Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetrakis(pyridine-2-carboxylato-κ^2N,O)palladium(IV) dihydrate

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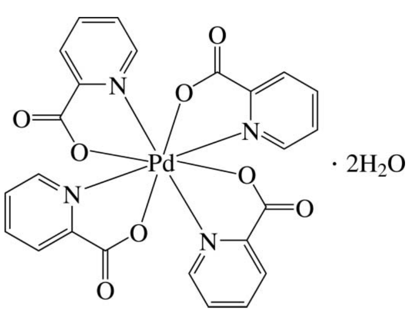
Received 23 September 2009; accepted 27 September 2009

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.034; wR factor = 0.104; data-to-parameter ratio = 16.7.

The asymmetric unit of the title compound, $[Pd(C_6H_4NO_2)_4]\cdot 2H_2O$, consists of a quarter of a neutral Pd^{IV} complex and half of a solvent water molecule. In the complex, the Pd^{IV} ion is located on a fourfold inversion axis and eight-coordinated in a distorted dodecahedral environment by four N and four O atoms from four symmetry-related pyridine-2-carboxylate (pic) anionic ligands. In the crystal, the water molecule is involved in O—H⋯O hydrogen bonding, and weak intermolecular C—H⋯O hydrogen bonds occur. There are also intermolecular π–π interactions between adjacent pyridine rings, with a centroid–centroid distance of 3.715 (3) Å.

Related literature

For details of polyhedra with coordination number eight, see: Lippard & Russ (1968); Muetterties & Guggenberger (1974). For the synthesis and structure of the Pd(II)–pic complex, $[Pd(pic)_2]$, see: Qin *et al.* (2002). For the crystal structures of eight-coordinated M(III, IV)–pic complexes (M = Nb, Er or Bi), see: Ooi *et al.* (1996); Soares-Santos *et al.* (2003); Callens *et al.* (2008). For the crystal structures of Pd(II) in an environment of eight O atoms, see: Izarova *et al.* (2009).



Experimental

Crystal data

$[Pd(C_6H_4NO_2)_4]\cdot 2H_2O$
M_r = 630.84
Tetragonal, $P4_2/n$
a = 11.1621 (5) Å
c = 9.5880 (9) Å
V = 1194.59 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.85 mm^{-1}
T = 296 K
0.23 × 0.14 × 0.07 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.804, T_{max} = 0.942
8399 measured reflections
1485 independent reflections
1074 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.104
S = 1.21
1485 reflections
89 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −1.00 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3O⋯O2^{i}	0.87	2.04	2.879 (5)	161
C1—H1⋯O2^{ii}	0.93	2.55	3.233 (5)	131
C2—H2⋯O3^{iii}	0.93	2.59	3.420 (6)	149

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

This study was supported financially by the Special Research Program of Chonnam National University, 2009.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2464).

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supplementary materials

Acta Cryst. (2009). E**65**, m1274 [**doi:10.1107/S1600536809039270**]

Tetrakis(pyridine-2-carboxylato-κ^2N,O)palladium(IV) dihydrate

N.-H. Kim and **K. Ha**

Comment

The asymmetric unit of the title compound, $[Pd(C_6H_4NO_2)_4].2H_2O$, contains a quarter of a neutral Pd^{IV} complex and one half of a solvent water molecule (Fig. 1). In the crystal, the complex has the symmetry elements C_2 and S_4, and its point group is S_4 and the Pd atom lies on the special position at (1/4, 1/4, 1/4) (Wyckoff letter a). The water molecule is disposed about a twofold rotation axis through O atom with the special position at (3/4, 1/4, *z*) (Wyckoff letter e). In the complex, the Pd^{4+} ion is eight-coordinated in a distorted dodecahedral environment (Fig. 2) by four N and four O atoms from four distinct pyridine-2-carboxylate (pic) anionic ligands. All four ligands are coordinated in an *N*,*O*-chelation mode with the considerably different Pd—O and Pd—N bond lengths [Pd—O = 2.097 (3) Å, Pd—N = 2.373 (3) Å] and the five-membered chelate ring has an O—Pd—N bite angle of 72.07 (12)°. On the contrary, the Pd—O and Pd—N bond lengths in the Pd(II)-pic complex, $[Pd(pic)_2]$, are almost equal [Pd—O = 2.003 (2) Å, Pd—N = 1.998 (2) Å] and the bite angle of the chelate ring is 82.36 (9)° (Qin *et al.*, 2002). The C═O bond length [1.215 (5) Å] and the C—O bond length [1.314 (5) Å] are typical and similar to values in the complex $[Pd(pic)_2]$ (Qin *et al.*, 2002). In the crystal structure, the water molecule is involved in O—H···O hydrogen bonding and weak intermolecular C—H···O hydrogen bonds occur (Table 1 and Fig. 3). There are also intermolecular π-π interactions between adjacent pyridine rings, with a centroid-centroid distance of 3.715 (3) Å.

Experimental

Single crystals of the title compound were unexpectedly obtained by reacting pyridine-2-carboxylic acid (0.721 g, 5.86 mmol), 1,6-diaminohexane (0.160 g, 1.38 mmol) and Na_2PdCl_4 (0.200 g, 0.68 mmol) in H_2O (10 ml) for 24 h at room temperature. Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH_3CN solution of the white reaction product.

Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.93 Å, O—H = 0.87 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$]].

Figures

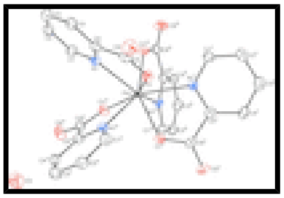


Fig. 1. The structure of the title compound, with displacement ellipsoids drawn at the 30% probability level for non-H atoms [Symmetry codes: (*a*) 1/2 - *x*, 1/2 - *y*, *z*, (*b*) *y*, 1/2 - *x*, 1/2 - *z*, (*c*) 1/2 - *y*, *x*, 1/2 - *z*]. H atoms are omitted.

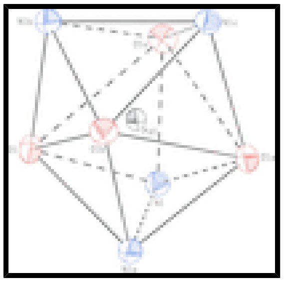


Fig. 2. View of the distorted dodecahedral geometry around the Pd atom.

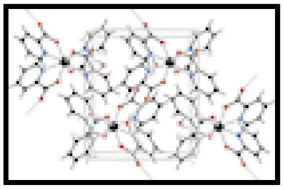


Fig. 3. View of the unit-cell contents of the title compound. Hydrogen-bond interactions are drawn with dashed lines.

Tetrakis(pyridine-2-carboxylato-κ^2*N*,*O*)palladium(IV) dihydrate

Crystal data

$[Pd(C_6H_4NO_2)_4]\cdot 2H_2O$

M_r = 630.84

Tetragonal, $P4_2/n$

Hall symbol: -P 4bc

a = 11.1621 (5) Å

b = 11.1621 (5) Å

c = 9.5880 (9) Å

α = 90°

β = 90°

γ = 90°

V = 1194.59 (14) Å^3

Z = 2

F_{000} = 636

D_x = 1.754 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 3500 reflections

θ = 2.6–28.3°

μ = 0.85 mm^{-1}

T = 296 K

Block, colorless

0.23 × 0.14 × 0.07 mm

Data collection

Bruker SMART 1000 CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 296 K

φ and ω scans

Absorption correction: Multi-scan (*SADABS*; Bruker, 2000)

T_{min} = 0.804, T_{max} = 0.942

8399 measured reflections

1485 independent reflections

1074 reflections with $I > 2\sigma(I)$

R_{int} = 0.045

θ_{max} = 28.3°

θ_{min} = 2.6°

$h = -14 \rightarrow 14$

$k = -14 \rightarrow 10$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 2.1364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.21$	$(\Delta/\sigma)_{max} < 0.001$
1485 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
89 parameters	$\Delta\rho_{min} = -1.00$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.2500	0.2500	0.2500	0.02277 (17)
O1	0.0856 (2)	0.3186 (3)	0.3193 (3)	0.0380 (7)
O2	−0.0577 (3)	0.3299 (3)	0.4796 (4)	0.0570 (10)
N1	0.1892 (3)	0.1367 (3)	0.4471 (4)	0.0334 (8)
C1	0.2408 (4)	0.0371 (4)	0.4990 (5)	0.0416 (10)
H1	0.3108	0.0087	0.4581	0.050*
C2	0.1927 (4)	−0.0243 (4)	0.6114 (5)	0.0449 (11)
H2	0.2298	−0.0930	0.6454	0.054*
C3	0.0889 (4)	0.0180 (5)	0.6722 (5)	0.0491 (12)
H3	0.0561	−0.0210	0.7489	0.059*
C4	0.0343 (4)	0.1187 (4)	0.6182 (4)	0.0406 (10)
H4	−0.0360	0.1482	0.6574	0.049*
C5	0.0863 (4)	0.1755 (4)	0.5038 (5)	0.0366 (10)
C6	0.0317 (4)	0.2821 (4)	0.4335 (5)	0.0371 (9)
O3	0.7500	0.2500	0.1567 (7)	0.092 (2)
H3O	0.7183	0.3148	0.1215	0.137*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02072 (19)	0.02072 (19)	0.0269 (3)	0.000	0.000	0.000
O1	0.0315 (15)	0.0398 (17)	0.0426 (17)	0.0077 (12)	−0.0017 (14)	0.0034 (14)

O2	0.0388 (19)	0.066 (2)	0.066 (2)	0.0183 (16)	0.0149 (17)	0.0011 (19)
N1	0.0312 (18)	0.0364 (19)	0.0326 (18)	0.0020 (14)	0.0007 (15)	0.0005 (15)
C1	0.040 (3)	0.035 (2)	0.049 (3)	0.0050 (18)	0.000 (2)	0.003 (2)
C2	0.053 (3)	0.040 (3)	0.042 (3)	−0.004 (2)	−0.007 (2)	0.006 (2)
C3	0.052 (3)	0.056 (3)	0.040 (3)	−0.006 (2)	0.001 (2)	0.006 (2)
C4	0.039 (2)	0.056 (3)	0.027 (2)	−0.004 (2)	0.0044 (18)	−0.006 (2)
C5	0.035 (2)	0.034 (2)	0.041 (2)	−0.0023 (17)	−0.0010 (18)	−0.0059 (19)
C6	0.032 (2)	0.038 (2)	0.041 (2)	−0.0005 (18)	0.0022 (19)	−0.006 (2)
O3	0.121 (6)	0.064 (4)	0.090 (5)	0.002 (4)	0.000	0.000

Geometric parameters (Å, °)

Pd1—O1^{i}	2.097 (3)	N1—C1	1.347 (5)
Pd1—O1^{ii}	2.097 (3)	C1—C2	1.386 (6)
Pd1—O1^{iii}	2.097 (3)	C1—H1	0.9300
Pd1—O1	2.097 (3)	C2—C3	1.380 (7)
Pd1—N1^{ii}	2.373 (3)	C2—H2	0.9300
Pd1—N1^{iii}	2.373 (3)	C3—C4	1.380 (7)
Pd1—N1^{i}	2.373 (3)	C3—H3	0.9300
Pd1—N1	2.373 (3)	C4—C5	1.393 (6)
O1—C6	1.314 (5)	C4—H4	0.9300
O2—C6	1.215 (5)	C5—C6	1.497 (6)
N1—C5	1.343 (5)	O3—H3O	0.87
O1^{i}—Pd1—O1^{ii}	95.77 (5)	N1^{ii}—Pd1—N1	74.42 (17)
O1^{i}—Pd1—O1^{iii}	143.04 (17)	N1^{iii}—Pd1—N1	129.37 (10)
O1^{ii}—Pd1—O1^{iii}	95.77 (5)	N1^{i}—Pd1—N1	129.37 (10)
O1^{i}—Pd1—O1	95.77 (5)	C6—O1—Pd1	123.4 (3)
O1^{ii}—Pd1—O1	143.04 (17)	C5—N1—C1	118.8 (4)
O1^{iii}—Pd1—O1	95.77 (5)	C5—N1—Pd1	113.3 (3)
O1^{i}—Pd1—N1^{ii}	71.43 (12)	C1—N1—Pd1	127.7 (3)
O1^{ii}—Pd1—N1^{ii}	72.07 (12)	N1—C1—C2	122.0 (4)
O1^{iii}—Pd1—N1^{ii}	145.42 (12)	N1—C1—H1	119.0
O1—Pd1—N1^{ii}	78.64 (12)	C2—C1—H1	119.0
O1^{i}—Pd1—N1^{iii}	78.64 (12)	C3—C2—C1	118.9 (4)
O1^{ii}—Pd1—N1^{iii}	71.43 (12)	C3—C2—H2	120.5
O1^{iii}—Pd1—N1^{iii}	72.07 (12)	C1—C2—H2	120.5
O1—Pd1—N1^{iii}	145.42 (12)	C2—C3—C4	119.5 (5)
N1^{ii}—Pd1—N1^{iii}	129.37 (10)	C2—C3—H3	120.3
O1^{i}—Pd1—N1^{i}	72.07 (12)	C4—C3—H3	120.3
O1^{ii}—Pd1—N1^{i}	145.42 (12)	C3—C4—C5	118.8 (4)
O1^{iii}—Pd1—N1^{i}	78.64 (12)	C3—C4—H4	120.6
O1—Pd1—N1^{i}	71.43 (12)	C5—C4—H4	120.6
N1^{ii}—Pd1—N1^{i}	129.37 (10)	N1—C5—C4	121.9 (4)

N1^{iii}—Pd1—N1^{i}	74.42 (17)	N1—C5—C6	115.0 (4)
O1^{i}—Pd1—N1	145.42 (12)	C4—C5—C6	123.1 (4)
O1^{ii}—Pd1—N1	78.64 (12)	O2—C6—O1	122.9 (4)
O1^{iii}—Pd1—N1	71.43 (12)	O2—C6—C5	121.3 (4)
O1—Pd1—N1	72.07 (12)	O1—C6—C5	115.8 (4)
O1^{i}—Pd1—O1—C6	−141.3 (3)	N1^{iii}—Pd1—N1—C1	24.3 (4)
O1^{ii}—Pd1—O1—C6	−33.7 (3)	N1^{i}—Pd1—N1—C1	127.2 (4)
O1^{iii}—Pd1—O1—C6	73.9 (3)	C5—N1—C1—C2	−1.9 (7)
N1^{ii}—Pd1—O1—C6	−71.6 (3)	Pd1—N1—C1—C2	−176.7 (3)
N1^{iii}—Pd1—O1—C6	140.4 (3)	N1—C1—C2—C3	−0.1 (7)
N1^{i}—Pd1—O1—C6	149.9 (3)	C1—C2—C3—C4	1.3 (7)
N1—Pd1—O1—C6	5.6 (3)	C2—C3—C4—C5	−0.4 (7)
O1^{i}—Pd1—N1—C5	71.4 (4)	C1—N1—C5—C4	2.8 (6)
O1^{ii}—Pd1—N1—C5	155.0 (3)	Pd1—N1—C5—C4	178.3 (3)
O1^{iii}—Pd1—N1—C5	−104.9 (3)	C1—N1—C5—C6	−176.3 (4)
O1—Pd1—N1—C5	−2.2 (3)	Pd1—N1—C5—C6	−0.7 (4)
N1^{ii}—Pd1—N1—C5	80.7 (3)	C3—C4—C5—N1	−1.6 (7)
N1^{iii}—Pd1—N1—C5	−150.8 (3)	C3—C4—C5—C6	177.4 (4)
N1^{i}—Pd1—N1—C5	−47.9 (3)	Pd1—O1—C6—O2	173.0 (3)
O1^{i}—Pd1—N1—C1	−113.6 (4)	Pd1—O1—C6—C5	−7.9 (5)
O1^{ii}—Pd1—N1—C1	−29.9 (4)	N1—C5—C6—O2	−175.7 (4)
O1^{iii}—Pd1—N1—C1	70.2 (4)	C4—C5—C6—O2	5.2 (7)
O1—Pd1—N1—C1	172.9 (4)	N1—C5—C6—O1	5.1 (6)
N1^{ii}—Pd1—N1—C1	−104.3 (4)	C4—C5—C6—O1	−173.9 (4)

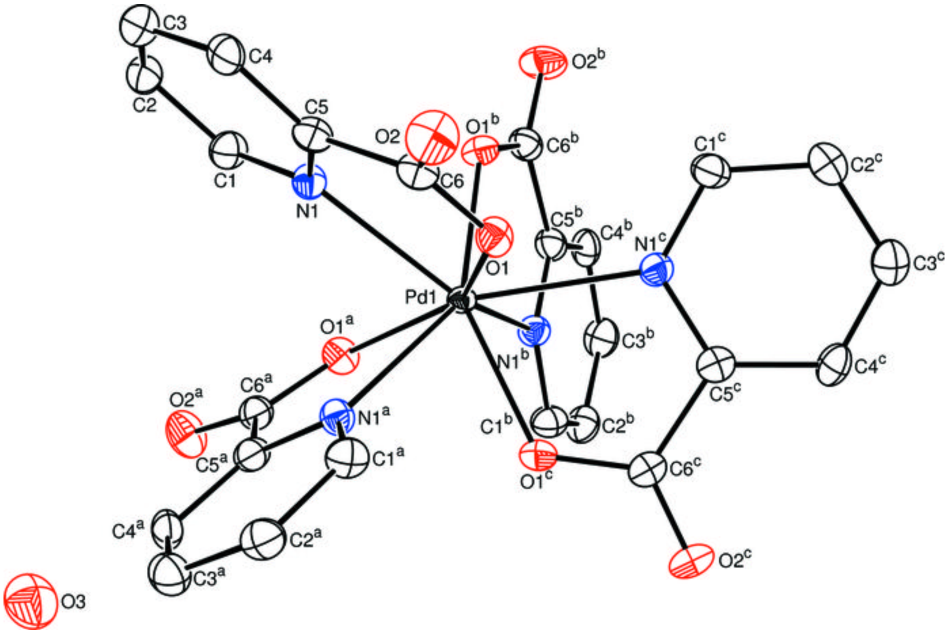
Symmetry codes: (i) $y, -x+1/2, -z+1/2$; (ii) $-x+1/2, -y+1/2, z$; (iii) $-y+1/2, x, -z+1/2$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O2^{iv}	0.87	2.04	2.879 (5)	161
C1—H1···O2^{v}	0.93	2.55	3.233 (5)	131
C2—H2···O3^{vi}	0.93	2.59	3.420 (6)	149

Symmetry codes: (iv) $-y+1, x+1/2, z-1/2$; (v) $x+1/2, y-1/2, -z+1$; (vi) $-x+1, -y, -z+1$.

Fig. 1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C4
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O2
O1^b
C6^b
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N1
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O3

Fig. 2

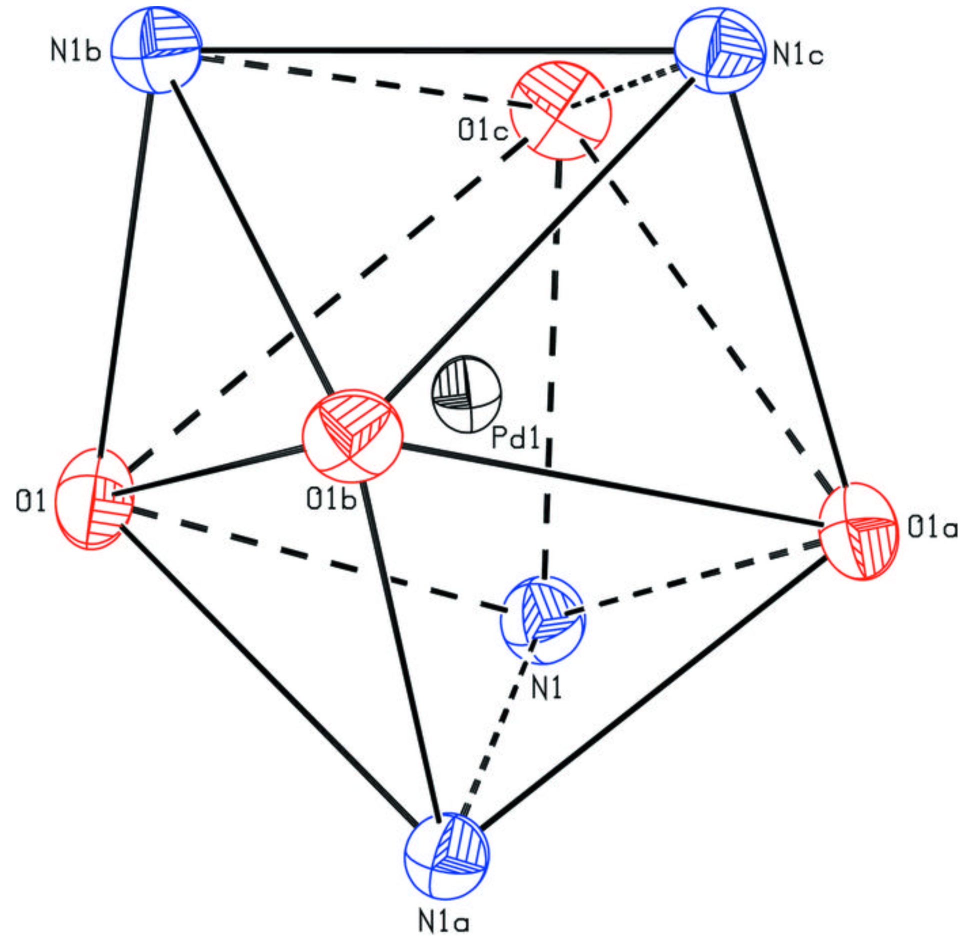

Fig. 3