metal-organic papers

trans-Dibromobis(N,N′-dimethylethane-1,2-diamine-κ^2N,N')nickel(II)

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The title compound, $[NiBr_2(C_4H_{12}N_2)_2]$, 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 bromide 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. 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)
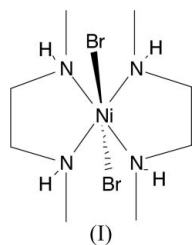
The title complex is a centrosymmetric pseudo-octahedral nickel(II) complex of *trans* geometry with two dimethylethylenediamine ligands providing four N atoms that serve as an equatorial plane for the octahedral arrangement, with the additional bromide ions in the axial positions. The title complex is isostructural with *trans*-dichlorobis(N,N′-dimethylethane-1,2-diamine-κ^2N,N')nickel(II) (Ariyananda & Norman, 2006).

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 2.119 (2) and 2.127 (2) Å. The Ni—Br distance of 2.6712 (4) Å falls into the upper quartile of similar distances (2.572 Å; Orpen *et al.*, 1989). Not only are the nickel(II)-to-ligand atom distances long in the title complex, the analogous chloride complex (Ariyananda & Norman, 2006) and aqua
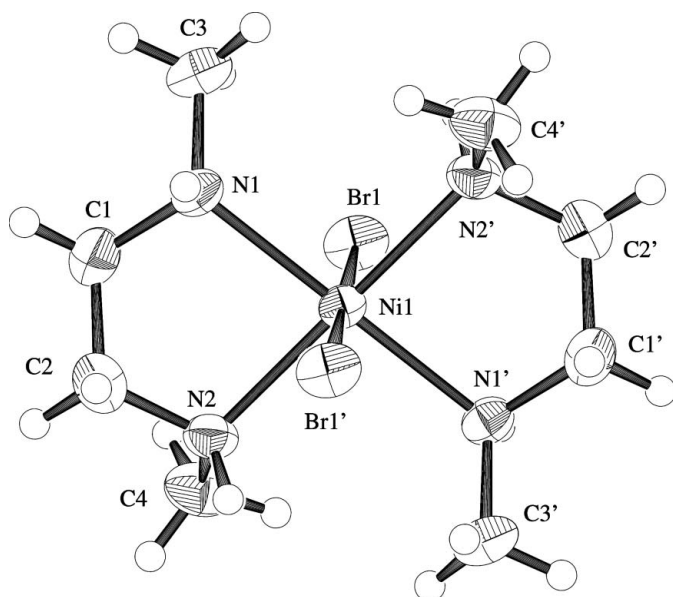
Figure 1
View of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Atoms with the suffix a are at the symmetry position $(1 - x, 1 - y, 1 - z)$. The minor set of disordered methyl H atoms has been omitted.
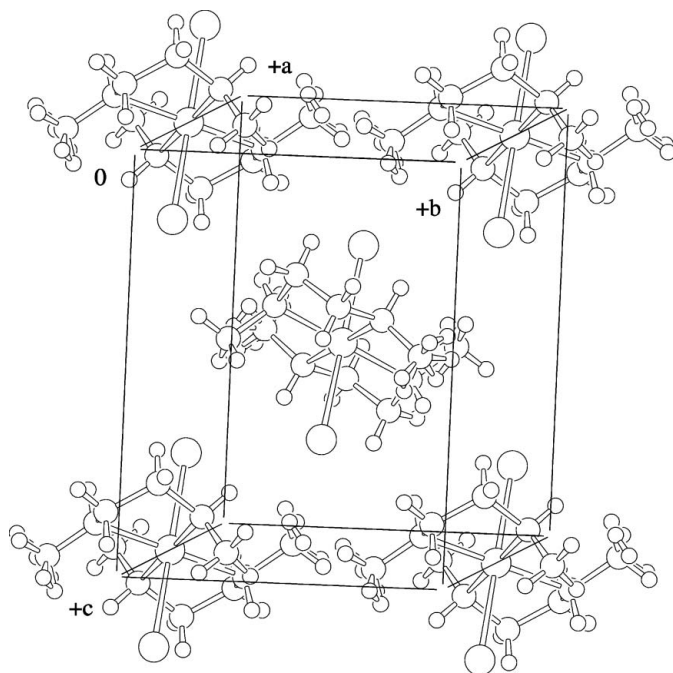
Figure 2
Packing diagram of (I).

complex, namely *trans*-diaqua(N,N'-dimethylethane-1,2-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 bromide ions, at $(x, \frac{1}{2} - y, z - \frac{1}{2})$ and $(x, \frac{3}{2} - y, z - \frac{1}{2})$.

The title compound has been reported previously (Pajunen & Luukkonen, 1969). While the distances and angles agree within 3σ with those reported previously, the current values have greater precision. H atoms were not included in that previous report, so the authors did not comment on the methyl disorder. One of the N—CH$_3$ groups exhibits disorder in the methyl group. This disorder ws modeled with two groups of H atoms with an occupancy ratio of 0.81:0.19.

Experimental

Crystal data

[NiBr$_2$(C$_4$H$_{12}$N$_2$)$_2$]	$Z = 2$
$M_r = 394.81$	$D_x = 1.836$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 7.8731$ (5) Å	$\mu = 8.35$ mm^{-1}
$b = 8.6501$ (4) Å	$T = 295$ K
$c = 10.6902$ (7) Å	Irregular fragment, blue
$\beta = 101.206$ (5)°	$0.22 \times 0.15 \times 0.10$ mm
$V = 714.16$ (7) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	1427 independent reflections
ω–2θ scans	1277 reflections with $I > 3\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.070$
$T_{min} = 0.269$, $T_{max} = 0.434$	$\theta_{max} = 75.1°$
4858 measured reflections	3 standard reflections frequency: 120 min intensity decay: 1.5%

Refinement

Refinement on F^2	Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(F_o) + 0.0036\|F_o\|^2]$
$R[F^2 > 2\sigma(F^2)] = 0.072$	
$wR(F^2) = 0.147$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.88$ e Å^{-3}
1277 reflections	$\Delta\rho_{min} = -1.02$ e Å^{-3}
71 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—Br1	2.6712 (4)	Ni1—N1^i	2.119 (2)
Ni1—Br1^i	2.6712 (4)	Ni1—N2	2.127 (2)
Ni1—N1	2.119 (2)	Ni1—N2^i	2.127 (2)
Br1—Ni1—N1	90.72 (6)	Br1^i—Ni1—N2	85.35 (7)
Br1—Ni1—N1^i	89.28 (6)	Br1^i—Ni1—N2^i	94.65 (7)
Br1—Ni1—N2	94.65 (7)	N1—Ni1—N2	84.2 (1)
Br1—Ni1—N2^i	85.35 (7)	N1—Ni1—N2^i	95.8 (1)
Br1^i—Ni1—N1	89.28 (6)	N1^i—Ni1—N2	95.8 (1)
Br1^i—Ni1—N1^i	90.72 (6)	N1^i—Ni1—N2^i	84.2 (1)

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—H1···Br1[ii]	0.95	2.80	3.603 (2)	143
N1—H2···Br1[iii]	0.95	2.93	3.705 (2)	139

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

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 the electron density in a difference map to orient the group. The occupancy of one of the H atoms (H10) was refined. The occupancy 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 (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 = 0.81) and a methyl orientation of lesser occupancy (H10–H12 = 0.19). The largest residual electron density is located 0.77 Å from atom Br1, and the deepest hole is 0.96 Å from H12 and 1.22 Å from H14.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MAXUS* (Mackay *et al.*, 1999); 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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