trans-Bis(azido-κN)bis(pyridine-2-carboxamide-κ²N¹,O²)nickel(II)

Marijana Đaković and Zora Popović*

Department of Chemistry, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia
Correspondence e-mail: zpopovic@chem.pmf.hr

In the title compound, $[Ni(N_3)_2(C_6H_6N_2O)_2]$, the Ni^{II} atom lies on an inversion centre. The distorted octahedral nickel(II) coordination environment contains two planar trans-related N,O-chelating picolinamide ligands in one plane and two monodentate azide ligands perpendicular to this plane. Molecules are linked into a three-dimensional framework by N—H···N hydrogen bonds.

Comment

Considerable attention has been paid to heteroleptic metal complexes of biologically important ligands owing to their pharmacological effects as drugs in various biological and medicinal processes. Sometimes the metal complexes are more effective than the free ligands. The azide ion, N_3^-, binds metal ions in a variable manner, giving rise to terminal, end-on bridging and end-to-end bridging modes (Cortes et al., 1994; Ribas et al., 1999; Hong & Do, 1999; Liu et al., 2004). The established various intriguing structures of azide–metal complexes, spanning from discrete molecules to three-dimensional arrays, not only enrich the stereochemistry of the transition metal ions, but also give deeper insight into the role of metal ions in the aforementioned processes on a more fundamental level regarding azide inhibition of the metabolism of mitochondria (Yuwen et al., 2000). As part of our ongoing research (Đaković et al., 2007a,b) on the preparation and characterization of metal pseudohalide complexes with small organic molecules of biological interest, we synthesized the title complex, (I).

To the best of our knowledge, the title compound is the first azide complex incorporating a pyridine monocarboxamide. Until now, only three Ni complexes with picolinamide (pia) have been reported, viz. two octahedral complexes, [Ni(pia-N,O)₂(H₂O)₂]Cl₂ (Masuko et al., 1967) and [Ni(pia-N,O)₂-(H₂O)₂](sac)₂·4H₂O (sac is saccharinate; Paşaoğlu et al., 2004), and one square-planar complex, [Ni(pia-N,N)₂]·2H₂O (Chang et al., 1968; Nawata et al., 1967). In the octahedral complexes, two pia ligands coordinate to the nickel(II) ion as bidentate

ligands through the pyridine N and the carboxamide O atoms, thus forming five-membered chelate rings in one plane, while two aqua ligands lie perpendicular to this plane. In the square-planar complex, the coordination environment is established by four N atoms, two endocyclic and two from the carboxamide units. The deprotonation of the amide N atom is performed by raising the pH to 11.5 with addition of sodium carbonate.

(I)
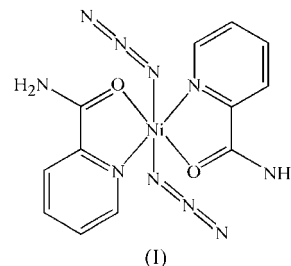
In (I), the octahedrally coordinated Ni^{II} atom is located on a crystallographic inversion centre. The coordination environment is occupied by two N,O-chelating picolinamide ligands in one plane and by two terminal azide ligands perpendicular to this plane (Fig. 1). The Ni1—O1 bond distance (Table 1) is slightly longer than in other octahedral nickel(II) complexes with picolinamide {2.030 (1) Å in [Ni(pia)₂(H₂O)₂](sac)₂·4H₂O (Paşaoğlu et al., 2004) and 2.045 Å in [Ni(pia)₂(H₂O)₂]-Cl₂ (Masuko et al., 1967)}, while the Ni1—N1 bond distance is consistent with those in the already mentioned compounds. The angles indicating the largest distortion from ideal octahedral geometry are the small bite angles, O1—Ni1—N1, in the picolinamide ligand (Table 1).

The pia ligands are nearly planar. Atoms N1, C1, C6 and O1 of the chelate ring have an r.m.s. deviation from their mean plane of 0.008 Å. Atom Ni1 deviates from this plane by 0.212 (2) Å, so that the chelate ring puckering can best be described as an envelope on Ni1. According to the Cambridge Structural Database (CSD, Version 5.28 of 2007; Allen, 2002), ten crystal structures of octahedral bis-pia complexes have been published so far, nine with trans- and just one with cis-related pia ligands. In the trans complexes, the dihedral angles between the planes of the pyridine ring and the amide group and between those of the pyridine and chelate rings are in the
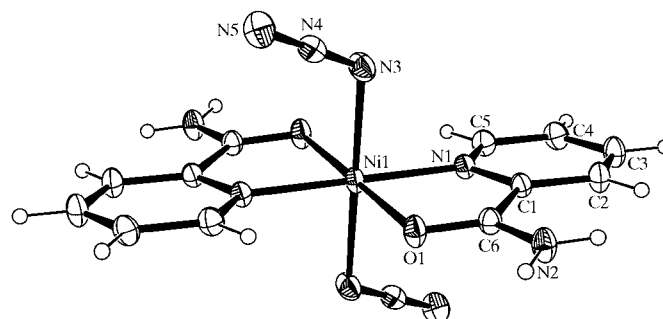
Figure 1
The title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

ranges 1.0–4.7 and 1.6–3.7°, respectively, while in the *cis* complex, the dihedral angles are much larger, *viz.* 14.1 and 22.7°, respectively. In the title compound, the aforementioned dihedral angles are 5.4 (1) and 3.3 (1)°, respectively; it could therefore be concluded that the pia ligand in (I) is among the less planar ones in *trans*-pia complexes, probably because of the short H⋯H intramolecular contact of 2.13 Å between atoms H2 (at C2) and H7 (at N2), which is also one of the shortest found in this class of compounds.

The azide ligands in (I) are coordinated in a nonlinear mode to the central metal ion (Table 1). In other reported nickel(II) complexes with monodentate azide ligands, the analogous angles are in the range 103–151°, according to 98 structures obtained from the CSD. The azide ligands are usually slightly bent and the already mentioned search of the CSD shows that the azide bond angle in terminal azides is between 175 and 180°. In complex (I), the azide N—N—N bond angle also deviates slightly from linearity (Table 1).

The crystal structure is predominantly determined by hydrogen bonding. Typical amide N—H⋯O hydrogen bonds of the $R_2^2(8)$ type are not found. Instead, an extensive network of N—H⋯N hydrogen bonding is established. The geometric parameters are given in Table 2. There are two N—H⋯N hydrogen bonds in the crystal structure (Fig. 2). The N2—H8⋯N5^{iii} bond [symmetry code: (iii) $-x + 2, -y + 1, -z + 1$], involving the amide N atom and the outer atom, N5^{iii}, of an adjacent azide ligand, forms $R_2^2(16)$ rings between two neighbouring molecules. The other interaction, N2—H7⋯N3^{ii} [symmetry code: (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$], between the same amide N atom and the coordinated azide atom, N3^{ii}, of a different adjacent molecule, links the molecules into zigzag $C_2^2(12)$ chains. The combination of these hydrogen-bonding interactions links the molecules into an infinite three-dimensional network.
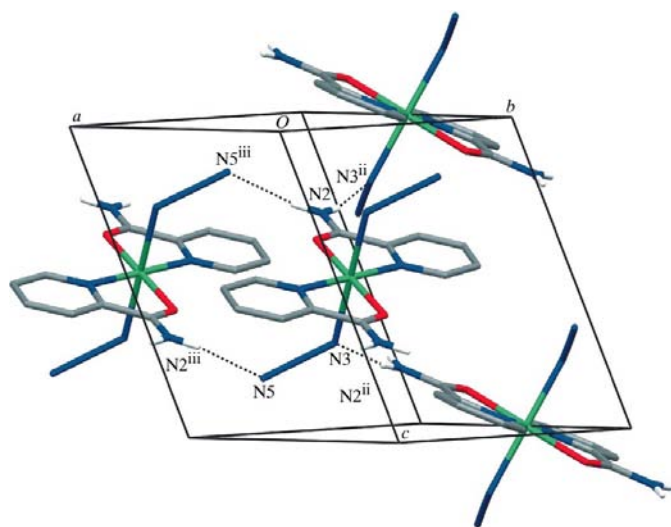

Figure 2
A perspective view of the packing of the title compound, showing the hydrogen bonds as dashed lines. H atoms have been omitted for clarity. [Symmetry codes: (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $-x + 2, -y + 1, -z + 1$.]

Experimental

Aqueous solutions of picolinamide (0.24 g, 2 mmol in 20 ml of H_2O) and nickel(II) nitrate hexahydrate (0.29 g, 1 mmol in 20 ml of H_2O) were mixed together. To the resulting solution was added an aqueous solution of sodium azide (0.13 g, 2 mmol in 10 ml of H_2O). The reaction mixture was left to stand for 4 d until green crystals of (I) suitable for X-ray analysis were obtained (yield 0.25 g, 65%). IR (KBr pellet, ν, cm^{-1}): 3281 (*m–s*), 3124 (*s*), 3079 (*m–s*), 2058 (*vs*), 2035 (*vs*), 1675 (*s*), 1620 (*m*), 1585 (*s*), 1568 (*s*), 1534 (*w*), 1425 (*s*), 1345 (*w*), 1310 (*m*), 1292 (*w*), 1276 (*w–m*), 1182 (*w*), 1158 (*w–m*), 1124 (*m*), 1094 (*w*), 1056 (*w*), 1027 (*m*), 927 (*vw*), 825 (*w–m*), 790 (*w–m*), 771 (*s*), 705 (*w–m*), 668 (*m–s*), 663 (*m–s*), 654 (*m*), 619 (*w–m*), 514 (*w*), 452 (*w*). The crystals detonate without melting when warmed to 538 K.

Crystal data

$[Ni(N_3)_2(C_6H_6N_2O)_2]$	$V = 774.13$ (3) Å^3
$M_r = 387.01$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.6237$ (1) Å	$\mu = 1.29$ mm^{-1}
$b = 11.9574$ (2) Å	$T = 183$ K
$c = 9.5112$ (3) Å	$0.59 \times 0.30 \times 0.06$ mm
$\beta = 116.767$ (2)°	

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby detector	27299 measured reflections
	2257 independent reflections
	2023 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*CrysAlisPro*; Oxford Diffraction, 2007)	$R_{int} = 0.030$
$T_{min} = 0.490$, $T_{max} = 0.930$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.073$	
$S = 1.08$	
2257 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
123 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.073 (1)	Ni1—N3	2.137 (1)
Ni1—N1	2.032 (1)		
O1—Ni1—N1	79.96 (5)	N1—Ni1—N3	88.96 (5)
O1—Ni1—N3	87.89 (5)	N1—Ni1—N3^i	91.04 (5)
O1—Ni1—N1^i	100.04 (5)	Ni1—N3—N4	118.3 (1)
O1—Ni1—N3^i	92.12 (5)	N3—N4—N5	178.9 (2)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H7⋯N3^{ii}	0.87 (2)	2.20 (2)	3.046 (2)	168 (2)
N2—H8⋯N5^{iii}	0.88 (2)	2.15 (2)	3.021 (2)	172 (2)

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

Aromatic H atoms were fixed in geometrically calculated positions and refined using a riding model [C—H = 0.95 Å and U_{iso}(H) = $1.2U_{eq}$(C)]. H atoms on the carboxamide N atom were found in a difference Fourier map at the final stage of refinement and refined freely.

Data collection: *CrysAlisPro* (Oxford Diffraction, 2007); cell refinement: *CrysAlisPro*; data reduction: *CrysAlisPro*; 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 *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3065). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Chang, S. C., Park, D. Y. & Li, N. C. (1968). *Inorg. Chem.* **7**, 2144–2150.

Cortes, R., Lezama, L., Pizarro, J. L., Solans, X., Arriortua, M. I. & Rajo, T. (1994). *Angew. Chem. Int. Ed.* **33**, 2488–2489.

Đaković, M., Popović, Z., Giester, G. & Rajić-Linarić, M. (2007a). *Polyhedron.* In the press.

Đaković, M., Popović, Z., Giester, G. & Rajić-Linarić, M. (2007b). Sixteenth Croatian–Slovenian Crystallographic Meeting, 13–16 June 2007, Petrčane, Croatia. Book of Abstracts, p. 32.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Hong, C. S. & Do, Y. (1999). *Angew. Chem. Int. Ed.* **38**, 193–195.

Liu, C.-M., Gao, S., Xiong, D.-G., Liu, Z.-L., Jiang, F.-C. & Zhu, D.-B. (2004). *Angew. Chem. Int. Ed.* **43**, 990–994.

Masuko, A., Nomura, T. & Saito, Y. (1967). *Bull. Chem. Soc. Jpn*, **40**, 511–515.

Nawata, Y., Iwasaka, H. & Saito, Y. (1967). *Bull. Chem. Soc. Jpn*, **40**, 515–521.

Oxford Diffraction (2007). *CrysAlisPro.* Version 171.32. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Paşaoğlu, H., Tezcan, F., Yeşilel, O. Z., Ölmez, H., Içbudak, H. I. & Büyükgüngör, O. (2004). *Acta Cryst.* C**60**, m335–m337.

Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortes, R., Lezama, L. & Rojo, T. (1999). *Coord. Chem. Rev.* **193–195**, 1027–1068.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97.* University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Yuwen, L., Yi, L., Cunxin, W., Songsheng, Q. & Fengjiao, D. (2000). *Thermochim. Acta*, **351**, 51–54.