

Diazidobis(2,2'-dipyridylamine)nickel(II)
monohydrateMónica Villanueva,^a M. Karmele Urtiaga,^{b*} José L. Mesa^a and M. Isabel Arriortua^b^aDepartamento de Química Inorgánica, Facultad de Ciencias Universidad del País Vasco, Apartado 644, E-48080 Bilbao, Spain, and ^bDepartamento de Mineralogía y Petrología, Facultad de Ciencias Universidad del País Vasco, Apartado 644, E-48080 Bilbao, Spain

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Key indicators

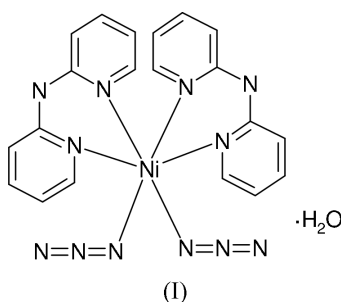
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.035
 wR factor = 0.093
Data-to-parameter ratio = 17.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The coordination environment of the Ni atom in the title compound, $[\text{Ni}(\text{N}_3)_2(\text{dpa})_2(\text{N}_3)_2] \cdot \text{H}_2\text{O}$ (dpa = 2,2'-dipyridylamine, $\text{C}_{10}\text{H}_9\text{N}_3$), is that of an octahedron, with the two azide ligands in a *cis* arrangement. The crystal structure of the complex is stabilized by hydrogen bonds involving the water molecule, resulting in a two-dimensional network in the (001) plane.

Comment

The 2,2'-dipyridylamine (dpa) ligand has several possible configurations for coordination. The *anti-anti* configuration, referring to the relation of the pyridyl N atoms to the amine H atom, has been found in many bidentate chelate complexes (e.g. Rodig *et al.*, 1981; Youngme *et al.*, 1998; Mesa *et al.*, 1998). The *syn-syn* configuration occurs in trinuclear complexes (Pyrka *et al.*, 1991; Wu *et al.*, 1990), and the *anti-syn* configuration exists in the dimer of the free ligand (Yang *et al.*, 1994).

Recently, we have begun a study of the polynuclear complexes of bivalent transition metals (e.g. Ni^{2+} , Mn^{2+} and Cu^{2+}) with bidentate ligands and pseudohalide groups. In order to determine the influence of the azide (N_3^-) ligand in structures of this type, we have synthesized the title complex, (I), $[\text{Ni}(\text{dpa})_2(\text{N}_3)_2] \cdot \text{H}_2\text{O}$, and report its structure here.



The crystal structure of (I) (Fig. 1) comprises coordination complexes and solvent water molecules in the ratio 1:1. The Ni atom is at the centre of an NiN_6 octahedron, formed by the four N atoms of the dpa ligands and the two N atoms of the terminal azides (Table 1). The two bidentate ligands have a *cis* disposition around the metal ion and are almost perpendicular to each other [$\text{N}3-\text{Ni}-\text{N}4$ 91.41 (6) and $\text{N}3-\text{Ni}-\text{N}6$ 172.30 (6)°]. Similarly, the azide ligands are *cis* to each other and are practically linear (Table 1).

An interesting feature of the structure of (I) is the formation of a two-dimensional structure stabilized by strong $\text{N}-\text{H} \cdots \text{N}$, $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds (Table 2). Thus, layers of complex molecules aggregate in the (001) plane and are connected to each other by water molecules, forming a sandwich-type array.

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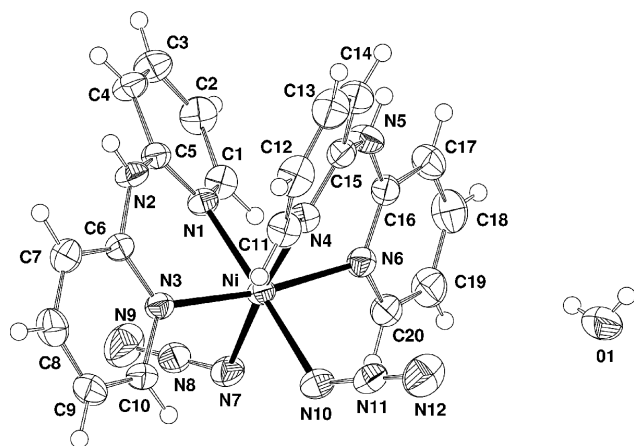


Figure 1
A view of the structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

[Ni(dpa)₂(N₃)₂·H₂O was synthesized from the reaction of NiCl₂·6H₂O (0.052 g, 0.219 mmol), 2,2'-dipyridylamine (0.075 g, 0.438 mmol) and NaN₃ (0.140 g, 2.150 mmol) in water (20 ml). The complex was isolated by filtration, washed with water and diethyl ether and dried over P₂O₅ for 1 h. Green prismatic single crystals of (I) were obtained by recrystallization from a methanol–water (1:1) solution of the complex. Analysis found: C 47.3, H 3.7, N 33.0, Ni 11.5%; calculated for C₂₀H₂₀N₁₂Ni: C 47.7, H 4.0, N 33.4, Ni 11.7%. The diffuse reflectance spectrum of (I) exhibits the essential characteristics of octahedrally coordinated Ni^{II} ions. Three absorption bands ascribed to the spin-allowed transitions ³A_{2g} → ³T_{2g} (F), ³T_{1g} (F) and ³T_{1g} (P) are observed at 9090, 15 150 and 26 665 cm⁻¹, respectively. The spin-forbidden transitions ³A_{2g} → ¹E_g and ¹T_{2g} can also be observed, at 13 890 and 21 275 cm⁻¹, respectively. The Dq and Racah (B and C) parameters were calculated by fitting the experimental frequencies to an energy-level diagram for octahedral d⁸ systems (Lever, 1984). The values obtained are Dq = 910, B = 975 and C = 3990 cm⁻¹. The resulting value for the B parameter supposes a reduction of ca 90% from that of the free Ni^{II} ions.

Crystal data

[Ni(N₃)₂(C₁₀H₉N₃)₂·H₂O
M_r = 503.17
Triclinic, P $\bar{1}$
a = 7.651 (3) Å
b = 9.268 (2) Å
c = 16.721 (4) Å
α = 79.36 (2)°
β = 84.17 (2)°
γ = 69.78 (2)°
V = 1092.6 (6) Å³
Z = 2
D_x = 1.530 Mg m⁻³

D_m = 1.55 Mg m⁻³
D_m measured by flotation in
CH₂Cl₂–CCl₄
Mo Kα radiation
Cell parameters from 25
reflections
θ = 8.1–13.3°
μ = 0.93 mm⁻¹
T = 293 (2) K
Prism, green
0.16 × 0.14 × 0.10 mm

Data collection

Enraf–Nonius CAD-4
diffractometer
ω/2θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
T_{min} = 0.863, T_{max} = 0.914
7053 measured reflections
6337 independent reflections
4806 reflections with I > 2σ(I)

R_{int} = 0.017
θ_{max} = 30.0°
h = -2 → 10
k = -12 → 13
l = -23 → 23
2 standard reflections
every 100 reflections
intensity decay: 1.8%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.035
wR(F²) = 0.093
S = 1.01
6337 reflections
368 parameters
Only coordinates of H atoms
refined

$$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.159P]$$

where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.027
Δρ_{max} = 0.44 e Å⁻³
Δρ_{min} = -0.27 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni–N1	2.1040 (16)	Ni–N6	2.1047 (16)
Ni–N3	2.0822 (15)	Ni–N7	2.1147 (17)
Ni–N4	2.1198 (16)	Ni–N10	2.1266 (18)
N1–Ni–N4	91.09 (6)	Ni–N7–N8	120.13 (13)
N1–Ni–N6	90.19 (6)	Ni–N10–N11	125.79 (14)
N3–Ni–N4	91.41 (6)	N7–N8–N9	178.2 (2)
N3–Ni–N6	172.30 (6)	N10–N11–N12	178.1 (2)
N7–Ni–N10	87.43 (7)		

Table 2

Hydrogen-bonding geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
N2–H21···N7 ⁱ	0.76 (3)	2.34 (3)	3.100 (3)	177 (3)
N5–H31···O1 ⁱ	0.84 (3)	2.02 (3)	2.852 (3)	169 (2)
O1–H40···N12 ⁱⁱ	0.76 (5)	2.18 (5)	2.928 (4)	168 (5)
O1–H41···N12 ⁱⁱⁱ	0.75 (4)	2.17 (4)	2.900 (4)	163 (4)

Symmetry codes: (i) x – 1, y, z; (ii) x, 1 + y, z; (iii) 1 – x, –y, 1 – z.

All H atoms were refined with a common U_{iso}(H) value. The ranges of the O–H, N–H and C–H distances were 0.73 (6)–0.76 (3), 0.75 (3)–0.83 (3) and 0.88 (3)–0.96 (3) Å, respectively.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: WinGX (Farrugia, 1999).

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