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Bis[1,3-bis(2-methyltetrazol-5-yl-κN^4)triazenido-κN^2]nickel(II)

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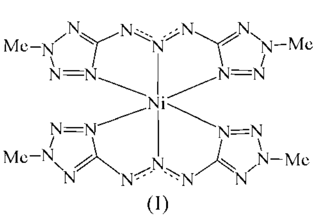
The title compound, [Ni(BMTT)$_2$], where BMTT is 1,3-bis(2-methyltetrazol-5-yl)triazenide ($C_4H_6N_{11}$), presents a molecular complex with tridentate ligands. The tridentate mode of the ligand is realised through the central N atom of the triazene group and two N atoms of the two tetrazole rings. The [Ni(BMTT)$_2$] molecule is the meridional isomer, with crystallographic $\overline{4}$ symmetry in space group $P4_2/n$. The nickel centre has a distorted octahedral environment, with two axial Ni—N bonds of 2.041 (2) Å and four equatorial Ni—N bonds of 2.0739 (14) Å. The molecules are linked together by van der Waals interactions only.

Comment

Over the past two decades, the coordination properties of the triazene ligands *R*–NH–N═N–*R*, where *R* is an aryl or heterocyclic group, have been intensively studied due to their versatility in coordination (Hanot *et al.*, 1999). The introduction of two *N*-substituted 5-tetrazolyl groups as the *R* substituents leads to polynitrogen binuclear heterocyclic compounds. These, similar to other bis(tetrazoles), are attractive as chelating agents (Voitekhovich *et al.*, 2002) and act as ligands for the synthesis of coordination polymers in one, two and three dimensions (Grunert *et al.*, 2004; Bronisz, 2004). However, complexes of bis(tetrazolyl)triazenes have not been described previously. We report here the crystal structure of a complex obtained by the reaction of 1,3-bis-(2-methyltetrazol-5-yl)triazene (HBMTT) with nickel(II) chloride in ethanol. In this reaction, 1,3-bis(2-methyltetrazol-5-yl)triazene undergoes deprotonation to form the thermally stable title bis(chelate) complex [Ni(BMTT)$_2$], (I) (Fig. 1).



(I)

The complex molecule contains an Ni^{II} cation and two deprotonated BMTT$^-$ ligands. The ligand shows tridentate chelating properties and is coordinated to the metallic centre through the N4 atoms of the two tetrazole rings and the central N8 atom of the triazene group. The molecule has crystallographic $\overline{4}$ symmetry and the reference Ni^{II} cation was selected as that lying at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{3}{4}$). Except for atom N8, which lies on the twofold rotation axis along ($\frac{1}{4}$, $\frac{1}{4}$, z), all remaining atoms occupy general positions.

The six N atoms around the Ni^{II} cation form a distorted octahedron, with two axial Ni—N8 bonds of 2.041 (2) Å and four longer equatorial Ni—N4 bonds of 2.0739 (14) Å. The complex is the meridional isomer, with a normalized bite *b* of 1.24 [$b = 2\sin(\alpha/2)$ (Kepert, 1982), where α is the N4—Ni—N8 angle in the case of (I)] and a tridentate bite angle N4—N8—N4^{ii} of *ca* 104.6° [symmetry code (ii) as in Fig. 1]. The observed meridional configuration of the ligands in (I) is in agreement with the predicted stabilization of the meridional isomer, rather than the symmetrical–facial and unsymmetrical–facial isomers, for ligands with a small normalized bite, $b < 1.3$, and/or for relatively rigid tridentate ligands with a tridentate angle greater than *ca* 100° (Kepert, 1982).

As a result of the formation of two adjacent five-membered Ni—N8—N7—C5—N4 rings for each ligand, the nitrogen octahedron is somewhat distorted. Thus, the axial–equatorial N8—Ni—N4 angles, with both N atoms belonging to the same ligand, are 76.58 (4)°, while the diequatorial angles, involving N atoms from two different ligands, are 93.086 (19)°. The coordination geometry in (I) is very similar to that found previously in [Ni(BATT)$_2$]·4H$_2$O, where HBATT is 1,3-bis(5-amino-1,2,4-triazol-3-yl)triazene (Hanot *et al.*, 1999).

The entire BMTT ligand in (I), with twofold rotation symmetry, is nearly planar; the mean deviation of the ligand atoms from the best least-squares plane is 0.0542 (17) Å. Each half of the ligand is planar to within 0.0132 (14) Å, the angle between the planes of these parts being 7.46 (3)°. The one-tetrazole ring bond lengths are shown in Table 1. The formal

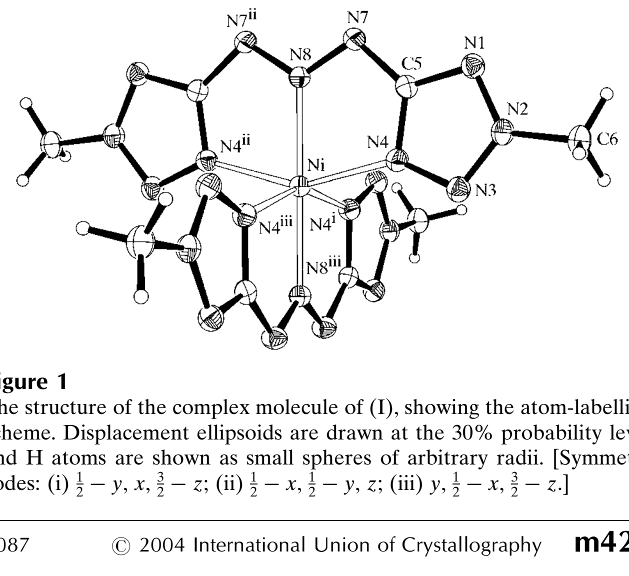


Figure 1
The structure of the complex molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $\frac{1}{2}-y, x, \frac{3}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, z$; (iii) $y, \frac{1}{2}-x, \frac{3}{2}-z$.]

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single bond N2—N3 is the shortest in the ring, whereas the N4—C5 bond is the longest. The remaining bonds have values in the range 1.326 (2)–1.339 (2) Å. The tetrazole ring is planar to within 0.0006 (10) Å. The geometry of the tetrazole ring in (I) is similar to that observed previously in copper(II) complexes of 2-substituted tetrazoles (van den Heuvel *et al.*, 1983; Bronisz, 2002; Lyakhov, Gaponik, Degtyarik & Ivashkevich, 2003*a*,*b*; Lyakhov, Gaponik, Degtyarik *et al.*, 2003). The deprotonated triazene bridge N7—N8—N7^{ii} is symmetrical. The bond lengths and angles at N7 and N8 indicate hybridization rather close to sp^3 and sp^2, respectively.

Because of the lack of hydrogen bonds in the structure of (I), the crystal packing is determined by van der Waals interactions only.

Experimental

1,3-Bis(2-methyltetrazol-5-yl)triazene was prepared by treating 5-amino-2-methyltetrazole with nitric acid and sodium nitrite, according to the method of Hattori *et al.* (1956). Complex (I) was synthesized by slow evaporation (20 d) of a solution composed of nickel(II) chloride hexahydrate (0.24 g, 1 mmol) and 1,3-bis(2-methyltetrazol-5-yl)triazene (0.21 g, 1 mmol) in ethanol (30 ml) at room temperature. The resulting dark-red prismatic crystals of (I) were found to be thermally stable and to decompose at temperatures greater than 520 K.

Crystal data

$[Ni(C_4H_6N_{11})_2]$
$M_r = 475.09$
Tetragonal, $P4_2/n$
$a = 9.5785$ (15) Å
$c = 9.713$ (2) Å
$V = 891.2$ (3) Å^3
$Z = 2$
$D_x = 1.770$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 19.6$–$22.3°$
$\mu = 1.15$ mm^{-1}
$T = 293$ (2) K
Prism, dark red
0.38 × 0.36 × 0.20 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.670$, $T_{max} = 0.803$
3195 measured reflections
1315 independent reflections
1139 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.1°$
$h = -13 \rightarrow 13$
$k = -4 \rightarrow 13$
$l = -6 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.121$
$S = 1.07$
1315 reflections
72 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.1594P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N8	2.041 (2)	N2—C6	1.460 (2)
Ni—N4	2.0740 (14)	N3—N4	1.326 (2)
N1—C5	1.338 (2)	N4—C5	1.354 (2)
N1—N2	1.339 (2)	C5—N7	1.382 (2)
N2—N3	1.312 (2)	N7—N8	1.3040 (17)
N8—Ni—N4	76.58 (4)	N8—N7—C5	108.13 (14)
N4^i—Ni—N4	93.088 (19)	N7^{ii}—N8—N7	117.3 (2)

Symmetry codes: (i) $\frac{1}{2}-y, x, \frac{3}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, z$.

The H atoms of the methyl groups were placed in geometrically calculated positions, with C—H distances of 0.96 Å, and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *R*3*m Software* (Nicolet, 1980); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1336). Services for accessing these data are described at the back of the journal.

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