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trans-Bis(dicyanamido-*N*)tetrakis(4-methylimidazole-*N*¹)nickel(II)

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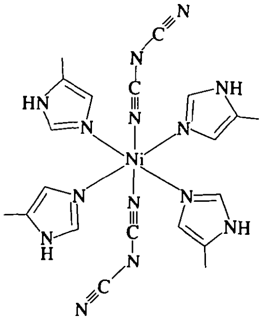
Abstract

The first crystal structure of a dicyanamide nickel(II) complex, $[Ni(C_2N_3)_2(C_4H_6N_2)_4]$, is reported. The central atom is octahedrally coordinated by four N atoms from four 4-methylimidazole ligands and by two N atoms from two terminally bonded dicyanamide anions. The Ni—N distances are in the range 2.090 (2) to 2.210 (2) Å.

Comment

In the course of our study of nucleophilic addition in the coordination sphere of the metal atom complexes in the system M^{II}–X^-–L–CH_3OH–H_2O [M = Cu^{II}, Ni^{II}; X = $N(CN)_2$, $ONC(CN)_2$; L = pyridine or a base of the pyrazole type] (Kožíšek, Hvastijová & Kohout, 1990; Hvastijová, Kožíšek, Kohout & Jäger, 1995; Hvastijová, Kožíšek, Kohout & Díaz, 1995), the title compound, $[Ni\{N(CN)_2\}_2(4\text{-meiz})_4]$ (4-meiz is 4-methylimidazole), (I), was prepared in monocrystal form.



(I)

The X-ray analysis of (I) shows that the crystal structure consists of separate $[Ni\{N(CN)_2\}_2(4\text{-meiz})_4]$ molecules. There are two symmetrically independent molecules in the unit cell, each with the metal atom lying on a centre of symmetry. In both molecules, the central Ni^{II} atom is pseudo-octahedrally coordinated with an NiN_6 chromophore. Dicyanamide anions are terminally bonded in *trans* positions.

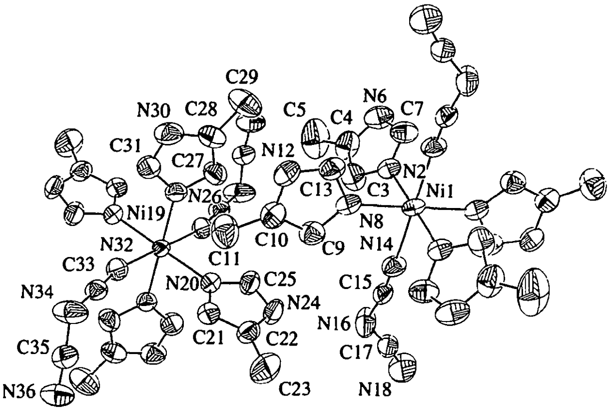


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids given at 50% probability levels. Each metal atom lies on a centre of inversion and H atoms are not shown.

Experimental

A solution of $Ni(NO_3)_2$ (2.5 mmol) in 5 ml of water and a solution of $KN(CN)_2$ (5.1 mmol) in 10 ml of water were added to a solution of 4-methylimidazole (10.5 mmol) in 15 ml of methanol. From the resulting turquoise solution, violet crystals of (I) were isolated.

Crystal data

$[Ni(C_2N_3)_2(C_4H_6N_2)_4]$
M_r = 519.24
Triclinic
$P\bar{1}$
a = 9.448 (3) Å
b = 9.918 (3) Å
c = 15.173 (5) Å
α = 107.85 (2)°
β = 93.67 (2)°
γ = 104.74 (2)°
V = 1293.1 (7) Å^3
Z = 2
D_x = 1.334 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 48 reflections
θ = 16.9–29.8°
μ = 0.787 mm^{-1}
T = 293 (2) K
Block
0.590 × 0.240 × 0.075 mm
Violet

Data collection

Stoe Stadi-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (*SHELX76*; Sheldrick, 1976)
T_{min} = 0.763, T_{max} = 0.904
8280 measured reflections
7523 independent reflections

5669 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.019
θ_{max} = 29.98°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0370$
$wR(F^2) = 0.1118$
$S = 1.113$
7489 reflections
339 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.4257P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.042$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni1	0	0	0	0.03853 (9)
N2	−0.0151 (2)	0.1403 (2)	0.13140 (11)	0.0465 (4)
C3	0.0319 (3)	0.1341 (3)	0.2170 (2)	0.0663 (6)
C4	0.0130 (3)	0.2488 (3)	0.2865 (2)	0.0679 (7)
C5	0.0476 (4)	0.2934 (5)	0.3908 (2)	0.118 (2)
N6	−0.0472 (2)	0.3254 (2)	0.24223 (14)	0.0663 (5)
C7	−0.0636 (3)	0.2563 (2)	0.1491 (2)	0.0580 (5)
N8	0.2275 (2)	0.0438 (2)	0.04806 (12)	0.0456 (4)
C9	0.3003 (2)	−0.0279 (2)	0.0917 (2)	0.0540 (5)
C10	0.4450 (2)	0.0490 (2)	0.1220 (2)	0.0537 (5)
C11	0.5694 (3)	0.0229 (4)	0.1730 (2)	0.0790 (8)
N12	0.4613 (2)	0.1710 (2)	0.09562 (14)	0.0607 (5)
C13	0.3303 (2)	0.1637 (2)	0.0522 (2)	0.0566 (5)
N14	−0.0475 (2)	−0.1809 (2)	0.05014 (13)	0.0508 (4)
C15	−0.0767 (2)	−0.2677 (2)	0.08593 (14)	0.0464 (4)
N16	−0.0921 (2)	−0.3612 (3)	0.1316 (2)	0.0783 (7)
C17	−0.2168 (3)	−0.4587 (2)	0.1235 (2)	0.0567 (5)
N18	−0.3175 (3)	−0.5503 (3)	0.1215 (2)	0.0937 (8)
Ni19	1/2	0	1/2	0.03534 (8)
N20	0.3782 (2)	−0.1425 (2)	0.36880 (11)	0.0426 (3)
C21	0.4243 (2)	−0.2377 (2)	0.29782 (15)	0.0509 (5)
C22	0.3106 (3)	−0.3190 (2)	0.2275 (2)	0.0566 (5)
C23	0.3009 (4)	−0.4357 (4)	0.1361 (2)	0.0986 (11)
N24	0.1921 (2)	−0.2723 (2)	0.25571 (13)	0.0589 (5)
C25	0.2368 (2)	−0.1668 (2)	0.3404 (2)	0.0542 (5)
N26	0.5393 (2)	0.1796 (2)	0.45108 (12)	0.0454 (4)
C27	0.4417 (3)	0.2218 (3)	0.4018 (2)	0.0571 (5)
C28	0.5119 (3)	0.3427 (3)	0.3812 (2)	0.0596 (6)
C29	0.4585 (4)	0.4331 (4)	0.3313 (2)	0.0943 (11)
N30	0.6561 (2)	0.3741 (2)	0.4180 (2)	0.0664 (5)
C31	0.6674 (3)	0.2745 (2)	0.4591 (2)	0.0622 (6)
N32	0.6976 (2)	−0.0440 (2)	0.45719 (13)	0.0492 (4)
C33	0.7844 (2)	−0.0990 (2)	0.4283 (2)	0.0479 (4)
N34	0.8906 (2)	−0.1515 (2)	0.3949 (2)	0.0857 (8)
C35	0.8835 (2)	−0.2888 (2)	0.3804 (2)	0.0523 (5)
N36	0.8910 (3)	−0.4064 (2)	0.3662 (2)	0.0692 (6)

Table 2. *Selected geometric parameters (Å, °)*

Ni1—N2	2.090 (2)	Ni19—N26	2.090 (2)
Ni1—N14	2.114 (2)	Ni19—N20	2.107 (2)
Ni1—N8	2.115 (2)	Ni19—N32	2.120 (2)
N14—C15	1.140 (2)	N32—C33	1.135 (2)
C15—N16	1.304 (3)	C33—N34	1.305 (3)
N16—C17	1.291 (3)	N34—C35	1.294 (3)
C17—N18	1.127 (3)	C35—N36	1.141 (3)
N2—Ni1—N14	89.81 (7)	N26—Ni19—N20	90.71 (7)
N2—Ni1—N8	87.89 (7)	N26—Ni19—N32	90.62 (7)
N14—Ni1—N8	89.25 (7)	N20—Ni19—N32	90.67 (7)
C15—N14—Ni1	172.2 (2)	C33—N32—Ni19	164.8 (2)
N14—C15—N16	172.6 (2)	N32—C33—N34	175.2 (2)
C17—N16—C15	122.0 (2)	C35—N34—C33	120.6 (2)
N18—C17—N16	172.8 (3)	N36—C35—N34	173.5 (2)

Non-H atoms were refined anisotropically. H atoms were refined as riding on their parent C/N atoms and five parameters were refined per methyl group. The crystal was bounded by the faces $(0\bar{1}0)$, (010), $(1\bar{1}1)$, $(\bar{1}1\bar{1})$, $(10\bar{1})$, $(00\bar{1})$ and $(1\bar{1}0)$. The structure was solved by Patterson methods and refined on F^2 by least-squares methods.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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8-[1,2-Bis(diphenylphosphino)ethane]-9,10-μ-hydrido-8-rhoda-7-thia-*nido*-undecaborane(10)–Dichloromethane (2/1)

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Abstract

The solid-state structure of the title compound, $[Rh(B_9H_{10}S)(C_{26}H_{24}P_2)].0.5CH_2Cl_2$, has a *nido* cluster geometry but, apparently, only a *closo* electron count. This anomaly is rationalized in terms of long range *ortho*-phenyl agostic C—H···Rh interactions.