O1—Ag1—O1^{ii}	111.4 (1)	O2^{iii}—Ag1—Ag1^{i}	147.5 (1)
O1—Ag1—O2^{iii}	82.8 (2)	Ag1—O1—C1	118.6 (6)
O2^{i}—Ag1—O1	157.0 (2)	Ag1—O1^{ii}—C1^{ii}	118.6 (5)
O2^{i}—Ag1—O1^{ii}	81.0 (2)	Ag1—O2^{i}—C1^{i}	128.8 (5)
O2^{iii}—Ag1—O1^{ii}	64.3 (2)	Ag1—O2^{iii}—C1^{iii}	122.1 (4)
O2^{i}—Ag1—O2^{iii}	120.3 (1)	O1—C1—O2	128.4 (7)
O1—Ag1—Ag1^{i}	83.0 (2)	O1—C1—C1^{iv}	117 (1)
O1^{ii}—Ag1—Ag1^{i}	148.2 (1)	O2—C1—C1^{iv}	115.1 (9)
O2^{i}—Ag1—Ag1^{i}	77.3 (2)		

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

Data were collected using $\theta/2\theta$ scans with a variable scan rate of 1.98–14.5° $\min^{-1}$ and employing background counts for 0.25 of the total scan time on each side. The scan width was $[1.9 + 2\theta(\alpha_2) - 2\theta(\alpha_1)]$. Refinement was by full-matrix least-squares method on F^2 using all reflections with $I_{hkl} > 0$.

Data collection: *Recentering θ/2θ Collection Program* in *XTL* (Syntex, 1973). Cell refinement: $P2_1$ in *XTL*. Data reduction: *TAPER* in *XTL*. 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, 1976). Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: VS1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diazidobis(2,2′-bipyridine)nickel(II) Monohydrate

M. Karmele Urtiaga* and M. Isabel Arriortua

Departamento de Mineralogía-Petrología, Universidad del País Vasco, Aptdo 644, 48080 Bilbao, Spain

Izaskun Gil De Muro and Roberto Cortes*

Departamento de Química Inorgánica, Universidad del País Vasco, Aptdo 644, 48080 Bilbao, Spain

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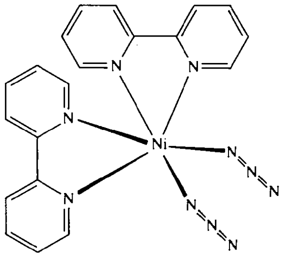
Abstract

The compound $[Ni(N_3)_2(bipy)_2].H_2O$ (I) (bipy = 2,2′-bipyridine) has been synthesized and its structure determined at room temperature. The coordination polyhedron of the Ni atom shows an octahedral topology with the two bipy and the two azido ligands in a *cis* arrangement. Two monomeric units form an outer-sphere dimer through hydrogen bonding with the water molecule to give the overall formula $[Ni(bipy)_2(N_3)_2]_2.2H_2O$.

Comment

Polynuclear nickel(II)–azido systems have been a focus of investigation in recent years (Arriortua, Cortés, Lezama, Rojo, Solans & Font-Bardia, 1990; Cortés, Urtiaga, Larramendi, Lezama, Arriortua & Rojo, 1992; Vicente, Escuer, Ribas, Salah El Fallah, Solans & Font-Bardia, 1994; Escuer, Vicente, Ribas, Salah El Fallah & Solans, 1994). Both dinuclear and chain structures have been obtained. The azide ion was chosen for its versatility of coordination; this includes both end-to-end and end-on bridging modes which lead to antiferromagnetic (Pierpoint, Hendrickson, Duggan, Wagner & Barefield, 1975) and ferromagnetic type interactions (Arriortua, Cortés, Lezama, Rojo, Solans & Font-Bardia, 1990), respectively, between the metallic centres.

The ligands selected to block the metal have been shown to play an important role in determining the final structure. The use of tridentate aromatic amine ligands, which favour *cis* coordination of the azido bridges, has led to dinuclear nickel(II) systems with end-on azido bridges, while the use of bidentate or tetradentate aliphatic amines, which favour *trans* coordination of the azido bridges, has led to nickel(II)–*trans*-azido chains. To our knowledge, no nickel(II)–*cis*-azido chains have been structurally characterized to date. The preparation of an appropriate precursor containing the azido ligands in the desired configuration may be useful in the synthesis of such *cis*-azido chain compounds. We decided, therefore, to prepare and characterize such a precursor using the 2,2′-bipyridine ligand, which has recently been shown to be able to give the required *cis* configuration of the pseudohalide ligands (Urtiaga, Pizarro, Cortés, Goñi & Larramendi, 1994).



(I)

The structure of the title compound with atom numbering is shown in Fig. 1. The Ni atom is at the centre of an NiN_6 coordination polyhedron formed by the four N atoms of the two bipy ligands [Ni—N1*A* 2.114 (2), Ni—N2*A* 2.082 (2), Ni—N1*B* 2.090 (2), Ni—N2*B* 2.067 (2) Å] and the two N atoms of the terminal azides [Ni—N3*A* 2.102 (2), Ni—N3*B* 2.094 (2) Å]. The two bidentate ligands have a *cis* disposition around the metal ion, forming practically perpendicular planes [N1*A*—Ni—N1*B* 90.09 (7), N2*A*—Ni—N2*B* 171.65 (7)°]. The rigidity of these ligands causes the bond angles N1*A*—Ni—N2*A* and N1*B*—Ni—N2*B* [77.64 (7) and 78.19 (7)°, respectively] to deviate significantly from orthogonality. This causes the geometry about the Ni^{II} ion to deviate slightly from that of an ideal octahedron.

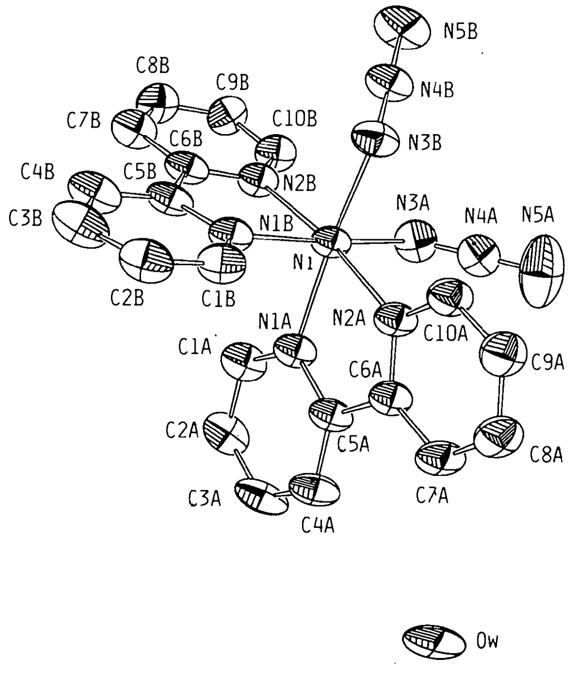


Fig. 1. View of $[Ni(bipy)_2(N_3)_2].H_2O$ showing the labeling of the non-H atoms. Displacement ellipsoids are drawn at the 50% level.

The azide ligands are practically linear [N3*A*—N4*A*—N5*A* 177.7 (3), N3*B*—N4*B*—N5*B* 178.6 (2)°] and form very similar angles (close to 120°) with the Ni^{II} ion.

The complex forms an outer-sphere dimer from two mononuclear units connected through hydrogen bonds between the water molecule and the terminal N atom of the coordinated azide groups [N5*A*···O*w* 2.965 (4), N5*B*^{i}···O*w* 2.900 (3) Å; symmetry code: (i) $-x$, $1-y$, $1-z$] (Fig. 2). The intermetallic bridging involves a large number of atoms, as reflected by the through space Ni···Ni^i distance of 10.94 (3) Å.

Infrared spectra of both complexes show the characteristic bands of the bipy ligand (McWhinnie & Miller, 1969) but displaced at higher frequencies and split by coordination to the metal. The more interesting bands are, however, those associated with the azido groups. The IR spectrum shows the band corresponding to the asymmetric stretch of the azido ion, $\nu_{as}(N_3)$, split at 2060 and 2025 cm^{-1}. This indicates that the azido ligand is bonded asymmetrically by its two terminal N atoms, in good agreement with the structural results involving the

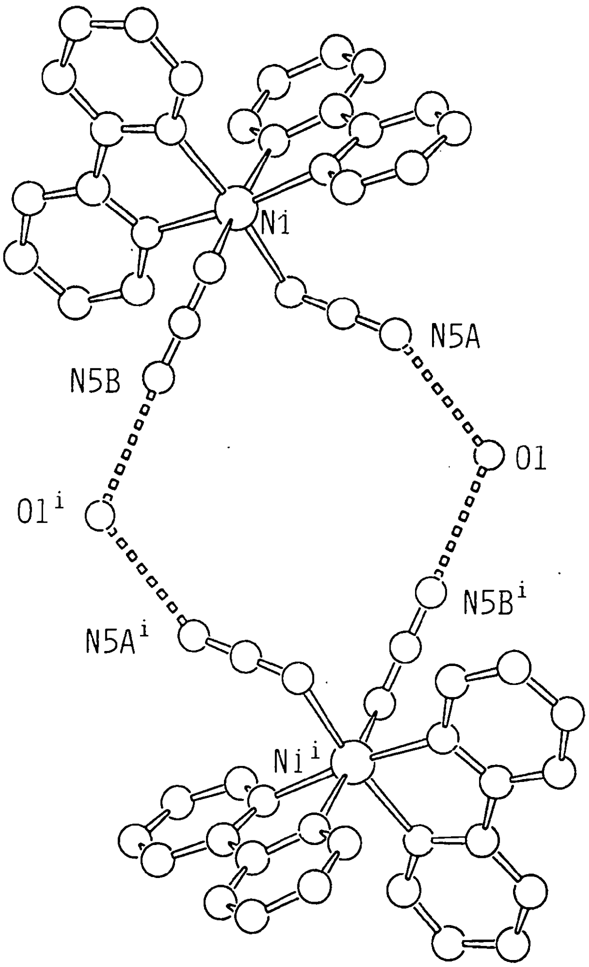


Fig. 2. The $[Ni(bipy)_2(N_3)_2]_2.2H_2O$ outer-sphere dimer formed by hydrogen bonding.

Ni—N(azido) bond and O*w*···N(azido) hydrogen bond. The symmetric stretch band, $\nu_s(N_3)$, appears at 1340 cm^{-1}, while that corresponding to $\delta(N_3)$ is split at 615 and 608 cm^{-1}. A similar situation is observed in the related copper(II) outer-sphere dimer $[Cu(pymep)(N_3)_2]_2.2H_2O$ (Rojo, Larramendi, Duran, Mesa, Vía & Arriortua, 1990).

Experimental

A solution containing 1 mmol of the $[Ni(bipy)_2Cl_2].2H_2O$ compound [previously prepared by reaction of nickel(II) chloride and 2,2′-bipyridine (1:2 ratio) in an acetone/ethanol mixture] dissolved in 10 ml of water was added to a saturated aqueous solution (10 ml) of sodium azide. The precipitate obtained immediately was filtered, washed with water and dried under vacuum for 12 h. This compound was recrystallized from an aqueous/methanol solution. Elemental analysis and atomic absorption results show good agreement with the stoichiometry. The density of the compound was measured by flotation in bromoform/chloroform.

Crystal data

$[Ni(N_3)_2(C_{10}H_8N_2)_2].H_2O$
$M_r = 473.14$
Triclinic
$P\overline{1}$
$a = 8.214\ (1)$ Å
$b = 10.264\ (1)$ Å
$c = 13.138\ (3)$ Å
$\alpha = 96.03\ (1)°$
$\beta = 87.13\ (1)°$
$\gamma = 110.18\ (1)°$
$V = 1033.8\ (3)$ Å^3
$Z = 2$
$D_x = 1.52$ Mg m^{-3}
$D_m = 1.49\ (1)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–14°$
$\mu = 0.976$ mm^{-1}
$T = 298$ K
Elongated prism
$0.37 \times 0.18 \times 0.13$ mm
Greenish brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5464 measured reflections
5322 independent reflections
4061 observed reflections [$I \geq 2.5\sigma(I)$]

$\theta_{max} = 28°$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity variation: 8.69%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.038$
$S = 1.23$
4061 reflections
344 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2|F_o| + 0.002|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	0.29908 (3)	0.21566 (2)	0.71538 (2)	2.87 (1)
N1*A*	0.4350 (2)	0.2850 (2)	0.8543 (1)	3.23 (4)
N2*A*	0.1012 (2)	0.1556 (2)	0.8245 (1)	3.31 (4)
N3*A*	0.2674 (2)	0.4102 (2)	0.7145 (2)	4.34 (5)
N1*B*	0.3636 (2)	0.0346 (2)	0.7042 (1)	3.27 (4)
N2*B*	0.5178 (2)	0.2693 (2)	0.6222 (1)	3.19 (4)
N3*B*	0.1319 (2)	0.1294 (2)	0.5919 (1)	4.21 (5)
N4*A*	0.1398 (2)	0.4323 (2)	0.7400 (2)	4.10 (5)
N5*A*	0.0176 (4)	0.4582 (3)	0.7668 (3)	8.54 (11)
C1*A*	0.6073 (3)	0.3454 (2)	0.8643 (2)	3.92 (6)
C2*A*	0.6858 (3)	0.3909 (2)	0.9588 (2)	4.42 (6)
C3*A*	0.5829 (3)	0.3738 (2)	1.0460 (2)	4.69 (7)
C4*A*	0.4054 (3)	0.3107 (2)	1.0375 (2)	4.20 (6)
C5*A*	0.3346 (2)	0.2679 (2)	0.9404 (1)	3.30 (4)
C6*A*	0.1461 (2)	0.2011 (2)	0.9226 (1)	3.28 (4)
C7*A*	0.0222 (3)	0.1848 (2)	1.0009 (2)	4.27 (6)
C8*A*	−0.1513 (3)	0.1189 (3)	0.9765 (2)	4.94 (7)
C9*A*	−0.1962 (3)	0.0701 (3)	0.8763 (2)	4.86 (7)
C10*A*	−0.0662 (3)	0.0916 (2)	0.8022 (2)	4.20 (6)
N4*B*	0.1490 (2)	0.1834 (2)	0.5154 (1)	3.76 (4)
N5*B*	0.1648 (3)	0.2340 (2)	0.4391 (2)	6.00 (6)
C1*B*	0.2743 (3)	−0.0836 (2)	0.7453 (2)	4.04 (6)
C2*B*	0.3300 (4)	−0.1963 (2)	0.7396 (2)	4.73 (6)
C3*B*	0.4831 (4)	−0.1881 (2)	0.6883 (2)	4.84 (7)
C4*B*	0.5736 (3)	−0.0681 (2)	0.6421 (2)	4.13 (5)
C5*B*	0.5102 (2)	0.0417 (2)	0.6515 (1)	3.23 (5)
C6*B*	0.5972 (2)	0.1736 (2)	0.6037 (1)	3.14 (4)
C7*B*	0.7463 (3)	0.1974 (2)	0.5435 (2)	3.99 (5)
C8*B*	0.8132 (3)	0.3228 (3)	0.4996 (2)	4.44 (6)
C9*B*	0.7319 (3)	0.4196 (2)	0.5173 (2)	4.23 (6)
C10*B*	0.5852 (3)	0.3902 (2)	0.5793 (2)	3.78 (5)
O*w*	−0.1379 (3)	0.6785 (2)	0.7603 (1)	6.08 (7)

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

Nickel coordination sphere			
Ni—N1*A*	2.114 (2)	Ni—N2*A*	2.082 (2)
Ni—N3*A*	2.102 (3)	Ni—N1*B*	2.090 (2)
Ni—N2*B*	2.067 (2)	Ni—N3*B*	2.094 (2)
Ni—Ni$^{\rm i}$	10.94 (3)		
N1*A*—Ni—N2*A*	77.64 (7)	N1*A*—Ni—N3*A*	90.02 (7)
N1*A*—Ni—N1*B*	90.09 (7)	N1*A*—Ni—N2*B*	95.37 (7)
N1*A*—Ni—N3*B*	171.04 (8)	N2*A*—Ni—N3*A*	91.03 (8)
N2*A*—Ni—N1*B*	97.07 (7)	N2*A*—Ni—N2*B*	171.65 (7)
N2*A*—Ni—N3*B*	93.62 (8)	N3*A*—Ni—N1*B*	171.73 (8)
N3*A*—Ni—N2*B*	93.56 (7)	N3*A*—Ni—N3*B*	92.15 (8)
N1*B*—Ni—N2*B*	78.19 (7)	N1*B*—Ni—N3*B*	89.01 (7)
N2*B*—Ni—N3*B*	93.17 (7)		
Average values in bipy ligand			
C—N	1.34 (1)	C—C	1.39 (3)
C—H	0.98 (2)		
C—C—C	30 (1)	C—N—C	118.7 (3)
C—C—N	29.5 (4)		
Azide groups			
N3*A*—N4*A*	1.173 (3)	N3*B*—N4*B*	1.177 (3)
N4*A*—N5*A*	1.154 (4)	N4*B*—N5*B*	1.159 (3)
Ni—N3*A*—N4*A*	124.4 (2)	Ni—N3*B*—N4*B*	122.1 (2)
N3*A*—N4*A*—N5*A*	177.7 (3)	N3*B*—N4*B*—N5*B*	178.6 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

Intensity data were corrected for Lorentz and polarization effects. The non-H atoms were refined anisotropically. H-atoms were obtained by difference Fourier synthesis and were refined isotropically. The structure was solved by the *MULTAN*11/84 (Main, Germain & Woolfson, 1984) program and refined by least-squares methods (*SHELX*76; Sheldrick, 1976). Molecular graphics were produced with the *SCHAKAL* program (Keller, 1988). Material for publication was prepared using *BONDLA* (Hall & Stewart, 1990) and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zinc(II) Complex of Urocanic Acid

NOBUO OKABE

Department of Pharmaceutical Sciences,
Kinki University, Kowakae 3-4-1, Higashiosaka,
Osaka 577, Japan

YOH SASAKI

Department of Science and Engineering,
Kinki University, Kowakae 3-4-1, Higashiosaka,
Osaka 577, Japan

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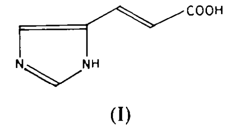
Abstract

In the title compound, tetraaquabis(4-imidazoleacrylato)zinc(II), [Zn($C_6H_5N_2O_2$)$_2$(H_2O)$_4$], the Zn atom has a quasi-octahedral coordination environment with four water O atoms in a square-planar arrangement and two N atoms of the imidazole ring in *trans* positions. The acrylic acid side chain is partially disordered. The imidazole ring and the carboxyl group have a *trans* configuration about the double bond and the carboxyl group is tilted towards the imidazole ring. The urocanic acid molecules are held together *via* hydrogen bonds involving all available H atoms.

Comment

Urocanic acid (I) is the first metabolic product of histidine. It has two geometrical isomers which display *trans* or *cis* configurations of the imidazole ring and the carboxyl group about the double bond of the acryl side chain. The biological activity of *trans*-urocanic acid (for example in the contraction of blood vessels or the lowering of blood pressure) is greater than that of *cis*-urocanic acid. Also, the major pathway of histidine metabolism is *via trans*-urocanic acid (Kurogochi, Fukui, Nakagawa & Yamamoto, 1957; Abrams & Borsook, 1952). The crystal structure of urocanic acid dihydrate was reported to compise molecules with the *trans* configuration (Hawkinson, 1977; Svinning & Sorum, 1979).



(I)

In order to investigate the interaction between imidazole compounds and zinc ions, zinc–urocanic acid complexes (1:2 and 1:1) were synthesized (Weitzel & Fretzdorff, 1956); tetrahedral coordination models were proposed for the *cis* configurations of each complex, but