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(2-Methylpropane-1,2-diamine-κ^2N,N')-[tris(2-aminoethyl)amine-κ^4N,N',N'',N''']-nickel(II) diperchlorate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.116
Data-to-parameter ratio = 14.4

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

In the title compound, [N($C_4H_{12}N_2$)($C_6H_{18}N_4$)](ClO_4)$_2$, the Ni^{II} atom is coordinated in a distorted octahedron by four N atoms of the tris(2-aminoethyl)amine (tren) ligand and by two N atoms of the 2-methylpropane-1,2-diamine (2-Mepn) ligand. The primary amino group of 2-Mepn at the C-2 position occupies the position *trans* to the tertiary amino group of tren. The complex cations and perchlorate anions are linked *via* N—H···O hydrogen bonds, forming one-dimensional zigzag chains along the [101] direction.

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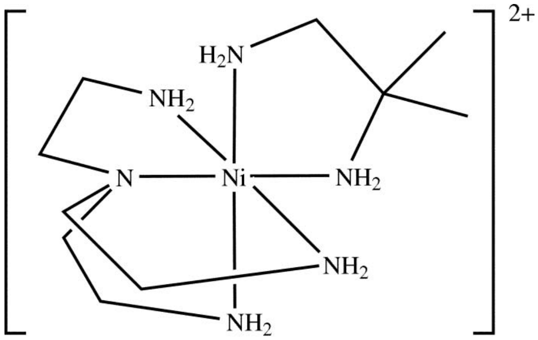
Comment

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 & White, 1993). In the present study, the synthesis and structure of the title nickel(II) complex, [Ni(tren)(2-Mepn)](ClO_4)$_2$, (I), is reported.



$2ClO_4^-$

(I)

In (I), the Ni^{II} atom is coordinated in a distorted octahedron by four N atoms of the tren ligand and by two N atoms of the 2-Mepn ligand (Fig. 1). The tetradentate tren ligand consists of three five-membered chelate rings in *gauche* conformations. Atom N6 of 2-Mepn occupies the position *trans* to the tertiary amino group of tren. Although the Ni—N1 and Ni—N3 bond lengths are significantly longer than the other four Ni—N distances, the Ni—N(tren) bond lengths in (I) are almost equal to the reported values in [Ni(tren)(en)](ClO_4)$_2$ (en is ethylenediamine; Misra *et al.*, 2002), [Ni(tren)(acetato)](ClO_4)$_2$ (Fun *et al.*, 1996), [Ni(tren)$_2$(C_2O_4)](ClO_4)$_2$ (Castro *et al.*, 1997) and [Ni(tren)(bpy)](ClO_4)$_2$ (bpy is pipyridine; Lin *et al.*, 2003).

In the bidentate ligand, the bond distance Ni—N5 [2.145 (3) Å] is longer than Ni—N6 [2.092 (3) Å]. This is due

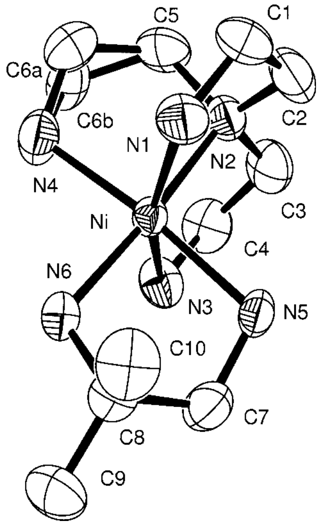


Figure 1
ORTEP3 drawing (Farrugia, 1997) of the cation of (I), showing the atom-labelling scheme, with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Atom C6 is disordered over two sites (C6*a* and C6*b*).

to the fact that atom N5 is oriented *cis* to the sterically hindered tertiary tren N atom. The chelate bite angle of the bidentate ligand is comparable with the reported bond angles of $[Ni(en)_3]^{2+}$, [82.1 (2)°; Mazhar-Ul-Haque *et al.*, 1970] and $[Ni(tren)(en)]^{2+}$ [82.0 (2)°; Misra *et al.*, 2002]. The molecular packing shows one-dimensional zigzag chains (Fig. 2) of hydrogen bonds (Table 2) between perchlorate ions and amino groups along the [101] direction.

Experimental

$Ni(tren)(ClO_4)_2$ was prepared according to the literature method of Lin *et al.* (2003). A solution of 2-Mepn (0.31 g, 3.0 mmol) in dry ethanol (50 ml) was added to a blue solution of $Ni(tren)(ClO_4)_2$ (0.80 g, 2.4 mmol) in dry ethanol (50 ml) at room temperature. The colour of the mixture changed to violet and the solution was continuously stirred for 3 h. The ethanol solution was then evaporated slowly and violet crystals (yield of 55%) precipitated out. Single crystals of (I) suitable for X-ray analysis were obtained on recrystallization from hot methanol.

Crystal data

$[Ni(C_4H_{12}N_2)(C_6H_{18}N_4)](ClO_4)_2$
$M_r = 492.01$
Monoclinic, *Cc*
$a = 14.532$ (2) Å
$b = 9.7074$ (13) Å
$c = 14.823$ (2) Å
$\beta = 96.167$ (2)°
$V = 2079.0$ (5) Å^3
$Z = 4$
$D_x = 1.572$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6541 reflections
$\theta = 2.5$–28.3°
$\mu = 1.24$ mm^{-1}
$T = 295$ (2) K
Plate, light violet
0.25 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.780$, $T_{max} = 0.906$
6541 measured reflections
4172 independent reflections
3560 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 28.3°$
$h = -17 \rightarrow 18$
$k = -6 \rightarrow 12$
$l = -19 \rightarrow 18$

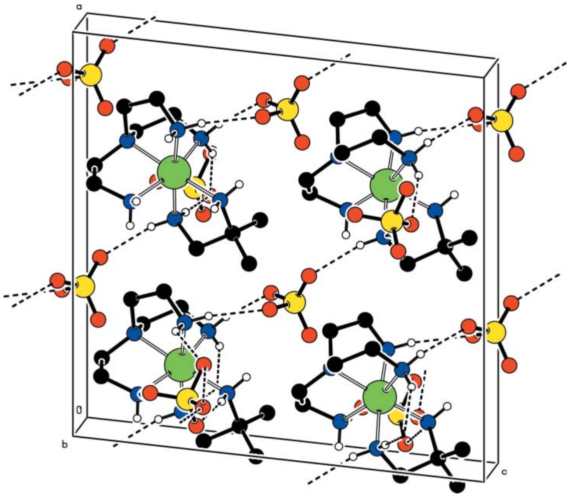


Figure 2
The one-dimensional zigzag chains of hydrogen bonds (dashed lines). One component of the disordered O– and C-atom sites has been omitted, as have the H atoms attached to C atoms.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.116$
$S = 0.91$
4172 reflections
290 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0953P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Absolute structure: Flack (1983), 1588 Friedel pairs
Flack parameter: 0.02 (2)

Table 1
Selected geometric parameters (Å, °).

Ni—N6	2.092 (3)	Ni—N5	2.145 (3)
Ni—N4	2.110 (4)	Ni—N3	2.166 (3)
Ni—N2	2.118 (4)	Ni—N1	2.176 (3)
N6—Ni—N4	92.86 (15)	N2—Ni—N3	81.17 (15)
N6—Ni—N2	175.65 (15)	N5—Ni—N3	87.19 (15)
N4—Ni—N2	82.85 (16)	N6—Ni—N1	100.04 (15)
N6—Ni—N5	80.82 (13)	N4—Ni—N1	93.30 (18)
N4—Ni—N5	173.51 (17)	N2—Ni—N1	80.97 (15)
N2—Ni—N5	103.45 (14)	N5—Ni—N1	89.29 (14)
N6—Ni—N3	98.36 (14)	N3—Ni—N1	160.46 (14)
N4—Ni—N3	92.30 (17)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O7*B*	0.90	2.21	3.069 (10)	158
N1—H1*A*···O7*A*	0.90	2.44	3.278 (10)	159
N1—H1*B*···O2^{i}	0.90	2.41	3.232 (8)	151
N3—H3*A*···O6*A*^{ii}	0.90	2.26	3.116 (10)	158
N3—H3*B*···O4*A*	0.90	2.39	3.281 (10)	170
N4—H4*A*···O3	0.90	2.38	3.030 (9)	129
N4—H4*B*···O6*B*	0.91	2.26	3.156 (10)	170
N4—H4*B*···O7*A*	0.91	2.40	3.160 (10)	139
N5—H5*A*···O5^{ii}	0.90	2.17	3.048 (9)	167
N5—H5*B*···O2^{i}	0.90	2.16	3.056 (6)	178
N6—H6*B*···O1	0.90	2.25	3.138 (6)	167

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

Acta Cryst. (2005). E**61**, m1398–m1400 Lin *et al.* • $[Ni(C_4H_{12}N_2)(C_6H_{18}N_4)](ClO_4)_2$ **m1399**

There is a positional disorder of atom C6 in the tren ligand. The site-occupancy factors of C6*a* and C6*b* were estimated as 75 and 25%, respectively. The H atoms bonded to C6*a* or C6*b* were positioned geometrically and restrained in both bond distances and angles (the *y* coordinate of atom H6*BD* being fixed to avoid oscillation). The other H atoms were placed in geometrically calculated positions (N—H = 0.90 Å and C—H = 0.96–0.97 Å) and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom) or 1.5$U_{\rm eq}$(C) for methyl H atoms. Two independent perchlorate ions show orientational disorder and two split states were assumed: Cl1/O1/O2/O3/(O4*A* or O4*B*) and Cl2/O5/O8/(O6*A*,O7*A* or O6*B*,O7*B*). The site-occupancy factors of O4*A*, O4*B*, O6*A*, O7*A*, O6*B* and O7*B* are each 0.5. The Cl—O distances of the two perchlorate ions were restrained to normal values. The abnormal O—Cl—O bond angles of the perchlorate ions [81 (1)–138 (1)°] suggest further complicated disorder.

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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m1400 Lin *et al.* • [Ni($C_4H_{12}N_2$)($C_6H_{18}N_4$)](ClO_4)$_2$ *Acta Cryst.* (2005). E**61**, m1398–m1400