trans-Dichlorobis(*N*,*N*′-dimethylethane-1,2-diamine-$\kappa^2 N$,*N*′)nickel(II)

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The title compound, $[NiCl_2(C_4H_{12}N_2)_2]$, is a molecular nickel(II) complex. The nickel(II) center is pseudo-octahedral six-coordinate with a *trans* geometry and is located on an inversion center. The molecules exhibit limited hydrogen bonding between the axial chloride ions and the secondary amine H atoms (each halide interacts with two H atoms) of adjacent molecules.

Comment

We have reported magneto-structural studies of nickel(II) dimers containing the $\{NiX\}_2$ core, where X is Cl and Br (Tong *et al.*, 1999, 2000; Xie & Norman, 2006), and observed that a bridging bromide mediates stronger ferromagnetic coupling between six-coordinate nickel(II) centers than does a bridging chloride for the same effective ferromagnetic coupling pathway. Consequently, we have been attempting the synthesis and structural characterization of additional examples. In this context, the title compound, (I), was prepared and characterized.


(I)
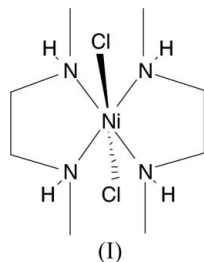
The title complex is a centrosymmetric pseudo-octahedral nickel(II) complex of *trans* geometry with two dimethyl-ethylenediamine ligands providing four N atoms that serve as an equatorial plane for the octahedral arrangement with the additional chloride ions in the axial positions. The title complex is isostructural with *trans*-dibromo(*N*,*N*′-dimethyl-ethane-1,2-diamine-$\kappa^2 N$,*N*′)nickel(II) (Ariyananda & Norman, 2006; Pajunen & Luukkonen, 1969).

It is somewhat surprising that all of the nickel(II)-to-ligand atom distances are somewhat long. The median value for six-coordinate secondary amine Ni—N distances reported by Orpen *et al.* (1989) is 2.098 Å while the upper quartile distance is 2.121 Å. The Ni—N distances in the title complex are 2.1204 (7) and 2.1243 (7) Å. The Ni—Cl distance of 2.4878 (2) Å falls into the upper quartile of similar distances (2.467 Å; Orpen *et al.*, 1989). Not only are the nickel(II)-to-ligand atom distances long in the title complex, the analogous bromide complex (Ariyananda & Norman, 2006) and aqua complex, namely *trans*-diaqua(*N*,*N*′-dimethylethane-1,2-
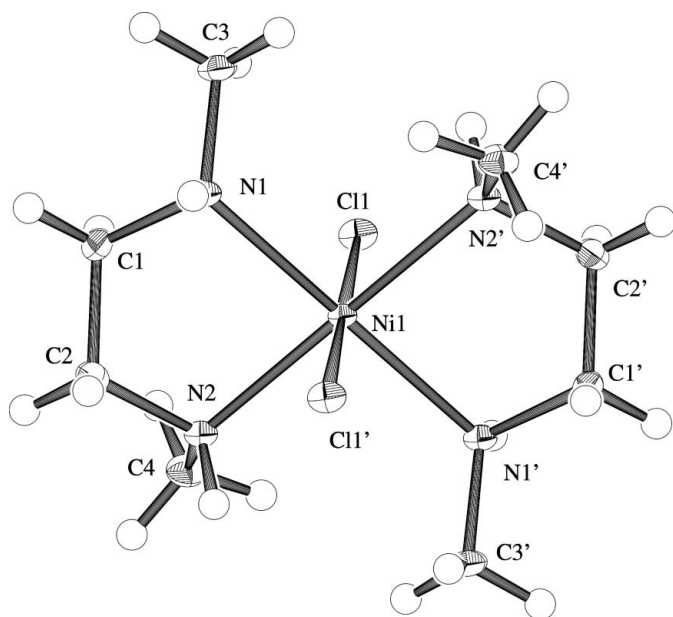
Figure 1
View of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Atoms with the suffix a are at the symmetry position $(1 - x, 1 - y, 1 - z)$. The minor set of disordered methyl H atoms has been omitted.
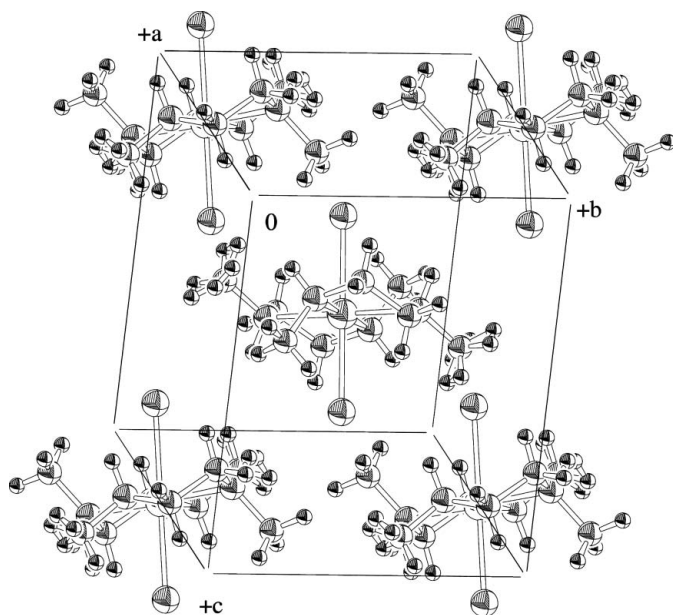
Figure 2
Packing diagram of (I).

diamine-$\kappa^2 N,N'$)nickel(II) dichloride dihydrate (Moore & Norman, 2006), also exhibit long nickel(II)-to-ligand atom distances. The observation that all of the distances are somewhat long suggests crowding about the nickel(II) center.

The title compound has two H atoms attached to N atoms capable of donating to a hydrogen bond, and these two H atoms exhibit close approaches to two adjacent chloride ions, at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. This pattern is also

observed for the analogous isostructural bromide complex (Ariyananda & Norman, 2006).

Experimental

Nickel(II) chloride hexahydrate (0.2382 g, 1.002 mmol) was dissolved in 10 ml of 5% aqueous methanol, heated to 323 K and stirred for 10 min, producing a green solution. N,N'-Dimethylethane-1,2-diamine (0.310 ml, 3.00 mmol) was added to the nickel(II) solution and heating continued for 10 min. The beaker containing the resultant blue solution was then placed in a desiccator containing ethyl acetate. Blue crystals appeared after several days.

Crystal data

[NiCl$_2$(C$_4$H$_{12}$N$_2$)$_2$]	$Z = 2$
$M_r = 305.91$	$D_x = 1.526$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.8639$ (2) Å	$\mu = 1.84$ mm^{-1}
$b = 8.5786$ (2) Å	$T = 100$ K
$c = 10.0186$ (3) Å	Fragment, blue
$\beta = 99.9252$ (10)°	$0.35 \times 0.30 \times 0.27$ mm
$V = 665.75$ (3) Å^3	

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler	15248 measured reflections
	2918 independent reflections
ω scans with κ offsets	2440 reflections with $I > 3\sigma(I)$
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	$R_{int} = 0.013$
	$\theta_{max} = 35.0°$
$T_{min} = 0.552$, $T_{max} = 0.609$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{max} = 0.58$ e Å^{-3}
$wR(F^2) = 0.081$	$\Delta\rho_{min} = -0.56$ e Å^{-3}
$S = 0.99$	Extinction correction: Zachariasen (1967)
2440 reflections	Extinction coefficient:
72 parameters	2.8 (5) $\times 10^{-6}$
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o) + 0.0009\|F_o\|^2]$	

Table 1
Selected geometric parameters (Å, °).

Ni1—Cl1	2.4878 (2)	Ni1—N1^i	2.1204 (7)
Ni1—Cl1^i	2.4878 (2)	Ni1—N2	2.1243 (7)
Ni1—N1	2.1204 (7)	Ni1—N2^i	2.1243 (7)
Cl1—Ni1—N1	90.57 (2)	Cl1^i—Ni1—N2	85.04 (2)
Cl1—Ni1—N1^i	89.43 (2)	Cl1^i—Ni1—N2^i	94.96 (2)
Cl1—Ni1—N2	94.96 (2)	N1—Ni1—N2	84.39 (3)
Cl1—Ni1—N2^i	85.04 (2)	N1—Ni1—N2^i	95.61 (3)
Cl1^i—Ni1—N1	89.43 (2)	N1^i—Ni1—N2	95.61 (3)
Cl1^i—Ni1—N1^i	90.57 (2)	N1^i—Ni1—N2^i	84.39 (3)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$Cl1^{ii}	0.95	2.65	3.4578 (7)	144
N1—H1$\cdots$Cl1^{iii}	0.95	2.85	3.6196 (7)	139

Symmetry codes: (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

The H atoms were placed in calculated positions (C—H = N—H = 0.95 Å) and assigned displacement parameters 1.2 times larger than the atoms to which they are bound. During refinement it became apparent that the *N*-methyl group associated with C3 is disordered. A second set of three H atoms was placed in calculated positions using electron density in a difference map to orient the group. The occupancy of one of the H atoms (H3) was refined. The occupancy of H4 and H5 (the remaining two H atoms of that methyl group) were constrained to the occupancy of H3. The occupancies of the H atoms of the other orientation of the methyl group (H13, H14 and H15) were constrained to one minus the refined occupancy. Displacement parameters for these H atoms were assigned to be the occupancy times 1.2 times the C3 displacement parameter. This gave a model with a methyl orientation of greater occupancy (H13–H15 = 0.91) and a methyl orientation of lesser occupancy (H3–H5 = 0.09).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); molecular graphics: *ORTEPII* (Johnson, 1976) in *TEXSAN*; software used to prepare material for publication: *TEXSAN for Windows*.

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