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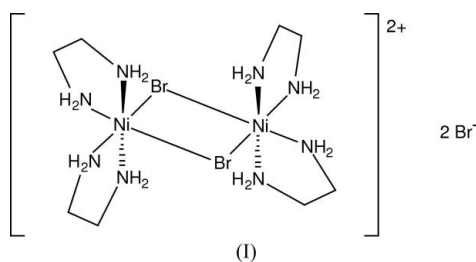
Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
R factor = 0.035
wR factor = 0.049
Data-to-parameter ratio = 22.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Di- μ -bromo-bis[bis(1,2-diaminoethane- κ^2N,N)-nickel(II)] dibromideThe title complex, $[\text{Ni}_2\text{Br}_2(\text{C}_2\text{H}_8\text{N}_2)_4]\text{Br}_2$, consists of two bromide anions and a complex dication. The dication is a centrosymmetric unit of two Ni atoms bridged unsymmetrically by two Br atoms. The Ni atoms are pseudo-octahedral, six-coordinate, with four N atoms from two 1,2-diaminoethane ligands completing the coordination environment.

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Comment

We have reported magneto-structural studies of nickel(II) dimers containing the $\{\text{Ni}X\}_2$ core, where X is Cl and Br (Tong *et al.*, 1999, 2000) and observed that a bridging bromide mediates stronger ferromagnetic coupling between 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 $\{\text{NiBr}\}_2$ core have been reported.Magnetic susceptibility studies of $[\text{Ni}_2\text{Br}_2(\text{en})_4]\text{Br}_2$, where en is 1,2-diaminoethane, were reported in 1972 (Ginsberg *et al.*, 1972). Earlier, limited structural details of $[\text{Ni}_2\text{Cl}_2(\text{en})_4]\text{Cl}_2$ and $[\text{NiBr}_2(\text{en})_4]\text{Br}_2$ were reported (Antsyshkina & Porai-Koshits, 1962). Subsequently, variations within the $\{\text{NiCl}\}_2$ core have been noted for the series $[\text{Ni}_2\text{Cl}_2(\text{en})_4]X_2$, where X is Cl^- , ClO_4^- and BPh_4^- (Journaux & Kahn, 1979; Bkouche-Waksman *et al.*, 1981), and these workers noted that the strength of the ferromagnetic coupling between the nickel(II) centers was inversely correlated to the sum of the Ni-Cl distances.The structure of the title compound, (I), consists of a centrosymmetric complex dication and two bromide counterions. The asymmetric unit (Fig. 1) consists of one half of the dication and a single bromide counter-ion. There is a close approach of one of the N atoms to the bromide counter-ion {the $\text{N} \cdots \text{Br}$ distance of $3.389(4) \text{ \AA}$ is similar to that reported for $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3)_3]\text{Br}_3$ (Ariyananda & Norman, 2003)}. The cationic portion of the title complex is a centrosymmetric unit of two Ni atoms bridged unsymmetrically by two Br atoms. The separation of the two Ni atoms is $3.992(1) \text{ \AA}$ and the Br separation is $3.586(1) \text{ \AA}$. The Ni atoms are pseudo-

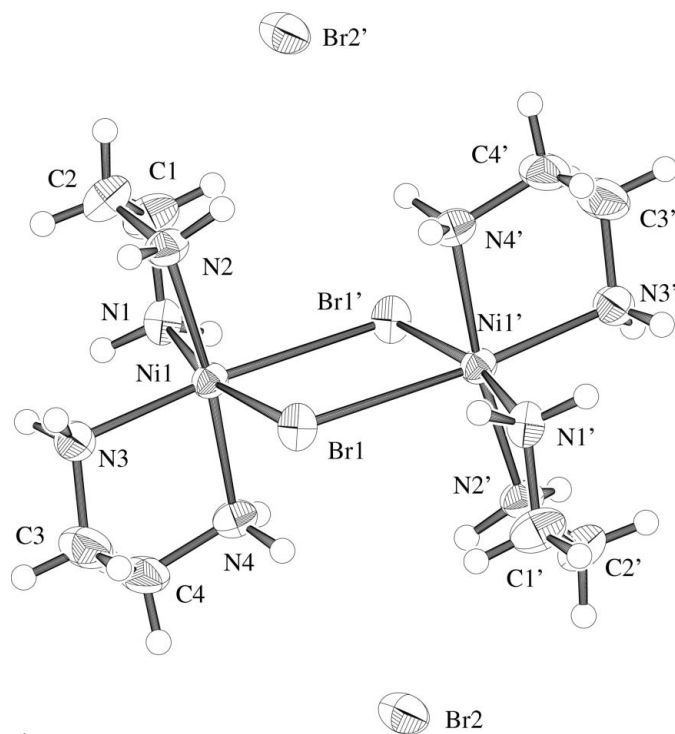


Figure 1
View of the structure of (I), with displacement ellipsoids drawn at the 50% probability level. Atoms marked with a ' are related to atoms not having a ' by $(1-x, -y, 1-z)$.

octahedral six-coordinate, with four N atoms from two en ligands completing the coordination environment. The difference in the Ni—Br distances (0.1105 Å) is pronounced, and appears to be typical of these types of dimers (see, for example, Tong *et al.*, 2000; L'Haridon & Bkouche-Waksman, 1978). Similar unsymmetric bridges are observed for the analogous chloride-bridged dimers (Tong *et al.*, 1999; Journaux & Kahn, 1979; Bkouche-Waksman *et al.*, 1981). The Ni—N distances for the title complex are very similar to those reported for the various $[\text{Ni}_2\text{Cl}_2(\text{en})_4]\text{X}_2$ complexes.

Preliminary attempts to produce various $[\text{Ni}_2\text{Br}_2(\text{en})_4]\text{X}_2$ complexes by attempted metathesis with a tenfold excess of various other anion sources failed, yielding only the title complex as the crystalline material.

Experimental

A modification of State's procedure was followed (State, 1960). Tris(1,2-diaminoethane)nickel(II) bromide (15.31 g, 38.39 mmol) and nickel(II) bromide trihydrate (5.71 g, 21.0 mmol) were dissolved in a mixture of 47.5 ml methanol and 2.5 ml water. The resultant deep-blue solution was refluxed for 10 min and then filtered. To prepare seed crystals, 4 ml acetone were slowly added to 3 ml of the blue solution. The resultant seed crystals were added to the remaining blue solution, followed by 100 ml acetone (dropwise). The resultant mixture was stirred for 10 min and the solids collected by vacuum filtration. The blue solid was recrystallized from 10% aqueous methanol. Absorption spectrum (10% aqueous methanol) λ_{max} (ϵ_{M}): 356.5 (5.80), 570.5 (3.61), 931.0 (4.84). ^1H NMR (300 MHz, CD_3OD): 97.

Crystal data

$[\text{Ni}_2\text{Br}_2(\text{C}_2\text{H}_8\text{N}_2)_4]\text{Br}_2$
 $M_r = 677.41$
 Monoclinic, $P2_1/n$
 $a = 6.6235$ (14) Å
 $b = 11.329$ (2) Å
 $c = 14.3470$ (17) Å
 $\beta = 94.753$ (15)°
 $V = 1072.9$ (3) Å³
 $Z = 2$

$D_x = 2.097$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 23.3$ – 25.1 °
 $\mu = 9.23$ mm⁻¹
 $T = 294$ K
 Prism, blue
 $0.50 \times 0.30 \times 0.30$ mm

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.035$, $T_{\text{max}} = 0.063$
 4342 measured reflections
 4049 independent reflections
 2250 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 32.5$ °
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 17$
 $l = -21 \rightarrow 21$
 3 standard reflections
 every 150 reflections
 intensity decay: 2.7%

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.049$
 $S = 1.04$
 2250 reflections
 101 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o) + 0.00106|F_o|^2]$

$(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.80$ e Å⁻³
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: $1.1(1) \times 10^{-6}$

Table 1

Selected geometric parameters (Å, °).

Br1—Ni1	2.6272 (8)	Ni1—N2	2.075 (4)
Br1—Ni1 ⁱ	2.7377 (8)	Ni1—N3	2.108 (4)
Ni1—N1	2.081 (4)	Ni1—N4	2.079 (4)
Ni1—Br1—Ni1 ⁱ	96.15 (2)	Br1 ⁱ —Ni1—N3	174.4 (1)
Br1—Ni1—Br1 ⁱ	83.85 (2)	Br1 ⁱ —Ni1—N4	91.8 (1)
Br1—Ni1—N1	168.2 (1)	N1—Ni1—N2	83.4 (2)
Br1—Ni1—N2	91.9 (1)	N1—Ni1—N3	95.1 (1)
Br1—Ni1—N3	95.7 (1)	N1—Ni1—N4	95.4 (1)
Br1—Ni1—N4	90.5 (1)	N2—Ni1—N3	90.3 (1)
Br1 ⁱ —Ni1—N1	85.8 (1)	N2—Ni1—N4	172.6 (2)
Br1 ⁱ —Ni1—N2	95.3 (1)	N3—Ni1—N4	82.5 (1)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H2 ⁱⁱ ⋯Br2 ⁱⁱ	0.95	2.44	3.389 (4)	172

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

H atoms were positioned geometrically ($C-H = 0.95$ Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN for Windows*; molecular graphics:

ORTEPII (Johnson, 1976); software used to prepare material for publication: *TEXSAN for Windows*.

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