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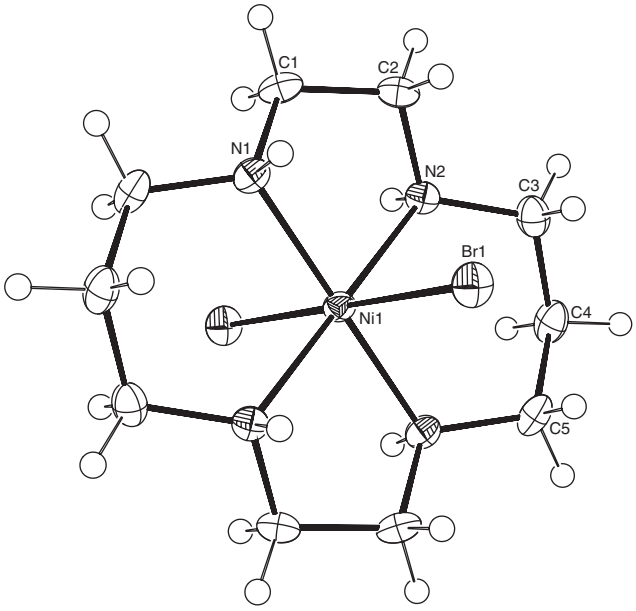
Crystal structure of trans-dibromido(1,4,8,11-tetraazacyclotetradecane)nickel(II), $C_{10}H_{24}Br_2N_4Ni$



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Abstract

$C_{10}H_{24}Br_2N_4Ni$, monoclinic, $P2_1/c$ (no. 14), $a = 6.9551(4)$ Å, $b = 12.6275(7)$ Å, $c = 8.7343(4)$ Å, $\beta = 109.1167(18)°$, $V = 724.79(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0226$, $wR_{ref}(F^2) = 0.0439$, $T = 223(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a solution of $NiBr_2$ (0.4940 g, 2.261 mmol) in H_2O (50 mL) was added 1,4,8,11-tetraazacyclotetradecane (0.4529 g, 2.261 mmol) and the mixture was stirred for 3 h at room temperature. After evaporation of the solvent, the residue was washed with MeOH and acetone, and dried at 50 °C, to give a violet powder (0.8560 g). Crystals were obtained by slow evaporation from a MeOH/acetone solution.

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Table 1: Data collection and handling.

Crystal:	Violet stick
Size:	0.17 × 0.12 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	68.4 cm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
$2\theta_{max}$, completeness:	56.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23002, 1810, 0.063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1556
$N(param)_{refined}$:	79
Programs:	Bruker programs [7], SHELX [8], ORTEP-3 [9], PLATON [10]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Ni1	0.0000	0.5000	0.5000	0.01629(9)
Br1	−0.20782(3)	0.47376(2)	0.70838(3)	0.02400(7)
N1	0.0476(3)	0.65389(13)	0.5815(2)	0.0193(4)
H1	−0.0316	0.6637	0.6561	0.023*
N2	0.2760(3)	0.46927(14)	0.67581(19)	0.0182(4)
H2	0.3790	0.4691	0.6199	0.022*
C1	0.2651(3)	0.66118(17)	0.6817(3)	0.0227(5)
H1A	0.2878	0.7241	0.7511	0.027*
H1B	0.3498	0.6672	0.6118	0.027*
C2	0.3221(3)	0.56225(18)	0.7850(2)	0.0230(4)
H2A	0.4672	0.5635	0.8485	0.028*
H2B	0.2440	0.5586	0.8601	0.028*
C3	0.2970(3)	0.36721(18)	0.7611(3)	0.0244(5)
H3A	0.2071	0.3664	0.8271	0.029*
H3B	0.4373	0.3594	0.8340	0.029*
C4	0.2440(3)	0.27415(17)	0.6430(3)	0.0258(5)
H4A	0.3224	0.2812	0.5686	0.031*
H4B	0.2882	0.2087	0.7048	0.031*
C5	0.0196(3)	0.26272(17)	0.5425(3)	0.0248(5)
H5A	−0.0026	0.1933	0.4895	0.030*
H5B	−0.0627	0.2661	0.6145	0.030*

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Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.98 Å, d(N—H) = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$. The highest peak (0.52 e Å^{-3}) and the deepest hole (−0.41 e Å^{-3}) in the difference Fourier map are located 1.11 Å and 0.848 Å from the atoms H2A and Ni1, respectively.

Discussion

This contribution is part of my continuing interest in the structural chemistry of 1,4,8,11-tetraazacyclotetradecane (cyclam) compounds [1–4]. The crystal structure of the related chlorido complex [$NiCl_2$(cyclam)] has been determined previously [5, 6].

In the title complex trans-[$NiBr_2$(cyclam)], the central Ni(II) ion is six-coordinated in a slightly distorted octahedral manner by four N atoms from the tetradentate cyclam ligand, occupying the four equatorial positions and two bromido ligands in the axial positions. The Ni atom is located on an inversion center, and therefore the asymmetric unit contains one half of the complex and the NiN_4 moiety is exactly planar. The Ni—N bond lengths are almost equal (d(Ni—N) = 2.0589(17) Å and 2.0648(16) Å). The six-membered chelate rings are in the stable chair conformations and the N1—C1—C2—N2 torsion angle of 56.9(2)° displays the gauche conformation for the group within the five-membered chelate rings. In the crystal structure, the complexes are stacked in columns along [100]. Inter- and intramolecular N—H···Br hydrogen bonds with d(N···Br) = 3.2939(17)–3.5074(17) Å further stabilize the crystal structure.

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