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trans-Diaquabis(*N*,*N*-dimethylethane-1,2-diamine-κ^2N,N')nickel(II) dichloride dihydrate: a redetermination at 90 K

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The crystal structure of the centrosymmetric title compound, $[Ni(C_4H_{12}N_2)_2(H_2O)_2]Cl_2\cdot2H_2O$, has been reported previously at room temperature by Ihara, Satake, Fujimoto, Senda, Suzuki & Uehara [*Bull. Chem. Soc. Jpn* (1991), **64**, 2349–2352]. At room temperature, the five-membered chelate ring displays disorder over *gauche* and eclipsed conformations, whereas at 90 K no such disorder is observed. The present redetermination shows better agreement of bond lengths with expected values.

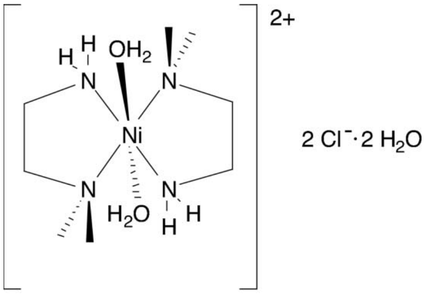
Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.042
wR factor = 0.091
Data-to-parameter ratio = 36.9

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

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. We do not know if this observation is general since very few compounds containing the $\{NiBr\}_2$ core, with six-coordinate nickel(II), have been reported. 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 compound contains a dicationic nickel(II) complex, two chloride counter-ions and two solvent water molecules. The dication is a centrosymmetric pseudo-octahedral nickel(II) complex of *trans* geometry with two *N*,*N*′-dimethylethylenediamine ligands providing four N atoms that serve as an equatorial plane for the bipyramidal arrangement. The axial positions are occupied by water molecules. The same arrangement was observed for a similar complex using *N*,*N*′-dimethylethylenediamine (Moore & Norman, 2006).

The structure of the title compound has been reported previously (Ihara *et al.*, 1991) at room temperature. In that report, the five-membered chelate ring was disordered (75:25) over *gauche* and eclipsed conformations, which also resulted in

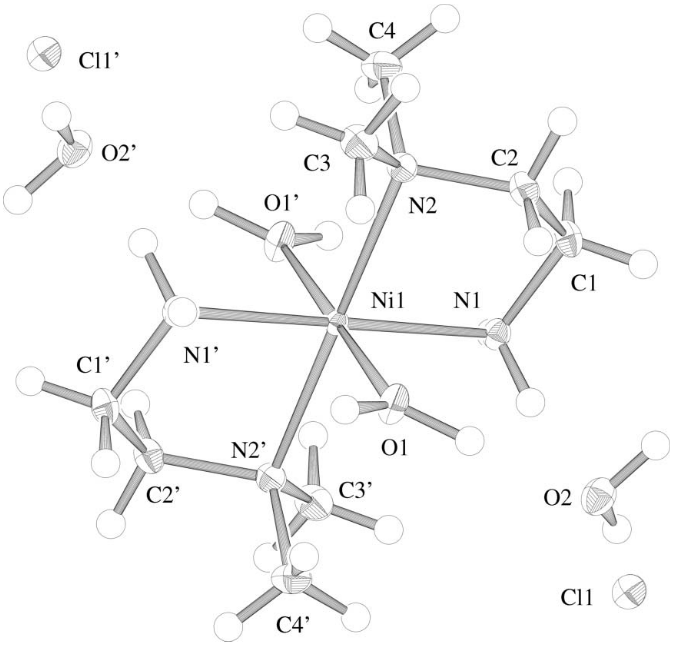


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Primed atoms are related to unprimed ones by the symmetry operation (2 − *x*, −*y*, 2 − *z*). The minor set of disordered methyl H atoms has been omitted.

two sets of *N*,*N*′-dimethyl positions. Consequently some of the distances and angles within the *N*,*N*′-dimethylethylenediamine unit in that report (Ihara *et al.*, 1991) differ significantly from the current report [for example, $C-NH_2$ = 1.473 (3) previously *versus* 1.491 (2) Å in the present structure]. The nickel(II)-to-ligand distances are not significantly different in the two reports.

The $Ni-NH_2$ distance [2.0845 (9) Å] is within one σ below the mean distance (2.097 Å) reported by Orpen *et al.* (1989), while the $Ni-NMe_2$ distance [2.182 (1) Å] falls in the upper quartile (2.177 Å) of six-coordinate tertiary amine Ni—N distances reported by Orpen *et al.* (1989). The Ni—O distance [2.1013 (9) Å] is near the upper quartile (2.105 Å) distance for Ni^{II}–water distances (Orpen *et al.*, 1989).

The title compound exhibits extensive hydrogen bonding. The axial water molecule hydrogen bonds through H13 to an adjacent chloride ion at (1 + *x*, *y*, *z*) and through H14 to the solvent water molecule (O2) in the same asymmetric unit. The solvent water molecule hydrogen bonds to two chloride ions, one in the same asymmetric unit and the other at ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$). The primary amine also hydrogen bonds to two chloride ions, one in the same asymmetric unit and the other at (1 − *x*, −*y*, 2 − *z*). Thus, the chloride ion accepts five hydrogen bonds.

Experimental

N,*N*′-Dimethylethane-1,2-diamine (0.160 ml, 1.46 mmol) was dissolved in 50 ml of an CH_2Cl_2–CH_3OH (1:1 *v*/*v*) mixture. Nickel(II) chloride hexahydrate (0.116 g, 0.488 mmol) was added, giving a turquoise solution, which was covered with a watch glass. After 14 d, all of the solvent had evaporated and the residue was dissolved in methanol (3 ml). The beaker containing the resultant filtered solution was then placed in a desiccator containing ethyl acetate. After 2 d, all of the solvent had evaporated and the residue was dissolved in methanol (2 ml). The beaker containing the blue solution was then placed in a second desiccator containing acetone. Blue crystals appeared after several days.

Crystal data

$[Ni(C_4H_{12}N_2)_2(H_2O)_2]Cl2\cdot 2H_2O$
M_r = 377.97
Monoclinic, $P2_1/n$
a = 7.4277 (10) Å
b = 13.003 (2) Å
c = 9.548 (2) Å
β = 107.787 (7)°
V = 878.1 (3) Å^3
Z = 2
D_x = 1.429 Mg m^{-3}
Mo *Kα* radiation
μ = 1.42 mm^{-1}
T = 90 K
Plate, light blue
0.30 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
ω scans with κ offsets
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.675, T_{max} = 0.871
14844 measured reflections
4003 independent reflections
3323 reflections with $I > 3\sigma(I)$
R_{int} = 0.023
θ_{max} = 35.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.091
S = 1.03
3323 reflections
90 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.00106|F_o|^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 3.4 (5) × 10^6

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.1013 (9)	N2—C2	1.480 (2)
Ni1—N1	2.0845 (9)	N2—C3	1.479 (2)
Ni1—N2	2.182 (1)	N2—C4	1.483 (2)
N1—C1	1.491 (2)	C1—C2	1.525 (2)
N1—Ni1—O1	90.05 (4)	C3—N2—C4	107.3 (1)
N1—Ni1—O1^i	89.95 (4)	C3—N2—Ni1	113.30 (7)
N1—Ni1—N2	83.03 (4)	C2—N2—C4	109.86 (9)
N1—Ni1—N2^i	96.97 (4)	C2—N2—Ni1	102.76 (7)
O1—Ni1—N2	87.62 (4)	C4—N2—Ni1	114.44 (7)
O1—Ni1—N2^i	92.38 (4)	N1—C1—C2	110.30 (9)
C1—N1—Ni1	111.03 (7)	N2—C2—C1	111.20 (9)
C3—N2—C2	109.08 (9)		

Symmetry code: (i) −*x* + 2, −*y*, −*z* + 2.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H13···Cl1^{ii}	0.95	2.17	3.1102 (9)	169
O1—H14···O2	1.01	1.68	2.6868 (12)	177
O2—H15···Cl1	0.88	2.29	3.1558 (10)	167
O2—H16···Cl1^{iii}	0.91	2.27	3.1579 (11)	164
N1—H1···Cl1	0.95	2.60	3.4652 (11)	151
N1—H2···Cl1^{iv}	0.95	2.48	3.3601 (11)	154

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

The H atoms of the water molecules were located in difference maps. The remaining H atoms were placed in calculated positions (C—H = N—H = 0.95 Å). During refinement it became apparent that one of the *N*-methyl groups associated with C4 is disordered. A second set of three H atoms was placed in calculated positions using the electron density in a difference map to orient the group. The occupancy of one of the H atoms (H10) was refined. The occupancies of H11 and H12 (the remaining two H atoms of that methyl group) were constrained to the occupancy of H10. The occupancies of the H atoms of the other orientation of the methyl group (H17, H18 and H19) were constrained to one minus the refined occupancy. This gave a model with a methyl orientation of greater occupancy (H17–H19, 0.75) and a methyl orientation of lesser occupancy (H10–H12, 0.25). For all H atoms, $U_{\rm iso}(H) = 1.2U_{\rm eq}$ of the parent atom..

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); software used to prepare material for publication: *TEXSAN for Windows*.

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