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# Azido{2,4-dibromo-6-[(2-diethylaminoethylimino)methyl]phenolato}nickel(II)

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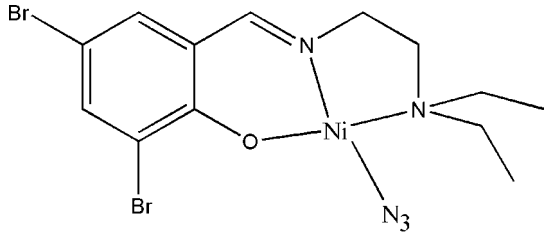
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.036; $wR$ factor = 0.080; data-to-parameter ratio = 18.1.

In the title mononuclear nickel(II) complex, $[Ni(C_{13}H_{17}Br_2N_2O)(N_3)]$, the $Ni^{II}$ atom is four-coordinated by the phenolate O, imine N and amine N atoms of one Schiff base ligand, and by the terminal N atom of an azide ligand, forming a square-planar geometry.

## Related literature

For related literature, see: Arıcı *et al.* (2005); Brückner *et al.* (2000); Diao (2007*a*); Diao (2007*b*); Diao, Huang *et al.* (2007); Diao, Shu *et al.* (2007); Harrop *et al.* (2003); Li *et al.* (2007); Marganian *et al.* (1995); Ren *et al.* (2002); Usman *et al.* (2003); Van Hecke *et al.* (2007).




## Experimental

*Crystal data*

$[Ni(C_{13}H_{17}Br_2N_2O)(N_3)]$
$M_r$ = 477.85
Monoclinic, $P2_1/c$
$a$ = 16.565 (2) Å
$b$ = 9.9972 (14) Å
$c$ = 10.1889 (15) Å
$\beta$ = 96.122 (2)°
$V$ = 1677.7 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 5.93 mm$^{-1}$
$T$ = 298 (2) K
0.20 × 0.20 × 0.18 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.384, $T_{max}$ = 0.415
(expected range = 0.318–0.344)
9529 measured reflections
3640 independent reflections
2428 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.080
$S$ = 1.02
3640 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.58 e Å$^{-3}$

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2359).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m2291 [ **doi:10.1107/S1600536807037592** ]

# Azido{2,4-dibromo-6-[(2-diethylaminoethylimino)methyl]phenolato}nickel(II)

**K. Li, S.-S. Huang, B.-J. Zhang, D.-L. Meng and Y.-P. Diao**

## Comment

Nickel(II) complexes with Schiff base ligands have received much attention in recent years (Marganian *et al.*, 1995). Some of the complexes have been found to have pharmacological and antitumor properties (Harrop *et al.*, 2003; Brückner *et al.*, 2000; Ren *et al.*, 2002). Nickel is also present in the active sites of several important classes of metalloproteins, as either a homodinuclear or a heterodinuclear species. We have recently reported a few transition metal complexes (Diao, Huang *et al.*, 2007; Diao, Shu *et al.*, 2007; Diao, 2007*a*,*b*). In order to further develop the coordination chemistry of such nickel complexes, we report herein the title new nickel(II) compound.

The $Ni^{II}$ atom in the mononuclear complex is four-coordinate in a square-planar geometry with one phenolate O, one imine N, and one amine N atoms of one Schiff base ligand and one terminal N atom of an azide ligand (Fig. 1). All the bond values (Table 1) subtended at the metal centres are comparable with the values observed in other Schiff base nickel(II) complexes (Arıcı *et al.*, 2005; Usman *et al.*, 2003; Van Hecke *et al.*, 2007; Li *et al.*, 2007).

## Experimental

3,5-Dibromosalicylaldehyde (0.1 mmol, 18.0 mg), *N*,*N*-diethylethane-1,2-diamine (0.1 mmol, 11.6 mg), sodium azide (0.1 mmol, 6.5 mg), and $Ni(NO_3)_2{\cdot}6H_2O$ (0.1 mmol, 29.0 mg) were dissolved in a methanol solution (10 ml). The mixture was stirred at room temperature for 30 min to give a red solution. After keeping the solution in air for a week, red block-like crystals were formed.

## Refinement

H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}$(methyl C).

## Figures

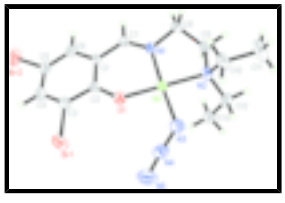


Fig. 1. The structure of the complex with 30% probability level.

**Azido{2,4-dibromo-6-[(2-diethylaminoethylimino)methyl]phenolato}nickel(II)**

*Crystal data*

| | |
|---|---|
| $[Ni(C_{13}H_{17}Br_2N_2O)(N_3)]$ | $F_{000} = 944$ |
| $M_r = 477.85$ | $D_x = 1.892$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 2309 reflections |
| $a = 16.565$ (2) Å | $\theta = 2.3$–$25.0$º |
| $b = 9.9972$ (14) Å | $\mu = 5.93$ mm$^{-1}$ |
| $c = 10.1889$ (15) Å | $T = 298$ (2) K |
| $\beta = 96.122$ (2)º | Block, red |
| $V = 1677.7$ (4) Å$^3$ | 0.20 × 0.20 × 0.18 mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3640 independent reflections |
| Radiation source: fine-focus sealed tube | 2428 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.032$ |
| $T = 298$(2) K | $\theta_{max} = 27.0$º |
| ω scans | $\theta_{min} = 2.4$º |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $h = -21 \rightarrow 18$ |
| $T_{min} = 0.384$, $T_{max} = 0.415$ | $k = -12 \rightarrow 11$ |
| 9529 measured reflections | $l = -12 \rightarrow 13$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | H-atom parameters constrained |
| $wR(F^2) = 0.080$ | $w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.1742P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3640 reflections | $\Delta\rho_{max} = 0.42$ e Å$^{-3}$ |
| 201 parameters | $\Delta\rho_{min} = -0.58$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ni1 | 0.28675 (2) | 0.75958 (4) | 0.36809 (4) | 0.03799 (13) |
| Br1 | 0.16019 (3) | 1.18409 (4) | 0.39701 (5) | 0.07939 (18) |
| Br2 | 0.00998 (3) | 0.98626 (5) | 0.83122 (5) | 0.07886 (18) |
| O1 | 0.21837 (14) | 0.9014 (2) | 0.3894 (2) | 0.0455 (6) |
| N1 | 0.23011 (15) | 0.6439 (2) | 0.4665 (3) | 0.0381 (6) |
| N2 | 0.35931 (16) | 0.6084 (3) | 0.3421 (3) | 0.0399 (7) |
| N3 | 0.34772 (18) | 0.8696 (3) | 0.2634 (3) | 0.0557 (8) |
| N4 | 0.35300 (19) | 0.9880 (4) | 0.2758 (3) | 0.0563 (8) |
| N5 | 0.3610 (3) | 1.1018 (4) | 0.2802 (4) | 0.0957 (14) |
| C1 | 0.14857 (18) | 0.8076 (3) | 0.5639 (3) | 0.0399 (8) |
| C2 | 0.16979 (19) | 0.9133 (3) | 0.4813 (4) | 0.0405 (8) |
| C3 | 0.1356 (2) | 1.0402 (3) | 0.5052 (4) | 0.0497 (9) |
| C4 | 0.0879 (2) | 1.0608 (4) | 0.6041 (4) | 0.0579 (11) |
| H4 | 0.0666 | 1.1453 | 0.6168 | 0.069* |
| C5 | 0.0711 (2) | 0.9553 (4) | 0.6862 (4) | 0.0523 (10) |
| C6 | 0.09968 (19) | 0.8300 (4) | 0.6656 (4) | 0.0503 (9) |
| H6 | 0.0867 | 0.7595 | 0.7191 | 0.060* |
| C7 | 0.17848 (19) | 0.6753 (3) | 0.5458 (3) | 0.0414 (8) |
| H7 | 0.1588 | 0.6070 | 0.5956 | 0.050* |
| C8 | 0.2532 (2) | 0.5030 (3) | 0.4539 (4) | 0.0462 (9) |
| H8A | 0.2226 | 0.4629 | 0.3774 | 0.055* |
| H8B | 0.2424 | 0.4532 | 0.5318 | 0.055* |
| C9 | 0.3422 (2) | 0.5013 (3) | 0.4386 (3) | 0.0451 (9) |
| H9A | 0.3576 | 0.4146 | 0.4066 | 0.054* |
| H9B | 0.3734 | 0.5176 | 0.5232 | 0.054* |
| C10 | 0.3358 (2) | 0.5630 (4) | 0.2019 (3) | 0.0550 (10) |
| H10A | 0.3403 | 0.6391 | 0.1440 | 0.066* |
| H10B | 0.2791 | 0.5368 | 0.1938 | 0.066* |
| C11 | 0.3845 (3) | 0.4478 (4) | 0.1518 (4) | 0.0873 (15) |
| H11A | 0.4404 | 0.4738 | 0.1534 | 0.131* |
| H11B | 0.3633 | 0.4258 | 0.0631 | 0.131* |
| H11C | 0.3806 | 0.3711 | 0.2076 | 0.131* |
| C12 | 0.4480 (2) | 0.6429 (4) | 0.3606 (4) | 0.0496 (9) |

| | | | | |
|---|---|---|---|---|
| H12A | 0.4613 | 0.6943 | 0.2851 | 0.060* |
| H12B | 0.4794 | 0.5609 | 0.3634 | 0.060* |
| C13 | 0.4724 (2) | 0.7220 (4) | 0.4846 (4) | 0.0592 (10) |
| H13A | 0.4438 | 0.8056 | 0.4805 | 0.089* |
| H13B | 0.5298 | 0.7386 | 0.4922 | 0.089* |
| H13C | 0.4592 | 0.6720 | 0.5599 | 0.089* |

*Atomic displacement parameters (Å$^2$)*

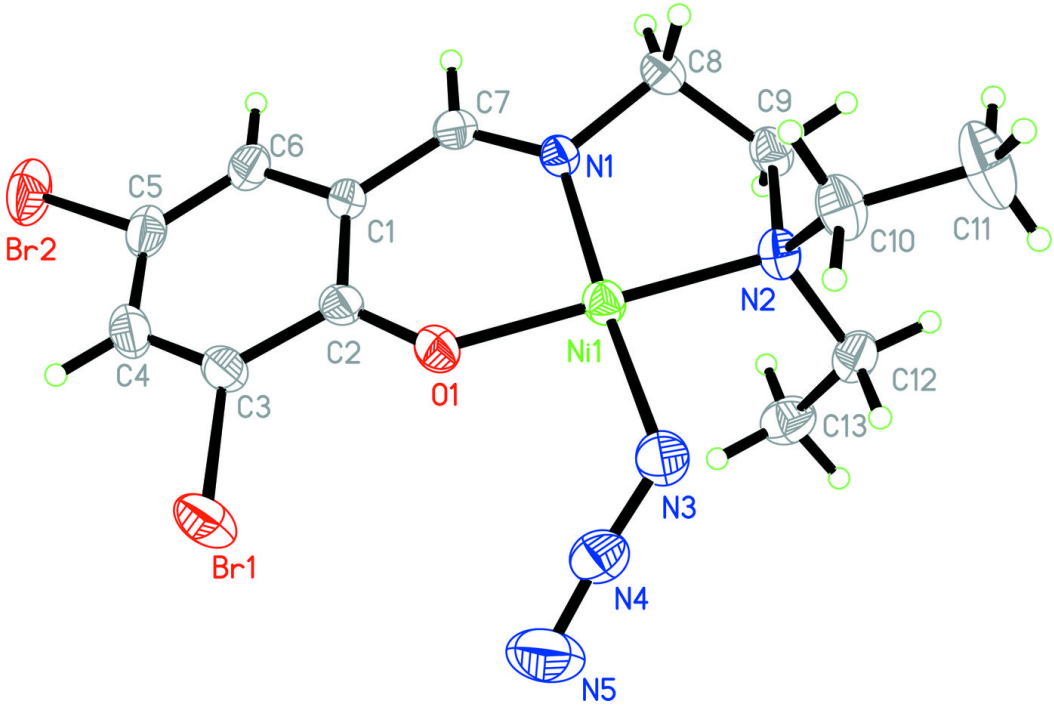
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0401 (2) | 0.0350 (2) | 0.0390 (3) | 0.00371 (19) | 0.00473 (18) | 0.00248 (19) |
| Br1 | 0.0849 (3) | 0.0361 (2) | 0.1165 (4) | 0.0036 (2) | 0.0078 (3) | 0.0110 (2) |
| Br2 | 0.0598 (3) | 0.0985 (4) | 0.0808 (4) | 0.0171 (2) | 0.0193 (2) | −0.0281 (3) |
| O1 | 0.0483 (14) | 0.0345 (13) | 0.0547 (16) | 0.0054 (11) | 0.0106 (12) | 0.0059 (11) |
| N1 | 0.0334 (15) | 0.0309 (14) | 0.0496 (18) | 0.0028 (12) | 0.0029 (13) | −0.0026 (12) |
| N2 | 0.0448 (16) | 0.0419 (16) | 0.0328 (16) | 0.0100 (13) | 0.0034 (13) | 0.0017 (12) |
| N3 | 0.067 (2) | 0.0494 (19) | 0.054 (2) | 0.0063 (16) | 0.0203 (16) | 0.0124 (16) |
| N4 | 0.065 (2) | 0.060 (2) | 0.046 (2) | −0.0041 (18) | 0.0141 (16) | 0.0124 (17) |
| N5 | 0.139 (4) | 0.061 (3) | 0.094 (3) | −0.028 (3) | 0.046 (3) | −0.002 (2) |
| C1 | 0.0310 (17) | 0.0342 (18) | 0.054 (2) | 0.0009 (14) | 0.0048 (16) | −0.0036 (16) |
| C2 | 0.0321 (18) | 0.0346 (18) | 0.053 (2) | −0.0019 (15) | −0.0038 (16) | −0.0042 (16) |
| C3 | 0.043 (2) | 0.0356 (19) | 0.069 (3) | 0.0013 (16) | −0.0037 (19) | −0.0038 (17) |
| C4 | 0.041 (2) | 0.048 (2) | 0.082 (3) | 0.0095 (18) | −0.006 (2) | −0.021 (2) |
| C5 | 0.037 (2) | 0.062 (3) | 0.058 (3) | 0.0040 (18) | 0.0061 (18) | −0.020 (2) |
| C6 | 0.0351 (19) | 0.055 (2) | 0.061 (3) | 0.0003 (17) | 0.0072 (18) | −0.0085 (19) |
| C7 | 0.0365 (19) | 0.0366 (18) | 0.051 (2) | −0.0031 (15) | 0.0051 (16) | 0.0022 (16) |
| C8 | 0.049 (2) | 0.0317 (17) | 0.059 (2) | 0.0020 (15) | 0.0076 (18) | −0.0005 (16) |
| C9 | 0.053 (2) | 0.0368 (18) | 0.045 (2) | 0.0096 (16) | 0.0068 (18) | 0.0044 (16) |
| C10 | 0.070 (2) | 0.057 (2) | 0.038 (2) | 0.016 (2) | 0.0014 (19) | −0.0036 (18) |
| C11 | 0.131 (4) | 0.074 (3) | 0.056 (3) | 0.043 (3) | 0.006 (3) | −0.015 (2) |
| C12 | 0.043 (2) | 0.055 (2) | 0.053 (2) | 0.0078 (17) | 0.0120 (18) | 0.0106 (19) |
| C13 | 0.048 (2) | 0.064 (3) | 0.064 (3) | −0.0058 (19) | 0.0007 (19) | 0.009 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ni1—O1 | 1.842 (2) | C5—C6 | 1.364 (5) |
| Ni1—N1 | 1.850 (3) | C6—H6 | 0.9300 |
| Ni1—N3 | 1.897 (3) | C7—H7 | 0.9300 |
| Ni1—N2 | 1.967 (3) | C8—C9 | 1.499 (5) |
| Br1—C3 | 1.883 (4) | C8—H8A | 0.9700 |
| Br2—C5 | 1.903 (4) | C8—H8B | 0.9700 |
| O1—C2 | 1.303 (4) | C9—H9A | 0.9700 |
| N1—C7 | 1.277 (4) | C9—H9B | 0.9700 |
| N1—C8 | 1.469 (4) | C10—C11 | 1.525 (5) |
| N2—C9 | 1.501 (4) | C10—H10A | 0.9700 |
| N2—C12 | 1.502 (4) | C10—H10B | 0.9700 |
| N2—C10 | 1.511 (4) | C11—H11A | 0.9600 |
| N3—N4 | 1.193 (4) | C11—H11B | 0.9600 |
| N4—N5 | 1.146 (4) | C11—H11C | 0.9600 |

| | | | |
|---|---|---|---|
| C1—C6 | 1.400 (5) | C12—C13 | 1.508 (5) |
| C1—C2 | 1.418 (5) | C12—H12A | 0.9700 |
| C1—C7 | 1.431 (4) | C12—H12B | 0.9700 |
| C2—C3 | 1.420 (4) | C13—H13A | 0.9600 |
| C3—C4 | 1.361 (5) | C13—H13B | 0.9600 |
| C4—C5 | 1.393 (5) | C13—H13C | 0.9600 |
| C4—H4 | 0.9300 | | |
| O1—Ni1—N1 | 93.63 (11) | C1—C7—H7 | 117.5 |
| O1—Ni1—N3 | 89.50 (12) | N1—C8—C9 | 106.8 (3) |
| N1—Ni1—N3 | 176.74 (13) | N1—C8—H8A | 110.4 |
| O1—Ni1—N2 | 179.04 (11) | C9—C8—H8A | 110.4 |
| N1—Ni1—N2 | 86.85 (11) | N1—C8—H8B | 110.4 |
| N3—Ni1—N2 | 90.00 (12) | C9—C8—H8B | 110.4 |
| C2—O1—Ni1 | 126.1 (2) | H8A—C8—H8B | 108.6 |
| C7—N1—C8 | 119.3 (3) | C8—C9—N2 | 108.4 (3) |
| C7—N1—Ni1 | 127.0 (2) | C8—C9—H9A | 110.0 |
| C8—N1—Ni1 | 113.6 (2) | N2—C9—H9A | 110.0 |
| C9—N2—C12 | 109.4 (2) | C8—C9—H9B | 110.0 |
| C9—N2—C10 | 111.0 (3) | N2—C9—H9B | 110.0 |
| C12—N2—C10 | 109.8 (3) | H9A—C9—H9B | 108.4 |
| C9—N2—Ni1 | 107.42 (19) | N2—C10—C11 | 116.8 (3) |
| C12—N2—Ni1 | 114.2 (2) | N2—C10—H10A | 108.1 |
| C10—N2—Ni1 | 104.97 (19) | C11—C10—H10A | 108.1 |
| N4—N3—Ni1 | 123.6 (3) | N2—C10—H10B | 108.1 |
| N5—N4—N3 | 175.2 (4) | C11—C10—H10B | 108.1 |
| C6—C1—C2 | 121.3 (3) | H10A—C10—H10B | 107.3 |
| C6—C1—C7 | 118.6 (3) | C10—C11—H11A | 109.5 |
| C2—C1—C7 | 120.1 (3) | C10—C11—H11B | 109.5 |
| O1—C2—C1 | 124.7 (3) | H11A—C11—H11B | 109.5 |
| O1—C2—C3 | 119.5 (3) | C10—C11—H11C | 109.5 |
| C1—C2—C3 | 115.8 (3) | H11A—C11—H11C | 109.5 |
| C4—C3—C2 | 122.4 (3) | H11B—C11—H11C | 109.5 |
| C4—C3—Br1 | 119.7 (3) | N2—C12—C13 | 113.4 (3) |
| C2—C3—Br1 | 117.8 (3) | N2—C12—H12A | 108.9 |
| C3—C4—C5 | 120.0 (3) | C13—C12—H12A | 108.9 |
| C3—C4—H4 | 120.0 | N2—C12—H12B | 108.9 |
| C5—C4—H4 | 120.0 | C13—C12—H12B | 108.9 |
| C6—C5—C4 | 120.5 (4) | H12A—C12—H12B | 107.7 |
| C6—C5—Br2 | 119.4 (3) | C12—C13—H13A | 109.5 |
| C4—C5—Br2 | 120.0 (3) | C12—C13—H13B | 109.5 |
| C5—C6—C1 | 119.9 (4) | H13A—C13—H13B | 109.5 |
| C5—C6—H6 | 120.0 | C12—C13—H13C | 109.5 |
| C1—C6—H6 | 120.0 | H13A—C13—H13C | 109.5 |
| N1—C7—C1 | 124.9 (3) | H13B—C13—H13C | 109.5 |
| N1—C7—H7 | 117.5 | | |

**Fig. 1**


C8
C7
C9
C6
N1
C5
C1
C10
C11
Br2
N2
Ni1
C2
C12
C4
O1
C3
C13
N3
Br1
N4
N5