{-}N_5)](ClO_4)_2\cdot H_2O$ has mono-protonated pentadentate diam in the 1*RS*,4*SR*,8*RS*,11*SR* (α) configuration, with one coordinated chloride ion, while β-$[Ni(diamH_2\text{-}N_4)](ClO_4)_2$, with both amine substituents protonated, has square-planar singlet ground-state Ni^{II} (Curtis *et al.*, 1993). The structure of the title compound, *trans*-β-$[NiCl(diamH_2\text{-}N_4)(H_2O)]Cl_3\cdot 3H_2O$, (I), with the formal composition $Ni^{2+}\cdot diam\cdot 2H^+\cdot 4Cl^-\cdot 4H_2O$ and which crystallizes from solutions of $[Ni(diam)]^{2+}$ in HCl, is now reported. It was uncertain if this triplet ground-state Ni^{II} compound had water or chloride ions completing the octahedral coordination.

The structural study shows triplet ground-state Ni^{II} in a planar coordination to the four intracyclic secondary amine N atoms of the diprotonated diam ligand, with one chloride ion and one water molecule *trans*-axially coordinated (Fig. 1 and Table 1). The diam ligand is achiral, but the four secondary amine groups become chiral centres when coordinated. The β-$[Ni(diam\text{-}N_4)]^{2+}$ cation is generally found to crystallize racemically, *e.g.* for *trans*-β-$[Ni(NCS)_2(diam\text{-}N_4)]$, with centrosymmetrically related molecules (Curtis *et al.*, 1993). However, the asymmetric coordination environment introduced by the dissimilar additional ligands for the cation of (I) leads to chirality of the cation and thence to the chiral space group $P2_1$ for the crystal. We believe an arbitrary choice was made from a crystal batch containing 50% of each enantiomeric crystal form. The related compounds *trans*-α-$[NiCl(diamH\text{-}N_5)](ClO_4)_2\cdot H_2O$ and *trans*-α-$[Cu(OClO_3)($diam-



(I)

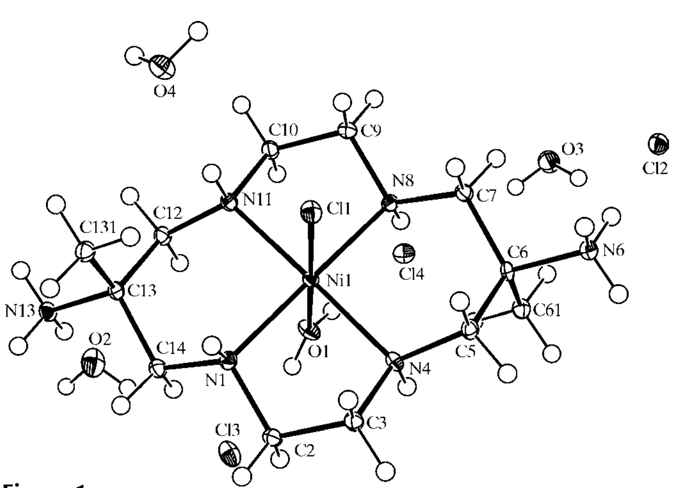


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level and with H atoms shown as circles of arbitrary radii.

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N_5)]ClO_4 (Bernhardt *et al.*, 1997) crystallize in the centrosymmetric space groups $P2_1/n$ and $P\bar{1}$, respectively, so this condition does not arise.

The four N atoms are coplanar [r.m.s. deviation 0.002 (1) Å], with the Ni atom displaced from this plane by 0.035 (1) Å towards the coordinated chloride ion. The cation has the 1*R*,4*R*,8*S*,11*S* (*β*) configuration usual for cyclic tetraamines in planar four-coordination, with *gauche*-conformation five-membered and chair-conformation six-membered chelate rings. The displacements of atoms from the N_4 plane (in Å, with an s.u. value of 0.002 Å unless specified) are −0.383 for atom C2, 0.356 for C3, 0.840 for C5, 0.450 for C6, 0.827 for C7, 0.405 for C9, −0.336 for C10, −0.865 for C12, −0.487 for C13, −0.828 for C14, −1.004 for C61, 1.279 (1) for N6, 0.957 for C131 and −1.353 (1) for N13.

The 6,13-diammonio substituents are equatorially oriented, as also reported for the amino/azonium substituents of *trans*-*β*-[Ni(NCS)$_2$(diam-N$_4$)], *trans*-*β*-[Cu(OClO$_3$)$_2$(diamH$_2$-N$_4$)]-(ClO$_4$)$_2$·6H$_2$O (Comba *et al.*, 1986), *trans*-*β*-[Cu(OClO$_3$)$_2$-(diamH$_2$-N$_4$)](ClO$_4$)$_2$·2H$_2$O (Bernhardt *et al.*, 1997), *trans*-*β*-[CoCl$_2$(diamH$_2$-N$_4$)][ZnCl$_4$]·0.5H$_2$O·0.5EtOH (Curtis *et al.*, 1992) and *trans*-*β*-[PtCl$_2$(diamH$_2$-N$_4$)]Cl$_2$(ClO$_4$)$_2$·4H$_2$O (Bernhardt *et al.*, 1992). The amino/azonium substituents are axially oriented for *trans*-*β*-[Cu(OClO$_3$)$_2$(diam-N$_4$)] (Lawrance *et al.*, 1986), *trans*-*β*-[Cu(diam-N$_4$)(H$_2$O)$_2$](ClO$_4$)$_2$ (Bernhardt *et al.*, 1997) and *trans*-*β*-[Pd(diamH$_2$-N$_4$)](ClO$_4$)$_4$ (Bernhardt *et al.*, 1990), as well as for *β*-diam-N$_4$ compounds of Ni^{II} and Cu^{II} with amido-substituted (Curtis & Puschmann, 2005; Curtis & Robinson, 2005) and anthracenylmethylamino-substituted diam (Bernhardt *et al.*, 1999, 2002). Disorder precluded making an unambiguous assignment of orientation of the substituents for *β*-[Ni(diamH$_2$-N$_4$)](ClO$_4$)$_2$ (Gainsford & Rae, 1993).

The mean Ni—N distance of 2.068 (3) Å (Table 1) is comparable to the values (Å) reported for other triplet ground-state Ni^{II} compounds of diam, *viz.* 2.071 (6) for *β*-[Ni(diam-N$_6$)](ClO$_4$)$_2$·H$_2$O, 2.07 (1) for *β*-[Ni(diam-N$_6$)]Cl$_2$, 2.06 (1) for *β*-[Ni(diam-N$_6$)][ZnCl$_4$]·1.5H$_2$O, 2.058 (6) for *trans*-*β*-[Ni(NCS)$_2$(diam-N$_4$)] and 2.058 (8) for *trans*-*α*-[NiCl(diamH-N$_5$)](ClO$_4$)$_2$·H$_2$O (Curtis *et al.*, 1993). This distance is clearly little affected by whether the substituent amine groups are coordinated, free or protonated. The Ni—Cl distance here is somewhat shorter than the value of 2.553 (1) Å observed for *trans*-*α*-[NiCl(diamH-N$_5$)](ClO$_4$)$_2$·H$_2$O (Curtis *et al.*, 1993) but similar to the value of 2.442 (2) Å found in a related dinickel(II) complex with perchlorate bound *trans* to the chloride ion (Szacilowski *et al.*, 2005).

The secondary amine groups, water molecules, and ammonium and chloride groups are linked into an extensive network by hydrogen bonding involving all the water and nitrogen-bound H atoms (Table 2).

Experimental

The title compound was prepared as reported by Curtis *et al.* (1993) (see scheme in *Comment*) and a crystal was grown by evaporation of an aqueous solution.

Crystal data

[NiCl($C_{12}H_{32}N_6$)(H_2O)]Cl_3·3H_2O
M_r = 533.01
Monoclinic, $P2_1$
a = 10.375 (1) Å
b = 10.532 (1) Å
c = 10.893 (1) Å
β = 103.610 (1)°
V = 1156.9 (2) Å^3
Z = 2

D_x = 1.530 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3552 reflections
θ = 3.1–28.2°
μ = 1.33 mm^{-1}
T = 273 (2) K
Block, blue–violet
0.40 × 0.40 × 0.32 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min}$ = 0.535, $T_{\max}$ = 0.653
6768 measured reflections

4243 independent reflections
3243 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.010
$\theta_{\max}$ = 28.2°
$h = -10 \rightarrow 12$
$k = -13 \rightarrow 11$
$l = -9 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.040
S = 0.97
4243 reflections
280 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.24 e Å^{-3}
$\Delta\rho_{\min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 313 Friedel pairs
Flack parameter: 0.012 (7)

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.069 (2)	Ni1—N11	2.062 (2)
Ni1—N4	2.063 (2)	Ni1—O1	2.177 (2)
Ni1—N8	2.077 (2)	Ni1—Cl1	2.4520 (5)
N1—Ni1—N4	85.53 (6)	N1—Ni1—O1	91.62 (6)
N1—Ni1—N8	178.16 (7)	N4—Ni1—O1	88.66 (6)
N1—Ni1—N11	94.28 (6)	N1—Ni1—Cl1	89.10 (4)
N4—Ni1—N8	94.34 (6)	N4—Ni1—Cl1	92.85 (4)
N4—Ni1—N11	177.96 (7)	O1—Ni1—Cl1	178.37 (4)
N8—Ni1—N11	85.78 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	0.91	2.37	3.270 (2)	169
N4—H4···Cl2^{ii}	0.91	2.48	3.323 (2)	154
N6—H6*D*···Cl2	0.89	2.26	3.147 (2)	173
N6—H6*E*···Cl4^{iii}	0.89	2.32	3.213 (2)	179
N6—H6*F*···Cl3^{iv}	0.89	2.27	3.129 (2)	163
N8—H8···Cl4	0.91	2.59	3.482 (2)	168
N11—H11···O4	0.91	2.25	3.128 (2)	161
N13—H13*D*···O4^{v}	0.89	1.97	2.854 (2)	176
N13—H13*E*···O2	0.89	1.86	2.750 (2)	175
N13—H13*F*···O3^{vi}	0.89	2.04	2.884 (2)	158
O1—H1*E*···Cl4	0.81 (2)	2.34 (2)	3.145 (2)	172 (2)
O1—H1*F*···Cl3	0.79 (2)	2.33 (2)	3.106 (2)	168 (2)
O2—H2*E*···Cl3	0.80 (2)	2.29 (2)	3.090 (2)	177 (2)
O2—H2*F*···Cl1^{vii}	0.85 (2)	2.36 (2)	3.201 (2)	173 (2)
O3—H3*E*···Cl4	0.81 (2)	2.47 (2)	3.272 (2)	169 (2)
O3—H3*F*···Cl2	0.82 (2)	2.66 (2)	3.352 (2)	142 (2)
O4—H4*E*···Cl4^{viii}	0.84 (2)	2.36 (2)	3.197 (2)	172 (3)
O4—H4*F*···Cl2^{vi}	0.84 (2)	2.28 (2)	3.113 (2)	169 (2)

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

Water H atoms were located in difference syntheses and their positions were refined with restrained O—H distances [O—H = 0.82 (2) Å] and H—O—H angles [H···H = 1.30 (4) Å]. All other H atoms were placed in calculated positions (C—H = 0.96 and 0.97 Å, and N—H = 0.89 and 0.91 Å) and treated as riding on their parent atoms, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C,N) for CH_2 and NH groups, and $1.5U_{\rm eq}$(C) for CH_3 groups. Interchange of the substituent methyl and ammonium sites caused an increase in R_1 from 0.0164 to 0.0286.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3.2* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3002). Services for accessing these data are described at the back of the journal.

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