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(1,3-Diaminopropane-κ^2N,N')[tris(2-aminoethyl)amine-κ^4N,N',N'',N''']nickel(II) bis(perchlorate)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.025
wR factor = 0.062
Data-to-parameter ratio = 15.3

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

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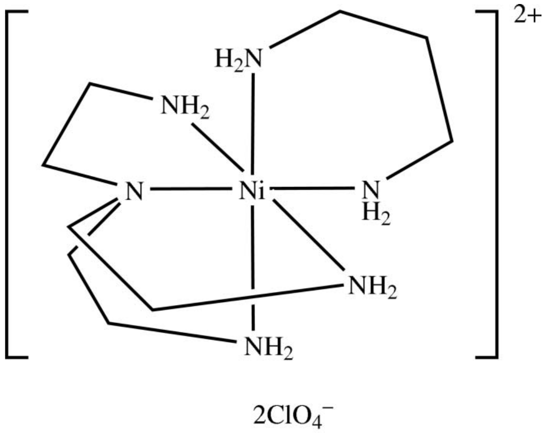
In the title compound, $[Ni(C_3H_{10}N_2)(C_6H_{18}N_4)](ClO_4)_2$, the Ni^{II} atom has a distorted octahedral coordination, formed by four N atoms of the tris(2-aminoethyl)amine (tren) ligand and two N atoms of the 1,3-diaminopropane (pn) ligand. The tren ligand consists of three five-membered chelate rings in *gauche* conformations and the pn ligand consists of a six-membered chelate ring in a chair conformation. In the crystal structure, a two-dimensional network of hydrogen bonds extends parallel to the (100) plane.

Comment

The effects of coordinated ligands on the thermodynamics and kinetics of ternary complex formation have received much attention because of their importance in studying catalytic reactions of enzymes, including a wide range of metal enzyme reactions (Hague *et al.*, 1993). In the present study, the synthesis and X-ray crystallographic structure analysis of the title compound, $[Ni(pn)(tren)](ClO_4)_2$ [tren is tris(2-aminoethyl)amine and pn is 1,3-diaminopropane], (I), is reported.



(I)

The Ni atom is six-coordinated by three primary amine groups and one tertiary amine group of the tren ligand, and by two primary amine groups of the pn ligand in a distorted octahedral geometry (Fig. 1). The tren ligand consists of three five-membered chelate rings in *gauche* conformations and the pn ligand consists of a six-membered chelate ring in a chair conformation. Atoms N1/N2/N4/N5 constitute the equatorial plane of the octahedron. The longer bond lengths of Ni—N3 [2.164 (2) Å] and Ni—N6 [2.148 (3) Å] are consistent with the fac that atoms N3 and N6 of the tren ligand are in the axial positions of the octahedron. The Ni—N(tren) bond lengths in (I) are almost equivalent to the reported values in $[Ni(tren)(en)]$ $(ClO_4)_2$ (en is ethylenediamine; Misra *et al.*,

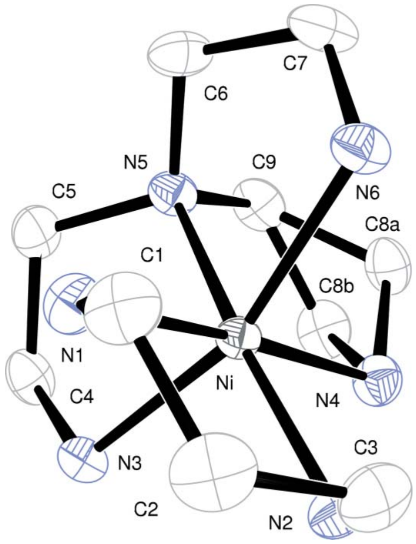


Figure 1
View of the complex cation in (I), showing the atom-labelling scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Atom C8 is disordered over two sites (C8*A* and C8*B*).

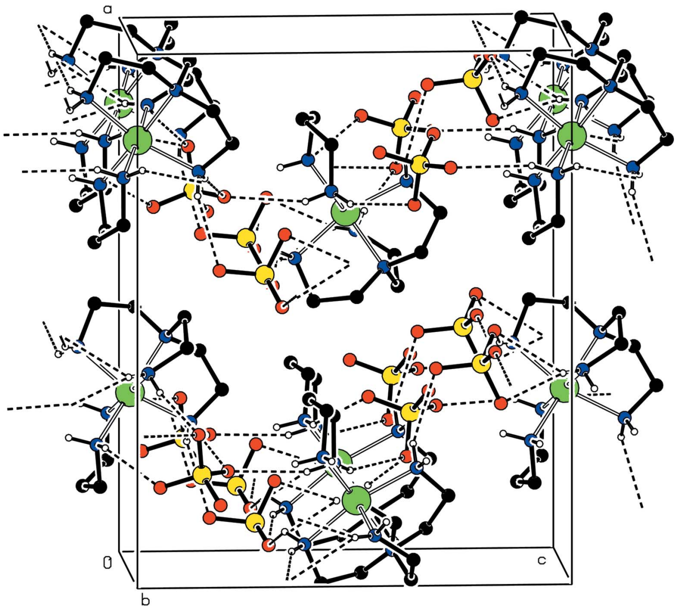


Figure 2
Two-dimensional zigzag chains of hydrogen bonding in the molecular packing of (I). Dashed lines indicate hydrogen bonds. Note that one of the disordered C-atom sites has been omitted, and H atoms attached to C atoms have been omitted for clarity.

2002), [Ni(tren)(acetato)]$(ClO_4)_2$ (Fun *et al.*, 1996), $[Ni(tren)_2(C_2O_4)_2](ClO_4)_2$ (Castro *et al.*, 1997), [Ni(tren)(phen)]$(ClO_4)_2$ (phen is 1,10-phenanthroline; Misra *et al.*, 2002), and [Ni(tren)(bpy)]$(ClO_4)_2$ (bpy is bypyridine; Lin *et al.*, 2003). In (I), one of the chelate rings of the tren ligand shows conformational disorder, similar to that observed in [Ni(tren)(2-Mepn)]$(ClO_4)_2$ (2-Mepn is 2-methylpropane-1,2-diamine; Lin *et al.*, 2005).

For the pn ligand, the Ni—N1 bond length is significantly longer than Ni—N2, suggesting the steric effect caused by the tertiary tren N group *cis* to the N1 atom. The chelate bite angle of the pn ligand in (I) [86.73 (8)°] is comparable to those in $[Ni(pn)_3](NO_3)_2$ (87.62–88.45°; Vezzosi *et al.*, 1985) and $[Ni(pn)_3](BF_4)_2$ [86.57 (18)–88.6 (2)°; Willett *et al.*, 2002]. The molecular packing (Fig. 2) exhibits a two-dimensional network of hydrogen bonds (Table 2) between perchlorate ions and amino groups extending parallel to the (100) plane.

Experimental

Compound (I) was prepared according to the literature method of Lin *et al.* (2003). A solution of Ni(tren)$(ClO_4)_2$ (0.80 g, 2.4 mmol in dry ethanol, 50 ml) was added dropwise to a solution of pn (0.20 g, 3.0 mmol in dry ethanol, 50 ml) with stirring at room temperature. The color of the mixture changed from blue to violet and the solution was stirred continuously for 3 h. The solution was then evaporated slowly and the violet crystals of (I) that precipitated out were filtered off and recrystallized from methanol.

Crystal data

$[Ni(C_3H_{10}N_2)(C_6H_{18}N_4)](ClO_4)_2$
$M_r = 477.98$
Orthorhombic, $Pna2_1$
$a = 16.876$ (2) Å
$b = 8.2937$ (9) Å
$c = 13.6237$ (16) Å
$V = 1906.9$ (4) Å^3
$Z = 4$
$D_x = 1.665$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3745 reflections
$\theta = 2.4$–28.3°
$\mu = 1.35$ mm^{-1}
$T = 295$ (2) K
Block, purple
0.30 × 0.25 × 0.20 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.692$, $T_{max} = 0.764$
11557 measured reflections
3745 independent reflections
3575 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 28.3°$
$h = -22 \rightarrow 21$
$k = -10 \rightarrow 11$
$l = -18 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.062$
$S = 0.95$
3745 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.65P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.026$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983), 1285 Friedel pairs
Flack parameter: 0.010 (12)

Table 1
Selected geometric parameters (Å, °).

Ni—N2	2.103 (2)	Ni—N6	2.148 (3)
Ni—N4	2.122 (2)	Ni—N3	2.164 (2)
Ni—N5	2.131 (2)	Ni—N1	2.169 (2)
N2—Ni—N4	89.62 (9)	N5—Ni—N3	81.56 (9)
N2—Ni—N5	170.99 (8)	N6—Ni—N3	161.12 (8)
N4—Ni—N5	81.39 (9)	N2—Ni—N1	86.73 (8)
N2—Ni—N6	100.11 (9)	N4—Ni—N1	175.91 (10)
N4—Ni—N6	94.20 (9)	N5—Ni—N1	102.23 (8)
N5—Ni—N6	81.37 (8)	N6—Ni—N1	88.28 (9)
N2—Ni—N3	98.01 (9)	N3—Ni—N1	87.50 (9)
N4—Ni—N3	91.17 (9)		

m1758 Lin *et al.* • $[Ni(C_3H_{10}N_2)(C_6H_{18}N_4)](ClO_4)_2$ *Acta Cryst.* (2005). E**61**, m1757–m1759

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{i}	0.90	2.53	3.357 (5)	154
N1—H1*B*···O2^{ii}	0.90	2.56	3.356 (4)	148
N2—H2*B*···O3	0.90	2.43	3.144 (4)	137
N3—H3*A*···O6	0.90	2.32	3.162 (4)	156
N3—H3*B*···O7^{i}	0.90	2.55	3.196 (4)	129
N4—H4*AA*···O1	0.90	2.28	3.100 (4)	152
N4—H4*AB*···O6	0.89	2.38	3.224 (4)	158
N4—H4*BA*···O1	0.89	2.28	3.100 (4)	153
N4—H4*BB*···O5	0.90	2.44	3.232 (5)	147
N6—H6*A*···O8^{iii}	0.90	2.51	3.172 (4)	131
N6—H6*B*···O2	0.90	2.24	3.138 (4)	176

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

There is a positional disorder of atom C8 of the tren ligand. The site-occupancy factors of C8*A* and C8*B* were estimated to be 0.60 and 0.40, respectively, based on their $U_{\rm eq}$ values. The positional disorder of the H atoms bonded to C9 and N4 was also considered (restrained distances for C9—H and N4—H were 0.97 and 0.90 Å, respectively). The H atoms bonded to C8*A* or C8*B* were positioned geometrically and their bond distances restrained (restrained distances for C8*A*—H and C8*B*—H were both 0.97 Å). The other H atoms were placed in geometrically calculated positions (N—H = 0.87–0.90 Å and C—H = 0.95–0.98 Å) and refined as riding [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom)].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Acta Cryst. (2005). E**61**, m1757–m1759 Lin *et al.* • $[\mathrm{Ni(C_3H_{10}N_2)(C_6H_{18}N_4)](ClO_4)_2}$ **m1759**