

Bis(1,5-diazacyclooctane-*N,N'*)- nickel(II) dibromide

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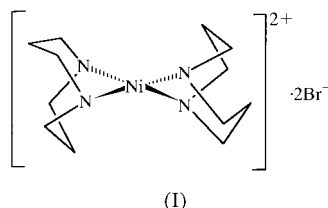
Received 19 June 2000

Accepted 22 August 2000

The crystal structure of the title complex, $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2]\text{Br}_2$, consists of discrete $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2]^{2+}$ cations and bromide counter-anions. The Ni^{II} ion is at the center of symmetry and is four-coordinated by four nitrogen donors of the mesocyclic ligand 1,5-diazacyclooctane (DACO) [$\text{Ni}-\text{N}$ 1.935 (2)–1.937 (2) Å]. The coordination geometry of Ni^{II} can be considered as square planar and both DACO ligands take the boat–chair conformation. The bromide anions are hydrogen bonded with the nitrogen donors of the ligands to form a macrocycle-like ring system.

Comment

1,5-Diazacyclooctane (DACO) is a typical example of a diazamacrocyclic ligand with several attractive features (Musker, 1992; Mills *et al.*, 1990; Grapperhaus & Darensbourg, 1998). Musker & Hussain (1966) first reported the Cu^{II} and Ni^{II} complexes of DACO, and deduced that the metal center appeared to be rigorously square-planar with both ligands arranged in the boat–chair conformation. However, the first crystal structure of DACO (Royer *et al.*, 1972), $[\text{Ni}(\text{DACO})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, showed that the trimethylene groups in DACO do not fold over as predicted but are arranged in a plane so that all the H atoms in the trimethylene groups are eclipsed. Another crystal structure of the same molecule (Hussain *et al.*, 1986) confirmed the above result, but the C–C bond distances in the methylene groups are significantly shorter than a normal sp^3 hybrid. A third structure determination (Boeyens *et al.*, 1984) showed that DACO rings were in



a boat–chair relationship as originally predicted due to the discovery of the molecular disorder in this structure. In order

to further examine this problem, we report herein the synthesis and crystal structure of a new Ni^{II} complex, $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2]\text{Br}_2$, (I), including the same cation, and in which both DACO rings are in the boat–chair conformation.

The structure of the title complex comprises discrete $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2]^{2+}$ cations and bromide counter-anions. A perspective view showing the $[\text{Ni}(\text{DACO})]^{2+}$ cation along the coordination plane is shown in Fig. 1. In the complex cation, the Ni^{II} center is four-coordinated, forming an exact plane with the Ni^{II} ion at the center of symmetry. Two independent Ni–N bond distances are nearly equivalent [$\text{Ni}1-\text{N}1$ 1.935 (2) and $\text{Ni}1-\text{N}2$ 1.937 (2) Å], but the chelate $\text{N}1-\text{Ni}-\text{N}2$ angle [86.68 (9)°] is slightly smaller than the non-chelate $\text{N}1-\text{Ni}1-\text{N}2^i$ angle [93.32 (9)°; symmetry code: (i) $1-x, -y, -z$]. The C–C bond distances in the methylene groups of DACO range from 1.512 (4) to 1.517 (4) Å, which suggests a normal aliphatic C–C bond with sp^3 hybrid. The DACO rings in the complexes take the boat–chair conformation, which has least non-bonding interaction and lowest energy. The bromide ions have no close contacts to the Ni^{II} centers, since the shortest axial distance for $\text{Ni} \cdots \text{Br}$ is 4.344 (3) Å. The central methylene C–H group of the boat form of the

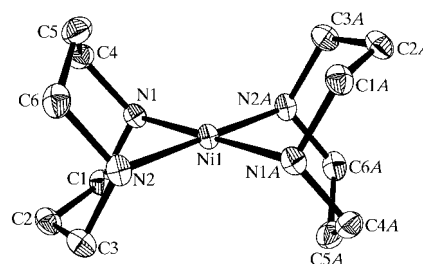


Figure 1
ORTEP (Johnson, 1976) view of the cation of the title complex shown with 30% probability ellipsoids.

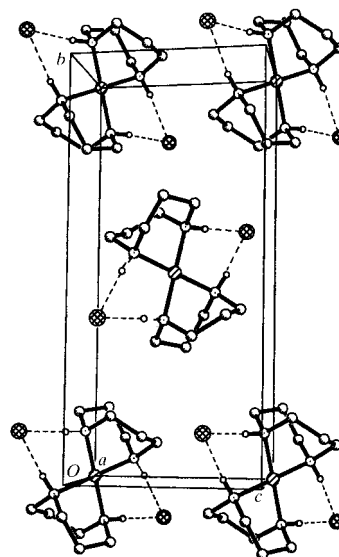


Figure 2
Molecular-packing diagram in the unit cell of (I) (H atoms not mentioned in the text have been omitted for clarity).

metalladiazacyclohexane rings shields the metal center in the complex with an $\text{H}\cdots\text{Ni}$ distance of 2.875 Å. Thus, this methylene hydrogen effectively blocks the axial coordination position to give this four-coordinated Ni^{II} complex. An important feature to note is that each $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2]^{2+}$ unit carries two bromide ions which are hydrogen bonded to the nitrogen donors of DACO (Fig. 2). These hydrogen bonds form a macrocycle-like ring system including a pair of $\text{N}\cdots\text{H}\cdots\text{Br}\cdots\text{N}\cdots\text{H}$ bridges. However, these bonds are relatively weak, with interatomic distances of 3.373 (4) ($\text{N1}\cdots\text{Br1}^{\text{ii}}$) and 3.313 (2) Å ($\text{N2}\cdots\text{Br1}^{\text{iii}}$), which are both in the range of weak hydrogen-bond distances (Stout & Jensen, 1968). Furthermore, the $\text{N1}-\text{H1C}\cdots\text{Br1}^{\text{ii}}$ and $\text{N2}-\text{H2C}\cdots\text{Br1}^{\text{iii}}$ hydrogen-bond angles are 165 and 168°, respectively [symmetry codes: (ii) $1-x, -y, 1-z$; (iii) $-1+x, y, -1+z$].

Experimental

The ligand 1,5-diazacyclooctane (DACO) dihydrobromide was prepared according to a literature method (Buhle *et al.*, 1943; Billman & Dorman, 1962). A mixture of $\text{Ni}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$ (373 mg, 1.5 mmol) and DACO dihydrobromide (822 mg, 3 mmol) was dissolved in methanol (30 ml) at room temperature. The ligand was neutralized by slow addition of KOH methanol solution to the above mixture, then the resulting yellow solution was allowed to stand for 5 d and yellow block-shaped crystals were deposited slowly with the evaporation of the solvent. Yield: 468 mg (70%). FT-IR data (KBr pellet, cm^{-1}): 3440 (*s*), 3096 (*vs*), 3056 (*vs*), 2957 (*m*), 2314 (*m*), 1618 (*m*), 1463 (*s*), 1425 (*s*), 1360 (*m*), 1262 (*m*), 1179 (*s*), 1106 (*s*), 1047 (*s*), 991 (*s*), 891 (*m*), 780 (*m*). Analysis calculated for the title complex: C 32.25, H 6.32, N 12.54%; found: C 32.11, H 6.40, N 12.38%.

Crystal data

$[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2]\text{Br}_2$	$D_x = 1.765 \text{ Mg m}^{-3}$
$M_r = 446.91$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3369 reflections
$a = 7.1366$ (5) Å	$\theta = 3.05\text{--}25.02^\circ$
$b = 16.0369$ (10) Å	$\mu = 5.898 \text{ mm}^{-1}$
$c = 7.4236$ (5) Å	$T = 293$ (2) K
$\beta = 98.1210$ (10)°	Prism, yellow
$V = 841.10$ (10) Å ³	$0.25 \times 0.20 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART 1000 diffractometer	1480 independent reflections
ω scans	1384 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (Stout & Jensen, 1968)	$R_{\text{int}} = 0.023$
$T_{\text{min}} = 0.321$, $T_{\text{max}} = 0.385$	$\theta_{\text{max}} = 25.02^\circ$
3428 measured reflections	$h = -6 \rightarrow 8$
	$k = -12 \rightarrow 19$
	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.2883P]$
$R(F) = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.146$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
1480 reflections	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$
88 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

$\text{Ni1}-\text{N2}$	1.935 (2)	$\text{C6}-\text{C5}$	1.512 (4)
$\text{Ni1}-\text{N1}$	1.937 (2)	$\text{N1}-\text{C1}$	1.496 (3)
$\text{C1}-\text{C2}$	1.512 (4)	$\text{N1}-\text{C4}$	1.502 (4)
$\text{C2}-\text{C3}$	1.517 (4)	$\text{N2}-\text{C6}$	1.498 (4)
$\text{C4}-\text{C5}$	1.514 (4)	$\text{C3}-\text{N2}$	1.492 (3)
$\text{N2}^{\text{i}}-\text{Ni1}-\text{N1}^{\text{i}}$	86.68 (9)	$\text{N2}-\text{C3}-\text{C2}$	112.8 (2)
$\text{N2}-\text{Ni1}-\text{N1}^{\text{i}}$	93.32 (9)	$\text{C3}-\text{N2}-\text{C6}$	113.9 (2)
$\text{N1}-\text{C1}-\text{C2}$	113.1 (2)	$\text{N2}-\text{C6}-\text{C5}$	112.1 (2)
$\text{C1}-\text{C2}-\text{C3}$	114.4 (2)	$\text{C6}-\text{C5}-\text{C4}$	113.8 (2)
$\text{N1}-\text{C4}-\text{C5}$	112.3 (2)		

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

H atoms were located from geometrical calculations and included in the structure-factor calculations as riding atoms, with $\text{N}-\text{H} = 0.91$ and $\text{C}-\text{H} = 0.97$ Å.

Data collection: SMART1000 Operation Manual (Bruker, 1998); cell refinement: SMART1000 Operation Manual; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXL97.

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 29771022 and 29971019), Tianjin Natural Science Foundation and the Trans-Century Talents Training Program Foundation from the State Education Ministry of China to XHB.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1103). Services for accessing these data are described at the back of the journal.

References

- Billman, J. H. & Dorman, L. C. (1962). *J. Org. Chem.* **27**, 2419–2422.
- Boeyens, J. A., Fox, C. C. & Hancock, R. D. (1984). *Inorg. Chim. Acta*, **87**, 1–4.
- Bruker (1998). SMART1000 Operation Manual and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Buhle, E. L., Moore, A. M. & Wiselogle, F. Y. (1943). *J. Am. Chem. Soc.* **65**, 29–32.
- Grapperhaus, C. A. & Darensbourg, M. Y. (1998). *Acc. Chem. Res.* **31**, 451–459.
- Hussain, M. S., Abmad, J., Haque, M. & Khattak, G. D. (1986). *Transition Met. Chem.* **11**, 155–159.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Mills, D. K., Reibenspies, J. H. & Darensbourg, M. Y. (1990). *Inorg. Chem.* **29**, 4364–4366.
- Musker, W. K. (1992). *Coord. Chem. Rev.* **117**, 133–157.
- Musker, W. K. & Hussain, M. S. (1966). *Inorg. Chem.* **5**, 1416–1419.
- Royer, D. J., Schievelbein, V. H., Kalyanaraman, A. R. & Bertrand, J. A. (1972). *Inorg. Chim. Acta*, **6**, 307–313.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Stout, G. H. & Jensen, L. H. (1968). In *X-ray Structure Determination: A Practical Guide*. New York: MacMillan.