Poly[(μ2-aqua-κ2O:O)(μ3-azido-κ3N1:N1:N3)(μ2-isonicotinato-κ2O:O′)lead(II)]

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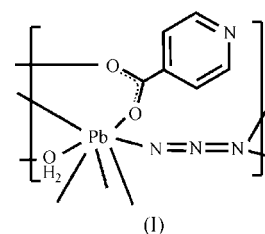
In the title compound, $[Pb(C_6H_4NO_2)(N_3)(H_2O)]_n$, the Pb ion is seven-coordinated by three N atoms from three azide ligands, two O atoms from two isonicotinate (inic) ligands and two O atoms from two coordinated water molecules, forming a distorted monocapped triangular prismatic coordination geometry. Each azide ligand bridges three Pb^{II} ions in a $\mu_{1,1,3}$ coordination mode to form a two-dimensional three-connected 6^3 topology network extending in the bc plane. The carboxylate group of the inic unit and the aqua ligand act as coligands to bridge Pb^{II} ions. Adjacent two-dimensional layers are connected by hydrogen-bonding interactions between the isonicotinate N atom and the water molecule, resulting in an extended three-dimensional network. The title complex is the first reported coordination polymer involving a p-block metal, an azide and a carboxylate.

Comment

In recent years, azide has attracted much attention not only for its versatile coordination mode as a bridging ligand, but also for its inherent advantages in the construction of materials with magnetic properties and potential applications (Yue *et al.*, 2008; Ray *et al.*, 2008; Liu *et al.*, 2007, 2006; Zeng *et al.*, 2005, 2006; Chen *et al.*, 2001). The synthetic strategy of choosing a different second ligand for propagating new motifs has been used to produce a large number of azide-bridged complexes (Cheng *et al.*, 2007; Liu *et al.*, 2005, 2006; Chen *et al.*, 2001). So far, most of the second ligands selected to coligate with the azide have been neutral (Escuer *et al.*, 2000; Gao *et al.*, 2003; Meyer *et al.*, 2003; Lewis *et al.*, 2004; Koner *et al.*, 2004). Anionic coligands have not been widely studied because of the added complication of having two different negative ligands that must co-exist and compete in the same molecule (Cheng *et al.*, 2007; Liu *et al.*, 2005, 2006; Chen *et al.*, 2001). Isonicotinic acid (Hinic), as a good source of a negative carboxylate ligand,

has been applied in transition-metal–azide systems to construct metal–organic frameworks and a few such complexes have been synthesized (Zeng *et al.*, 2006; Liu *et al.*, 2005, 2006). However, the combination of azide and a negative carboxylate coligand has been applied with p-block metals only rarely, with just one discrete compound reported (Fischer *et al.*, 1999). So far, coordination polymers of p-block metals with azide and carboxylate coligands have not been reported. In this context, we carried out the reaction of $[Pb_3(OH)_2(CO_3)_2]$ with NaN_3 and Hinic under hydrothermal conditions and isolated a novel Pb^{II} complex, $[Pb(inic)(N_3)(H_2O)]_n$, (I), the crystal structure of which is reported here. To the best of our knowledge, (I) is the first reported coordination polymer involving a p-block metal, an azide and a carboxylate.

(I)

Compound (I) crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit contains one Pb^{II} ion, one isonicotinate anion, one azide anion and one water molecule. The Pb^{II} center is seven-coordinated by three N atoms from three azide ligands, two O atoms from two inic ligands and two O atoms from two coordinated water molecules, forming a distorted monocapped triangular prismatic coordination geometry (Fig. 1); the triangular prism is formed by the triangles OW1[ii]–N1[iii]–N1 and O1–O2[i]–N3[iv], with end face O1–N3[iv]–OW1[ii]–N1[iii] and capping atom OW1. Each azide anion ligates three equivalent Pb^{II} ions in the $\mu_{1,1,3}$ coordination mode to form a honeycomb-like two-dimensional layer
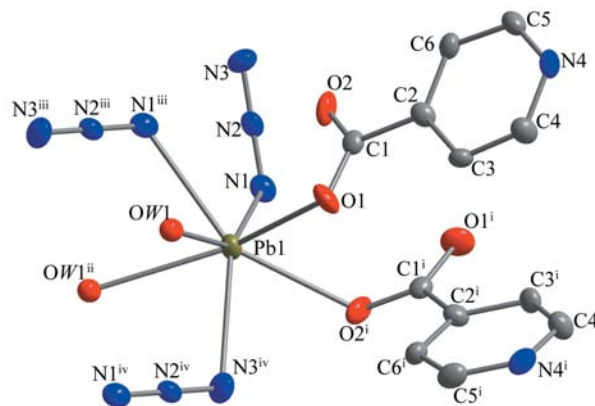

Figure 1
A view of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.]

structure (Fig. 2). The Pb—N bond lengths (Table 1) are similar to reported values (Marandi, Mirtamizdoust, Soudi & Fun, 2007; Marandi, Mirtamizdoust, Chantrapromma & Fun, 2007; Fischer *et al.*, 1999). The carboxylate group and the aqua ligand act as coligands with *syn–anti* carboxylate and μ_2-aqua bridging modes linking the Pb^{II} ions. The inic and aqua coligands are distributed on both sides of the two-dimensional layer. To emphasize the nature of the Pb-atom net bridged by azide, inic or aqua ligands, each Pb atom can be regarded as a three-connected node bridged to three nearest-neighbor Pb atoms by a pair of 'double-bridge' ligands [with Pb$\cdots$Pb separations of 4.480 (2) and 4.514 (1) Å, and Pb$\cdots$Pb$\cdots$Pb angles of 89.26 (1)–166.73 (1)°]. By defining each seven-coor-
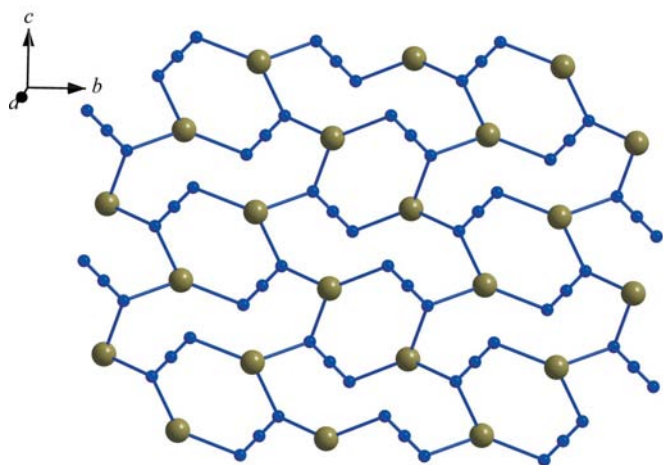

Figure 2
The two-dimensional coordination polymer formed by Pb^{II} ions and azide ligands in (I), viewed in the *bc* plane. The inic and aqua ligands have been omitted for clarity.
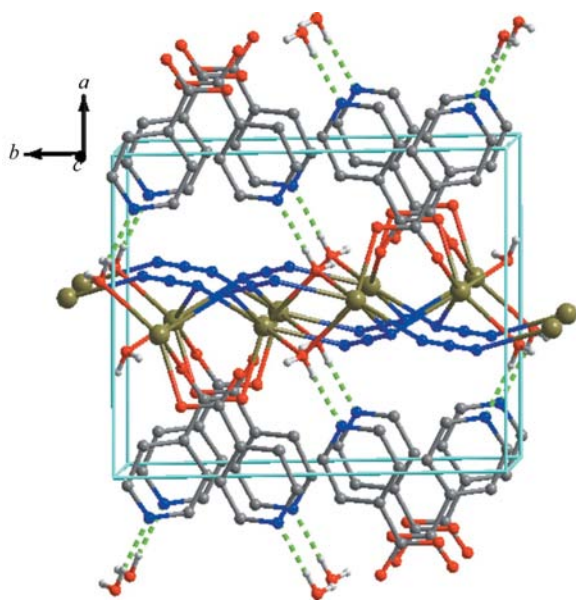

Figure 3
A packing diagram of (I), showing the water–isonicotinate O—H$\cdots$N hydrogen-bond network in the adjacent two-dimensional layers (dashed lines). H atoms not involved in hydrogen bonding have been omitted.

dinated Pb atom as a three-connected node, the two-dimensional network in (I) can be described as a two-dimensional three-connected topology with short and long Schläfli vertical symbols of 6^3 and 6.6.6 (Smith, 1978; O'Keeffe & Hyde, 1996, 1997). Within the two-dimensional layer, one hydrogen-bonding interaction is formed between an aqua ligand and a carboxylate O atom (Table 2). Adjacent two-dimensional layers are further interlinked by hydrogen-bonding interactions between the water molecule and the isonicotinate N atom into a three-dimensional supramolecular framework (Fig. 3).

Compared with the reported lead azide complexes [Pb(phen)(N$_3$)$_2$]$_n$ and {[Pb(deta)(N$_3$)]N$_3$}$_n$ (phen and deta are 1,10-phenanthroline and diethylenetriamine, respectively; Marandi, Mirtamizdoust, Soudi & Fun, 2007), the difference in the charge of the coligand [negative carboxylate in (I) *versus* neutral phen or deta] leads to a different ratio of Pb and N$_3$ [1:1 for (I) *versus* 1:2 for the other two complexes]. As a result, the three-dimensional framework of (I) is constructed from genuinely two-dimensional layers formed completely *via* the bridging ligand. By contrast, in the [Pb(phen)(N$_3$)$_2$]$_n$ and {[Pb(deta)(N$_3$)]N$_3$}$_n$ complexes, the three-dimensional supramolecular frameworks were constructed from quasi-two-dimensional layers, which were formed by a weak Pb—N interaction and lone-pair activity between adjacent one-dimensional chains.

Experimental

A mixture of [Pb$_3$(OH)$_2$(CO$_3$)$_2$] (0.25 mmol, 0.1939 g), NaN$_3$ (0.5 mmol, 0.0325 g), isonicotinic acid (0.3 mmol, 0.0330 g) and distilled water (8 ml) was sealed in a 25 ml Teflon-lined stainless steel autoclave and heated to 393 K for 3 d. After cooling to room temperature at a rate of 10 K h^{-1}, colorless crystals of the title compound suitable for X-ray analysis were isolated from the solution by filtration. **Caution:** Azide complexes are potentially explosive. Only a small amount of the material should be prepared and this should be handled with care.

Crystal data

[Pb(C$_6$H$_4$NO$_2$)(N$_3$)(H$_2$O)]	$V = 857.5$ (3) Å^3
$M_r = 389.34$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.815$ (2) Å	$\mu = 19.66$ mm^{-1}
$b = 12.963$ (3) Å	$T = 298$ (2) K
$c = 6.3422$ (13) Å	$0.18 \times 0.15 \times 0.10$ mm
$\beta = 105.33$ (3)°	

Data collection

Rigaku Mercury CCD area-detector diffractometer	5684 measured reflections
	1720 independent reflections
Absorption correction: multi-scan (*RAPID-AUTO*; Rigaku, 1998)	1660 reflections with $I > 2\sigma(I)$
$T_{min} = 0.038$, $T_{max} = 0.135$	$R_{int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.127$	
$S = 1.09$	
1720 reflections	$\Delta\rho_{max} = 3.03$ e Å^{-3}
133 parameters	$\Delta\rho_{min} = -3.02$ e Å^{-3}
3 restraints	

Table 1
Selected geometric parameters (Å, °).

Pb1—O1	2.518 (5)	Pb1—OW1[ii]	2.729 (5)
Pb1—OW1	2.662 (5)	Pb1—N1[iii]	2.744 (7)
Pb1—O2[i]	2.704 (6)	Pb1—N1	2.754 (7)
Pb1—OW1—Pb1[ii]	112.40 (17)	Pb1[i]—N1—Pb1	110.4 (2)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OW1—H1WA$\cdots$N4[v]	0.83 (3)	1.91 (4)	2.711 (8)	160 (8)
OW1—H1WB$\cdots$O2[iii]	0.83 (3)	1.98 (4)	2.790 (8)	164 (9)

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

Carbon-bound H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)]. Water H atoms were located in a difference Fourier map and were refined with an O—H distance restraint of 0.84 (1) Å [U_{iso}(H) = 1.2U_{eq}(O)].

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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