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# Diazidobis(2,2′-biimidazole)nickel(II)

**Zhong-Hai Ni,[a]* Zhi-Nan Cai,[b] Wei-Feng Zhong[a] and Shang-Zheng Wei[a]**

[a]School of Chemistry and Chemical Technology, Shandong University, Jinan 250100, People's Republic of China, and [b]Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Correspondence e-mail: nizhh@sdu.edu.cn

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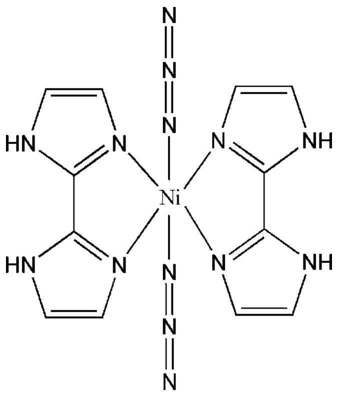
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.030; $wR$ factor = 0.069; data-to-parameter ratio = 12.1.

Green single crystals of the title compound, $[Ni(N_3)_2(C_6H_6N_4)_2]$, were obtained by reacting nickel(II) perchlorate with 2,2′-biimidazole ($H_2$bim) and sodium azide. The azide and $H_2$bim ligands are bonded to the Ni atom, which lies on an inversion centre, with approximately octahedral geometry. The azide anions are terminally bonded in two *trans* postitions. A two-dimensional supramolecular network is formed through hydrogen bonds between ligand $H_2$bim and azide N atoms.

## Related literature

For related literature, see: Albada *et al.* (2004); Atencio *et al.* (2004, 2005); Ding *et al.* (2005); Ghosh *et al.* (2006); Ghoshal *et al.* (2005); Sang & Xu (2006); Tadokoro & Nakasuji (2000); Xiao & Shreeve (2005).



## Experimental

### *Crystal data*

$[Ni(N_3)_2(C_6H_6N_4)_2]$
$M_r$ = 411.07
Monoclinic, $C2/c$
$a$ = 12.6974 (18) Å
$b$ = 8.8399 (10) Å
$c$ = 14.3537 (12) Å
$\beta$ = 91.803 (9)°
$V$ = 1610.3 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.24 mm$^{-1}$
$T$ = 293 (2) K
0.26 × 0.20 × 0.16 mm

### *Data collection*

Bruker P4 diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.743, $T_{max}$ = 0.820
1966 measured reflections
1505 independent reflections
1250 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022
3 standard reflections every 97 reflections intensity decay: none

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.069
$S$ = 1.02
1505 reflections
124 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$

### Table 1

Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$A$···N7$^{i}$ | 0.86 | 2.01 | 2.822 (3) | 157 |
| N4—H4$A$···N7$^{i}$ | 0.86 | 2.25 | 3.020 (3) | 149 |
| N4—H4$A$···N5$^{ii}$ | 0.86 | 2.55 | 3.044 (3) | 118 |

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

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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: HG2232).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m1570 [ **doi:10.1107/S1600536807021113** ]

# Diazidobis(2,2'-biimidazole)nickel(II)

**Z.-H. Ni, Z.-N. Cai, W.-F. Zhong** and **S.-Z. Wei**

## Comment

2,2'-biimidazole and its monoanion ligand Hbim$^-$ as well as its hydrogenated derivative 2,2'-biimidazoline play an important role in the molecular self-assembly and molecular recognition in chemical, physical and biological sciences, since they not only can be coordinated to metal centers as bidentate chelate but can act as donors in hydrogen bonding interactions usually leading to higher dimensional supramolecular structures (Atencio *et al.*, 2004; Ghosh *et al.*, 2006; Tadokoro & Nakasuji, 2000).

To date, a variety of supramolecular architectures involving polynuclear, one-, two- and three-dimensional molecular arrangements have been obtained based on the above mentioned multifunctional ligands (Atencio *et al.*, 2005; Ding *et al.*, 2005; Sang & Xu, 2006; Tadokoro & Nakasuji, 2000). More recntly, two novel dicyanamido-bridged one-dimensional polymeric complexes of manganese(II) have been reported using 2,2'-biimidazole as a bidentate chelate (Ghoshal *et al.*, 2005). It is well known that azide anion is an excellent bridging ligand and a good hydrogen bonds acceptant. Therefore, we hoped to obtain azide-bridged and hydrogen bonds-connected higher dimensional structures based on 2,2'-biimidazole and azide ligands and transitional metal ions through the control of their molar ratios. However, only a mononuclear complex $Ni(H_2bim)_2(N_3)_2$, (I), was obtained, and its molecular structure was reported herein.

An ORTEP drawing of the title complex is shown in Fig. 1. In the complex $Ni(H_2bim)_2(N_3)_2$, the central Ni atom is hexacoordinated by six N atoms from two $H_2bim$ ligands and two azide ions leading to an approximately octahedral structure. The basal plane of the octahedral coordination of the Ni(II) atom is formed by four N atoms from two bidentate chelating $H_2bim$ and the apical position is occupied by N atoms of two azide groups. The Ni—N bond distances range from from 2.0931 (19)Å to 2.153 (2) Å, which are similar to those of Ni—N bond in complex $[Ni(N_3)_2(C_6H_{10}N_4)_2]$ (Albada *et al.*, 2004). The Ni1—N5—N6 bond angle is 119.90 (18)°. The azide anion is nearly linear [N5—N6—N7 = 179.0 (3)°]. The N—N bond lengths of 1.180 (3)Å for N5—N6 and 1.173 (3)Å for N6—N7 are normal.

The $Ni(H_2bim)_2(N_3)_2$ units are connected together by the intermolecular hydrogen bonds involving uncoordinated $H_2bim$ ligand and azide nitrogen atoms as well as coordinated azide nitrogen atoms leading to two-dimensional supramolecular network.

In the IR spectrum the azide vibration is observed at 2053 cm$^{-1}$.

## Experimental

The ligand 2,2'-biimidazoline ($H_2bim$) was prepared according to the method reported in the literature (Xiao & Shreeve, 2005). A solid of 2,2'-biimidazoline (0.2 mmol) was added to the methanol solution (8 ml) of $Ni(ClO_4)_2.6H_2O$ (0.1 mmol) and a reseda solution was obtained. To the solution, a aqueous solution (5 ml) o f $NaN_3$ (0.6 mmol) was added carefully. The mixture was filtered and slowly evaporated to generate grass green single crystals suitable for X-ray diffraction analysis. (Yield 50%). Elemental analysis [found (calculated)] for $C_{12}H_{12}N_{14}Ni$: C 35.40 (35.12), H 3.01 (2.95), N 47.65% (47.81%).

## Refinement

H atoms bound to C and N atoms were visible in difference maps and were placed using the HFIX commands in SHELXL-97. A l l H atoms were allowed for as riding atoms (C—H 0.97 Å, N—H 0.86 Å).

## Figures

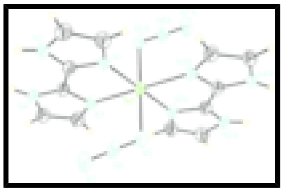

Fig. 1. A view of (I) with the unique atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

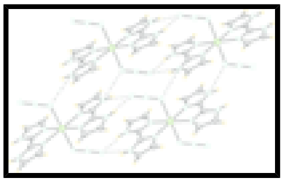

Fig. 2. The hydrogen-bonded network in (I). Hydrogen bonds are indicated by dashed lines.

## Diazidobis(2,2'-biimidazole)nickel(II)

### *Crystal data*

| | |
|---|---|
| $[Ni(N_3)_2(C_6H_6N_4)_2]$ | $F_{000}$ = 840 |
| $M_r$ = 411.07 | $D_x$ = 1.696 Mg m$^{-3}$ |
| Monoclinic, *C*2/*c* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -C 2yc | Cell parameters from 45 reflections |
| *a* = 12.6974 (18) Å | θ = 4.6–23.7° |
| *b* = 8.8399 (10) Å | μ = 1.24 mm$^{-1}$ |
| *c* = 14.3537 (12) Å | *T* = 293 (2) K |
| β = 91.803 (9)° | Block, green |
| *V* = 1610.3 (3) Å$^3$ | 0.26 × 0.20 × 0.16 mm |
| *Z* = 4 | |

### *Data collection*

| | |
|---|---|
| Bruker P4<br>diffractometer | $R_{int}$ = 0.022 |
| Radiation source: fine-focus sealed tube | $θ_{max}$ = 25.5° |
| Monochromator: graphite | $θ_{min}$ = 2.8° |
| *T* = 293(2) K | *h* = −1→15 |
| ω scans | *k* = −1→10 |
| Absorption correction: psi scan | *l* = −17→17 |

| | |
|---|---|
| (North *et al.*, 1968) | |
| $T_{\min} = 0.743$, $T_{\max} = 0.820$ | 3 standard reflections |
| 1966 measured reflections | every 97 reflections |
| 1505 independent reflections | intensity decay: none |
| 1250 reflections with $I > 2\sigma(I)$ | |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 2.2P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| $wR(F^2) = 0.069$ | $\Delta\rho_{\max} = 0.22$ e Å$^{-3}$ |
| $S = 1.02$ | $\Delta\rho_{\min} = -0.20$ e Å$^{-3}$ |
| 1505 reflections | Extinction correction: none |
| 124 parameters | |
| Primary atom site location: structure-invariant direct methods | |
| Secondary atom site location: difference Fourier map | |
| Hydrogen site location: inferred from neighbouring sites | |

### *Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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$^2$ > 2sigma(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* | $U_{\rm iso}$*/$U_{\rm eq}$ |
|---|---|---|---|---|
| Ni1 | 0.2500 | 0.7500 | 0.5000 | 0.04159 (13) |
| N1 | 0.23120 (16) | 0.5740 (2) | 0.40210 (14) | 0.0440 (5) |
| N2 | 0.27795 (17) | 0.3433 (2) | 0.36366 (14) | 0.0474 (5) |
| H2A | 0.3097 | 0.2574 | 0.3655 | 0.057* |
| N3 | 0.34697 (15) | 0.5856 (2) | 0.56318 (13) | 0.0429 (5) |
| N4 | 0.42338 (16) | 0.3636 (2) | 0.54714 (13) | 0.0452 (5) |
| H4A | 0.4399 | 0.2776 | 0.5237 | 0.054* |
| N5 | 0.11730 (17) | 0.6639 (2) | 0.57324 (15) | 0.0486 (5) |
| N6 | 0.10387 (17) | 0.5322 (3) | 0.57872 (14) | 0.0477 (5) |
| N7 | 0.0897 (2) | 0.4015 (3) | 0.58536 (18) | 0.0629 (6) |
| C1 | 0.1773 (2) | 0.5320 (3) | 0.32153 (18) | 0.0504 (6) |

| | | | | |
|---|---|---|---|---|
| H1A | 0.1287 | 0.5921 | 0.2888 | 0.061* |
| C2 | 0.2057 (2) | 0.3902 (3) | 0.29705 (18) | 0.0529 (7) |
| H2B | 0.1811 | 0.3356 | 0.2454 | 0.063* |
| C3 | 0.29009 (19) | 0.4563 (3) | 0.42548 (16) | 0.0407 (5) |
| C4 | 0.35389 (18) | 0.4631 (3) | 0.51081 (16) | 0.0404 (5) |
| C5 | 0.4630 (2) | 0.4248 (3) | 0.62848 (17) | 0.0496 (6) |
| H5A | 0.5125 | 0.3812 | 0.6694 | 0.060* |
| C6 | 0.4157 (2) | 0.5619 (3) | 0.63756 (17) | 0.0495 (6) |
| H6A | 0.4280 | 0.6292 | 0.6865 | 0.059* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0441 (2) | 0.0386 (2) | 0.0415 (2) | 0.0114 (2) | −0.00750 (18) | −0.00495 (19) |
| N1 | 0.0469 (11) | 0.0422 (12) | 0.0424 (11) | 0.0072 (10) | −0.0066 (9) | −0.0045 (9) |
| N2 | 0.0542 (12) | 0.0404 (12) | 0.0476 (11) | 0.0076 (10) | −0.0004 (10) | −0.0068 (10) |
| N3 | 0.0432 (11) | 0.0445 (12) | 0.0406 (10) | 0.0109 (10) | −0.0050 (9) | −0.0037 (9) |
| N4 | 0.0485 (12) | 0.0412 (11) | 0.0458 (11) | 0.0139 (10) | 0.0017 (9) | 0.0006 (9) |
| N5 | 0.0504 (12) | 0.0400 (13) | 0.0550 (13) | 0.0096 (10) | −0.0016 (10) | −0.0034 (10) |
| N6 | 0.0444 (12) | 0.0507 (15) | 0.0474 (12) | 0.0132 (11) | −0.0072 (10) | −0.0071 (10) |
| N7 | 0.0670 (16) | 0.0400 (14) | 0.0808 (17) | 0.0074 (12) | −0.0097 (13) | −0.0061 (12) |
| C1 | 0.0517 (15) | 0.0522 (16) | 0.0468 (14) | 0.0053 (13) | −0.0088 (12) | −0.0015 (12) |
| C2 | 0.0585 (16) | 0.0552 (17) | 0.0444 (14) | −0.0006 (14) | −0.0080 (12) | −0.0089 (12) |
| C3 | 0.0417 (12) | 0.0394 (13) | 0.0412 (12) | 0.0044 (11) | 0.0022 (10) | −0.0024 (10) |
| C4 | 0.0387 (12) | 0.0402 (13) | 0.0423 (12) | 0.0074 (11) | 0.0015 (10) | 0.0012 (10) |
| C5 | 0.0474 (14) | 0.0569 (17) | 0.0443 (13) | 0.0162 (13) | −0.0045 (11) | 0.0046 (12) |
| C6 | 0.0481 (14) | 0.0573 (16) | 0.0426 (13) | 0.0131 (13) | −0.0065 (11) | −0.0039 (12) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ni1—N3 | 2.0931 (19) | N4—C4 | 1.339 (3) |
| Ni1—N3$^{i}$ | 2.0931 (19) | N4—C5 | 1.368 (3) |
| Ni1—N1 | 2.105 (2) | N4—H4A | 0.8600 |
| Ni1—N1$^{i}$ | 2.105 (2) | N5—N6 | 1.180 (3) |
| Ni1—N5 | 2.153 (2) | N6—N7 | 1.173 (3) |
| Ni1—N5$^{i}$ | 2.153 (2) | C1—C2 | 1.354 (4) |
| N1—C3 | 1.319 (3) | C1—H1A | 0.9300 |
| N1—C1 | 1.376 (3) | C2—H2B | 0.9300 |
| N2—C3 | 1.342 (3) | C3—C4 | 1.448 (3) |
| N2—C2 | 1.368 (3) | C5—C6 | 1.361 (4) |
| N2—H2A | 0.8600 | C5—H5A | 0.9300 |
| N3—C4 | 1.323 (3) | C6—H6A | 0.9300 |
| N3—C6 | 1.374 (3) | | |
| N3—Ni1—N3$^{i}$ | 180.00 (9) | C4—N4—C5 | 107.1 (2) |
| N3—Ni1—N1 | 80.13 (8) | C4—N4—H4A | 126.5 |
| N3$^{i}$—Ni1—N1 | 99.87 (8) | C5—N4—H4A | 126.5 |
| N3—Ni1—N1$^{i}$ | 99.87 (8) | N6—N5—Ni1 | 119.90 (18) |

| | | | |
|---|---|---|---|
| N3$^{i}$—Ni1—N1$^{i}$ | 80.13 (8) | N7—N6—N5 | 179.0 (3) |
| N1—Ni1—N1$^{i}$ | 180.0 | C2—C1—N1 | 109.8 (2) |
| N3—Ni1—N5 | 90.09 (8) | C2—C1—H1A | 125.1 |
| N3$^{i}$—Ni1—N5 | 89.91 (8) | N1—C1—H1A | 125.1 |
| N1—Ni1—N5 | 89.46 (8) | C1—C2—N2 | 106.1 (2) |
| N1$^{i}$—Ni1—N5 | 90.54 (8) | C1—C2—H2B | 127.0 |
| N3—Ni1—N5$^{i}$ | 89.91 (8) | N2—C2—H2B | 127.0 |
| N3$^{i}$—Ni1—N5$^{i}$ | 90.09 (8) | N1—C3—N2 | 111.5 (2) |
| N1—Ni1—N5$^{i}$ | 90.54 (8) | N1—C3—C4 | 118.7 (2) |
| N1$^{i}$—Ni1—N5$^{i}$ | 89.46 (8) | N2—C3—C4 | 129.8 (2) |
| N5—Ni1—N5$^{i}$ | 180.0 | N3—C4—N4 | 111.8 (2) |
| C3—N1—C1 | 105.3 (2) | N3—C4—C3 | 118.0 (2) |
| C3—N1—Ni1 | 111.22 (15) | N4—C4—C3 | 130.2 (2) |
| C1—N1—Ni1 | 143.43 (18) | C6—C5—N4 | 106.4 (2) |
| C3—N2—C2 | 107.3 (2) | C6—C5—H5A | 126.8 |
| C3—N2—H2A | 126.3 | N4—C5—H5A | 126.8 |
| C2—N2—H2A | 126.3 | C5—C6—N3 | 109.4 (2) |
| C4—N3—C6 | 105.4 (2) | C5—C6—H6A | 125.3 |
| C4—N3—Ni1 | 111.78 (15) | N3—C6—H6A | 125.3 |
| C6—N3—Ni1 | 142.48 (18) | | |

Symmetry codes: (i) −*x*+1/2, −*y*+3/2, −*z*+1.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2A···N7$^{ii}$ | 0.86 | 2.01 | 2.822 (3) | 157 |
| N4—H4A···N7$^{ii}$ | 0.86 | 2.25 | 3.020 (3) | 149 |
| N4—H4A···N5$^{iii}$ | 0.86 | 2.55 | 3.044 (3) | 118 |

Symmetry codes: (ii) −*x*+1/2, −*y*+1/2, −*z*+1; (iii) *x*+1/2, *y*−1/2, *z*.

**Fig. 1**

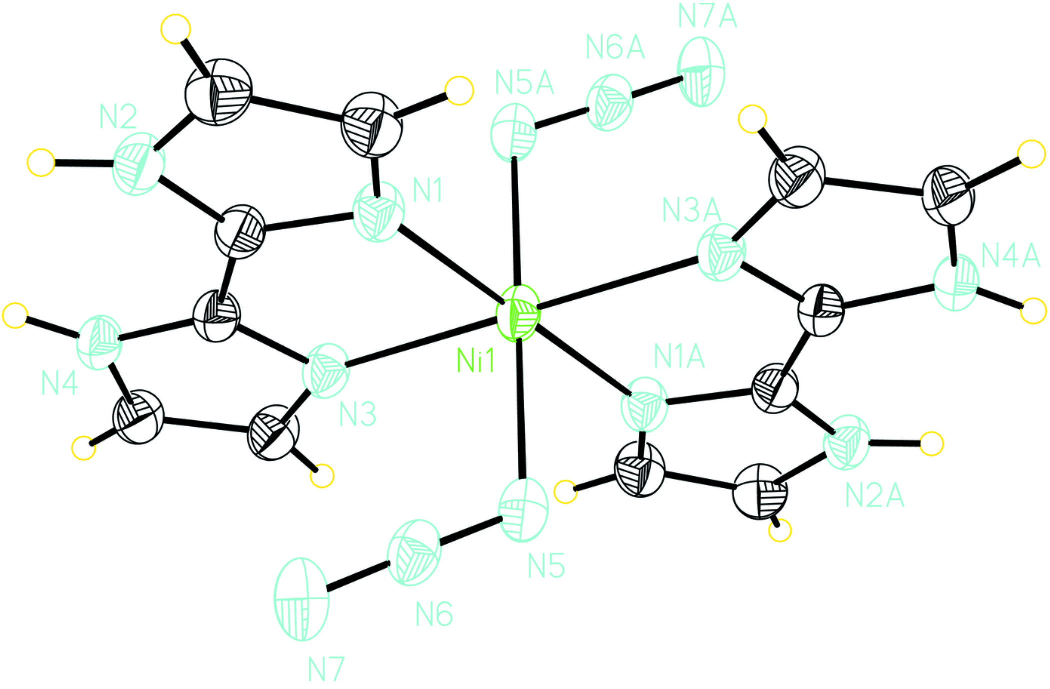

**Fig. 2**