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(Nitrato-κO)bis(pyridine-2-carboxamide-κ^2N^1,O)mercury(II) nitrate

Marijana Đaković and Zora Popović*

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

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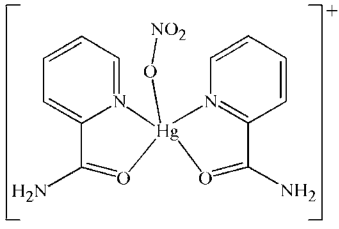
In the title compound, $[Hg(NO_3)(C_6H_6N_2O)_2]NO_3$, the Hg^{II} atom is five-coordinate. The distorted square-pyramidal mercury(II) coordination environment is achieved by two *N*,*O*-bidentate picolinamide ligands, with one *O*-monodentate nitrate ion in the apical position. A seven-coordinate extended coordination environment is completed by two additional weak Hg⋯O interactions, one from the coordinated nitrate ion and one from the other nitrate ion, to give seven-coordination. The molecules are linked into a two-dimensional network by N—H⋯O hydrogen bonds.

Comment

It is well known that the interaction of metal ions with bioactive ligands can improve their bioactivity profiles and, moreover, the inactive free ligands may acquire pharmacological properties (Krogsgaard-Larsen *et al.*, 2004). In this context, metal complexes are of central importance to many aspects of the structure and function of biologically active or potentially active ligands, and metal coordination is one of the most efficient strategies for designing repository, slow-release or long-acting drugs (Bharti *et al.*, 2000). We report here the preparation and structure analysis of the title compound, (I), as part of our systematic study of group 12 metal complexes with biologically important molecules (Popović, Pavlović, Vinković *et al.*, 2006; Popović, Matković-Čalogović *et al.*, 2007; Pavlović, Soldin *et al.*, 2007; Kukovec *et al.*, 2007). In addition to numerous mercury halide and pseudohalide complexes or adducts (Dean, 1978; Graddon, 1982; Holloway & Melnik, 1994; House *et al.*, 1994; Popović, Pavlović & Soldin, 2006), there are several papers dealing with mercury(II) nitrate complexes (Bullock & Tuck, 1965; Kamenar *et al.*, 1976; Grdenić *et al.*, 1978*a*,*b*, 1979; Buergi *et al.*, 1982; Müller *et al.*, 2005).



(I)

Compound (I) consists of $[Hg(NO_3)(pia)_2]^+$ complex cations (pia is picolinamide), with pia in its usual *N*,*O*-chelating mode, and nitrate anions (Fig. 1). The coordination polyhedron around the Hg^{II} ion in the complex cation can be described as a deformed square pyramid achieved through a [2N+3O] donor set of atoms. The two N and two O atoms in the coordination environment originate from two pia ligands, while the third O atom, O3, comes from a nitrate anion, with the Hg1—O3 bond length (Table 1) being 0.29 Å longer than the sum of the covalent radii of the atoms involved (1.57 + 0.66 = 2.23 Å; Matković-Čalogović, 1994). The lengths of the Hg—N and Hg—O bonds (Table 1) involving the pia ligands differ slightly from each other by 10.6σ and 17.0σ, respectively. The steric demand of the nitrate O atom covalently bound to the Hg^{II} ion is probably responsible for these bond-length differences. To the best of our knowledge, the only other report of a mercury(II) complex with a pia ligand is that of $[Hg(SCN)_2(pia)]_2$ (Đaković *et al.*, 2007), in which the Hg—N bond length of 2.239 (3) Å is slightly longer than those in (I) (by 5σ and 16σ) as a consequence of the three S atoms coordinated to Hg. Further elongation of Hg—N bonds was observed in the structure of [HgI(pic)(Hpic)] (Hpic is picolinic acid; Popović, Pavlović & Soldin, 2006), where Hg—N = 2.298 (3) Å, which is longer than those in (I) by 21σ and 30σ, due to the presence of the even larger iodide ligand. In (I), there are two additional weak Hg⋯O interactions. One is from atom O4 of the strongly coordinated nitrate ion [Hg1⋯O4 = 2.860 (2) Å] and the other is from the other symmetry-independent nitrate ion [Hg1⋯O6 = 2.813 (2) Å] (Fig. 1). These distances are within the sum of the van der Waals radii of these atoms (2.9–3.05 Å; Matković-Čalogović, 1994). Considering these interactions, the effective coordination polyhedron (Grdenić, 1965) around the Hg^{II} atom can be described as a distorted capped octahedron.

An interesting feature of the structure of (I) is the mutual spatial orientation of the chelate ligands; the planes defined by

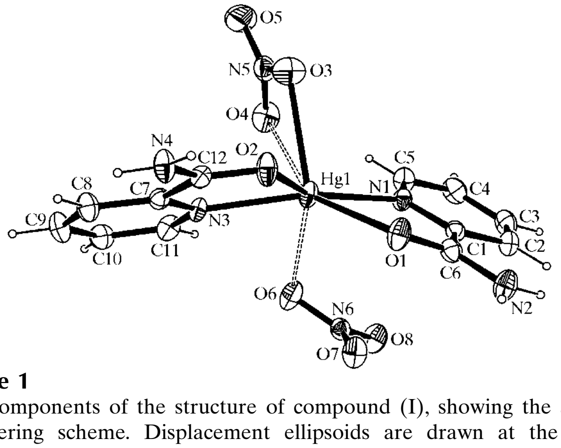


Figure 1
The components of the structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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atoms Hg1/N1/C1/C6/O1 and Hg1/N3/C7/C12/O2 intersect at an angle of 37.94 (1)°. This value is close to the corresponding dihedral angle of 40.5° in the similar ηcoordinated mercury compound, $[Hg(bipy)_2](NO_3)_2\cdot 2H_2O$ (bipy is 2,2′-bipyridyl; Grdenić *et al.*, 1979). Although both pia ligands in (I) are nearly planar, the conformations of the chelate rings differ significantly. The r.m.s. deviations of the chelate ring atoms N1/C1/C6/O1 and N2/C7/C12/O2 from their mean planes are 0.008 and 0.006 Å, respectively. Atom Hg1 deviates from these planes by 0.427 (4) and 0.006 (4) Å, respectively, and the chelate ring puckering of the former ring can best be described as an envelope on Hg1. The dihedral angles between the pyridine rings containing atoms N1 and N3 and their corresponding amide groups are 3.0 (1) and 2.1 (2)°, respectively, while the dihedral angles between these pyridine rings and their corresponding chelate rings are 3.1 (1) and 0.5 (1)°, respectively, which are in accordance with those found in similar Hg compounds, namely 2.2 (2) and 8.3 (2)° in $[Hg(SCN)_2(pia)]_2$, and 7.5 (2) and 1.7 (2)° in $[HgI(pic)_2(Hpic)]$.

The crystal structure of (I) is predominantly determined by N—H···O hydrogen bonding. The cation possesses two hydrogen-bond donors, *viz*. amide atoms N2 and N4, and both participate in intermolecular interactions. The combination of these interactions links the molecules into extended sheets which lie parallel to the (100) plane (Fig. 2). Hydrogen bonding within the sheets consists of a combination of reasonably short strong and, on average, more linear interactions with longer weaker and more bent interactions (Table 2). In the former group of interactions, two types of centrosymmetric ring motifs can be discerned. The 'standard' amide hydrogen-bond motif of $R_2^2(8)$ (Bernstein *et al.*, 1995) involves N4—H15···O2^{iv}, while two centrosymmetric $R_2^2(16)$ motifs, involving O atoms from the weakly coordinating nitrate anion, O7 and O8 (N2—H12···O8^{i} and N4—H14···O7^{iii}), are established (symmetry codes as in Table 2). The weaker interactions involve O atoms from the strongly coordinated nitrate ion. Atom O4, which already participates in coordination with atom Hg1, and atom O5 act as acceptors in bifurcated N2—H13···O4^{ii} and N2—H13···O5^{ii} hydrogen bonds, thereby forming an $R_1^2(4)$ graph-set motif.

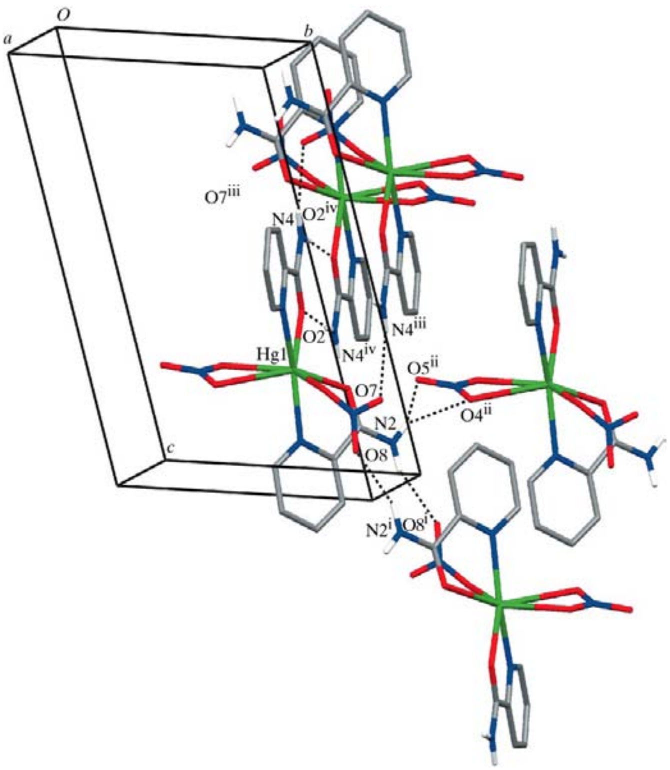

Figure 2
A perspective view of the packing of compound (I), showing the hydrogen bonds as dashed lines. Aromatic H atoms have been omitted for clarity. [Symmetry codes: (i) $1 - x, 2 - y, 2 - z$; (ii) $x, y + 1, z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $2 - x, 2 - y, 1 - z$.]

Experimental

To an aqueous solution (10 ml) of mercury(II) nitrate monohydrate (0.34 g, 0.1 mmol) containing a few drops of nitric acid (20% by weight), an aqueous solution (30 ml) of picolinamide (0.24 g, 0.2 mmol) was added. After a few hours, colourless crystals of (I) suitable for X-ray analysis were obtained. The crystals were filtered off, washed with water and dried in air (yield 0.52 g, 91.4%). IR (KBr pellet, ν, cm^{-1}): 3556 (*w-m*), 3406 (*s*), 3291 (*s*), 2395 (*w*), 2360 (*w*), 2343 (*w*), 1762 (*w*), 1680 (*s*), 1611 (*w-m*), 1590 (*s*), 1570 (*s*), 1473 (*w-m*), 1448 (*s*), 1431 (*s*), 1385 (*vs*), 1292 (*m-s*), 1255 (*m*), 1169 (*w*), 1118 (*w*), 1097 (*w-m*), 1045 (*w*), 1036 (*w*), 1024 (*vw*), 1013 (*w*), 999 (*m*), 825 (*m*), 766 (*w*), 746 (*m*), 715 (*vw*), 680 (*w*), 668 (*w-m*), 658 (*w*), 634 (*w*), 618 (*m*), 582 (*w-m*), 504 (*w*). The crystals decompose prior to melting.

Crystal data

$[Hg(NO_3)(C_6H_6N_2O)_2]NO_3$
$M_r = 568.87$
Triclinic, $P\overline{1}$
$a = 6.6594 (1)$ Å
$b = 9.5373 (2)$ Å
$c = 13.6949 (3)$ Å
$\alpha = 73.832 (2)°$
$\beta = 86.714 (2)°$
$\gamma = 75.399 (2)°$
$V = 808.34 (3)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 9.58$ mm^{-1}
$T = 183$ K
0.31 × 0.08 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Rubby detector
Absorption correction: multi-scan (*CrysAlisPro*; Oxford Diffraction, 2007)
$T_{min} = 0.187$, $T_{max} = 0.682$
38635 measured reflections
4719 independent reflections
4201 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.035$
$S = 1.02$
4719 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.47$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—O1	2.444 (2)	Hg1—N1	2.191 (2)
Hg1—O2	2.396 (2)	Hg1—N3	2.221 (2)
Hg1—O3	2.515 (2)		
O1—Hg1—O2	72.25 (5)	O2—Hg1—N1	137.45 (6)
O1—Hg1—O3	118.02 (6)	O2—Hg1—N3	71.17 (6)
O1—Hg1—N1	71.06 (6)	O3—Hg1—N1	98.25 (7)
O1—Hg1—N3	129.40 (6)	O3—Hg1—N3	88.90 (7)
O2—Hg1—O3	80.66 (6)	N1—Hg1—N3	151.19 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H12···O8^{i}	0.85 (3)	2.12 (3)	2.911 (3)	154 (3)
N2—H13···O4^{ii}	0.86 (3)	2.41 (3)	3.180 (3)	150 (2)
N2—H13···O5^{ii}	0.86 (3)	2.47 (3)	3.238 (3)	150 (2)
N4—H14···O7^{iii}	0.84 (3)	2.19 (3)	3.003 (2)	163 (3)
N4—H15···O2^{iv}	0.83 (3)	2.06 (3)	2.878 (3)	170 (2)

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

The aromatic H atoms were fixed in geometrically calculated positions and refined using a riding model, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The H atoms on the carboxamide N atom were found in a difference Fourier map at the final stage of refinement and refined freely. The largest peak of residual electron density lies 1.67 Å from atom Hg1 and 1.10 Å from atom N1.

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* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3068). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bharti, N., Maurya, M. R., Naqvi, F., Bhattacharya, A., Bhattacharya, S. & Azam, A. (2000). *Eur. J. Med. Chem.* **35**, 481–486.

Buergi, H. B., Fischer, E., Kunz, R. W., Parvez, M. & Pregosin, P. S. (1982). *Inorg. Chem.* **21**, 1246–1256.

Bullock, J. I. & Tuck, D. G. (1965). *J. Chem. Soc.* pp. 1877–1881.

Đaković, M., Popović, Z., Giester, G. & Rajić-Linarić, M. (2007). *Polyhedron*, doi:10.1016/j.poly.2007.09.014.

Dean, P. A. (1978). *Prog. Inorg. Chem.* **24**, 109–178.

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

Graddon, D. P. (1982). *Rev. Inorg. Chem.* **4**, 211–283.

Grdenić, D. (1965). *Q. Rev.* **19**, 303–328.

Grdenić, D., Kamenar, B. & Hergold-Brundić, A. (1978*a*). *Cryst. Struct. Commun.* **7**, 165–170.

Grdenić, D., Kamenar, B. & Hergold-Brundić, A. (1978*b*). *Cryst. Struct. Commun.* **7**, 245–250.

Grdenić, D., Kamenar, B. & Hergold-Brundić, A. (1979). *Croat. Chem. Acta*, **52**, 339–346.

Holloway, C. E. & Melnik, M. (1994). *Main Group Met. Chem.* **17**, 799–885.

House, D. A., Robinson, W. T. & McKee, V. (1994). *Coord. Chem. Rev.* **135**, 533–586.

Kamenar, B., Hergold-Brundić, A. & Sikirica, M. (1976). *Cryst. Struct. Commun.* **5**, 149–152.

Krogsgaard-Larsen, P., Liljefors, T. & Madsen, U. (2004). *Textbook of Drug Design and Discovery*, 3rd ed. London: Taylor and Francis.

Kukovec, B.-M., Popović, Z. & Pavlović, G. (2007). *Acta Cryst.* C**63**, m389–m391.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Matković-Čalogović, D. (1994). PhD thesis, University of Zagreb, Croatia.

Müller, J., Polonius, F.-A. & Roitzsch, M. (2005). *Inorg. Chim. Acta*, **385**, 1225–1230.

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

Pavlović, G., Soldin, Ž., Popović, Z. & Tralić-Kulenović, V. (2007). *Polyhedron*, **26**, 5162–5170.

Popović, Z., Matković-Čalogović, D., Popović, J., Vicković, I., Vinković, M. & Vikić-Topić, D. (2007). *Polyhedron*, **26**, 1045–1052.

Popović, Z., Pavlović, G. & Soldin, Ž. (2006). *Acta Cryst.* C**62**, m272–m274.

Popović, Z., Pavlović, G., Vinković, M., Vikić-Topić, D. & Rajić-Linarić, M. (2006). *Polyhedron*, **25**, 2353–2362.

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

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