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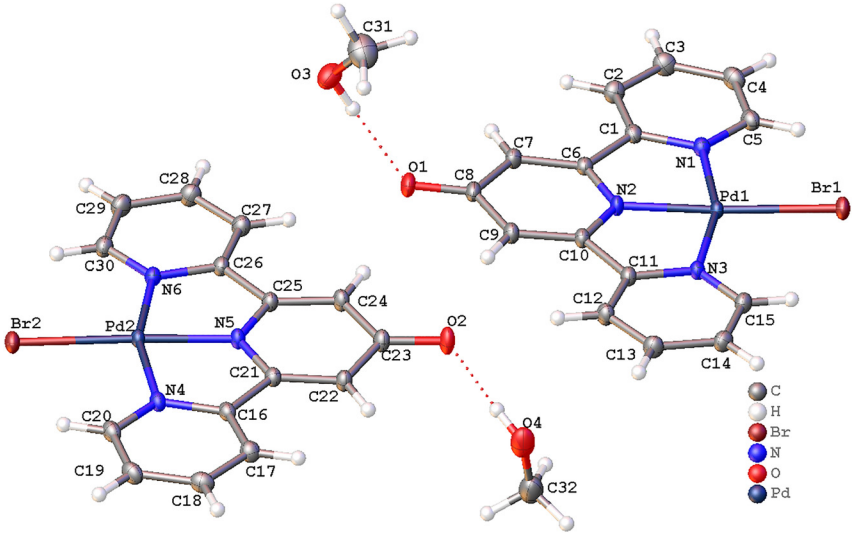
Crystal structure of bromido-(2,2′:6′,2″-terpyridine-4′-onato-κ^{3}N)palladium(II) methanol solvate



https://doi.org/10.1515/ncrs-2024-0343
Received August 19, 2024; accepted October 4, 2024;
published online October 16, 2024

Abstract

$C_{16}H_{14}BrN_3O_2Pd$, triclinic, $P\bar{1}$ (no. 2), a = 7.5162(5) Å, b = 12.5437(9) Å, c = 17.7525(12) Å, α = 73.149(2)°, β = 82.186(2)°, γ = 73.616(2)°, V = 1534.13(18) Å^3, Z = 4, T = 100(2) K, $R_{gt}(F)$ = 0.0208, $wR_{ref}(F^2)$ = 0.0573.

CCDC no.: 2377415

A part of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.15 × 0.10 × 0.06 mm
Wavelength:	Ga $K\alpha$ radiation (1.34139 Å)
μ:	8.72 mm^{-1}
Diffractometer, scan mode:	Bruker D8 venture, φ and ω
θ_{max}, completeness:	72.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	48198, 9168, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8,873
$N(param)_{refined}$:	420
Programs:	Bruker,[1] SHELX,[2–4] Diamond,[5] Olex2[6]

1 Source of materials

All the reagents and solvents were used as obtained without further purification. The ligand 2,6-bis(2-pyridyl)-4(1H)-pyridone (25.0 mg, 0.1 mmol) and palladium bromide (27.0 mg, 0.1 mmol) were thoroughly mixed and dissolved in 20.0 mL a mixed solution of methanol and acetonitrile (v:v = 1:1). The yellow solution was stirred vigorously at 333 K for 2 h and then filtered to remove some precipitate. The final resulting solution was kept at ambient condition. Yellow-brown block crystals were obtained seven days later at bottom of the vessel.

2 Experimental details

All the H atoms bound to carbon atoms were placed at their geometrically idealized positions and constrained to ride on their parent atoms with C–H = 0.95 Å (aromatic) and 0.98 Å (methyl), U_{iso}(H) = 1.2U_{eq} (aromatic) and 1.5U_{eq} (methyl). These two H atoms bound with O3 and O4 oxygen atoms

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.24570 (2)	1.13961 (2)	0.87041 (2)	0.01838 (4)
C1	0.1297 (2)	1.04707 (13)	0.64470 (9)	0.0147 (2)
C2	0.0441 (2)	1.10615 (14)	0.57444 (9)	0.0187 (3)
H2	0.031369	1.065222	0.538906	0.022*
C3	−0.0229 (2)	1.22528 (14)	0.55636 (9)	0.0210 (3)
H3	−0.080644	1.266530	0.508296	0.025*
C4	−0.0041 (2)	1.28330 (14)	0.60954 (10)	0.0211 (3)
H4	−0.048393	1.364763	0.598231	0.025*
C5	0.0804 (2)	1.22031 (13)	0.67953 (9)	0.0176 (3)
H5	0.091899	1.259802	0.716178	0.021*
C6	0.2074 (2)	0.92083 (12)	0.66960 (8)	0.0141 (2)
C7	0.2008 (2)	0.84113 (13)	0.63102 (9)	0.0163 (3)
H7	0.145498	0.866451	0.581727	0.020*
C8	0.2770 (2)	0.71995 (13)	0.66485 (9)	0.0163 (3)
C9	0.3609 (2)	0.68971 (13)	0.73914 (9)	0.0167 (3)
H9	0.415415	0.611265	0.764201	0.020*
C10	0.3617 (2)	0.77500 (12)	0.77380 (9)	0.0146 (2)
C11	0.4348 (2)	0.75792 (12)	0.85067 (8)	0.0144 (2)
C12	0.5187 (2)	0.65065 (13)	0.89824 (9)	0.0182 (3)
H12	0.534672	0.582952	0.881507	0.022*
C13	0.5788 (2)	0.64349 (13)	0.97049 (9)	0.0191 (3)
H13	0.635167	0.570723	1.004032	0.023*
C14	0.5558 (2)	0.74373 (14)	0.99329 (9)	0.0187 (3)
H14	0.597218	0.740489	1.042333	0.022*
C15	0.4716 (2)	0.84844 (13)	0.94355 (9)	0.0169 (3)
H15	0.456392	0.916966	0.959148	0.020*
N1	0.14632 (17)	1.10498 (11)	0.69686 (7)	0.0147 (2)
N2	0.28703 (18)	0.88698 (11)	0.73915 (7)	0.0141 (2)
N3	0.41064 (17)	0.85628 (10)	0.87369 (7)	0.0136 (2)
O1	0.27118 (17)	0.64407 (10)	0.63150 (7)	0.0211 (2)
Pd1	0.27793 (2)	1.00028 (2)	0.79471 (2)	0.01240 (4)
Br2	0.69846 (2)	−0.09628 (2)	0.61552 (2)	0.01836 (4)
C16	0.8032 (2)	0.01556 (12)	0.83456 (9)	0.0145 (2)
C17	0.8835 (2)	−0.03799 (13)	0.90644 (9)	0.0177 (3)
H17	0.887367	0.006101	0.941319	0.021*
C18	0.9582 (2)	−0.15653 (13)	0.92696 (9)	0.0196 (3)
H18	1.012809	−0.194337	0.976116	0.023*
C19	0.9522 (2)	−0.21915 (13)	0.87490 (10)	0.0197 (3)
H19	1.004755	−0.300062	0.887568	0.024*
C20	0.8681 (2)	−0.16203 (13)	0.80383 (9)	0.0177 (3)
H20	0.862355	−0.205116	0.768563	0.021*
C21	0.7211 (2)	0.14060 (12)	0.80652 (8)	0.0140 (2)
C22	0.7170 (2)	0.22341 (12)	0.84376 (9)	0.0159 (3)
H22	0.777002	0.202436	0.891645	0.019*
C23	0.6221 (2)	0.34179 (13)	0.81038 (9)	0.0168 (3)
C24	0.5415 (2)	0.36717 (12)	0.73609 (9)	0.0169 (3)
H24	0.477086	0.443808	0.711278	0.020*
C25	0.5583 (2)	0.27964 (12)	0.70117 (8)	0.0144 (2)
C26	0.4923 (2)	0.29155 (12)	0.62387 (9)	0.0147 (2)
C27	0.4026 (2)	0.39598 (13)	0.57487 (9)	0.0176 (3)
H27	0.380004	0.465450	0.590135	0.021*
C28	0.3464 (2)	0.39722 (14)	0.50301 (9)	0.0204 (3)
H28	0.283549	0.467623	0.468869	0.024*
C29	0.3828 (2)	0.29488 (14)	0.48165 (9)	0.0199 (3)
H29	0.345932	0.294580	0.432622	0.024*
C30	0.4736 (2)	0.19299 (14)	0.53257 (9)	0.0174 (3)
H30	0.498388	0.122992	0.517792	0.021*
N4	0.79476 (17)	−0.04715 (11)	0.78396 (7)	0.0145 (2)
N5	0.64389 (18)	0.16958 (11)	0.73660 (7)	0.0141 (2)
N6	0.52755 (17)	0.19071 (11)	0.60248 (7)	0.0144 (2)
O2	0.60970 (18)	0.42002 (10)	0.84444 (7)	0.0221 (2)
Pd2	0.66287 (2)	0.05112 (2)	0.68439 (2)	0.01267 (4)
C31	−0.1127 (3)	0.5446 (2)	0.69386 (13)	0.0401 (5)
H31A	−0.221004	0.516160	0.693016	0.060*
H31B	−0.153793	0.618795	0.707019	0.060*
H31C	−0.029826	0.488955	0.733546	0.060*
O3	−0.01756 (19)	0.55873 (12)	0.61951 (8)	0.0286 (3)
H3A	0.069984	0.588316	0.619104	0.043*
C32	0.9852 (3)	0.43833 (18)	0.91231 (13)	0.0355 (4)
H32A	1.063576	0.449045	0.947956	0.053*
H32B	0.931692	0.512805	0.875945	0.053*
H32C	1.060618	0.385311	0.882188	0.053*
O4	0.8411 (2)	0.39201 (11)	0.95671 (8)	0.0320 (3)
H4A	0.765095	0.391983	0.926121	0.048*

were initially found from the difference maps and then constrained to be at their ideal positions with O–H = 0.84 Å and the U_{iso}(H) = 1.5U_{eq}(O).

3 Comment

In recent years, terpyridine-based palladium metal complexes have been widely designed and applied in many fields such as medicine, materials science, chemical sensors, and catalysis.[7–10] Along with the various structural features, 4′-substituted terpyridine derivatives have interesting photophysical and electrochemical properties.[11] In this work, we have used 2,6-bis(2-pyridyl)-4(1H)-pyridone (TPD) and palladium bromide as the raw material.

The titled compound was crystallized in the triclinic $P\bar{1}$ space group with the asymmetric unit consisting of each two neutral Pd(TPD)Br coordination units and two methanol molecules, thus giving a z' = 2. These two independent coordination units have same configurations with the middle pyridine nitrogen atom trans to bromide atom and the ligand carbonyl group (O1 and O2), acting as acceptors, were hydrogen-bonded to solvent methanol molecules. For each Pd^{2+} ion, it adopted a distorted square-planar geometric configuration and was coordinated by a bromide atom and three nitrogen atoms of the terpyridine moiety of TPD which is similar to some Pd(II)-chloride analogs.[12] TPD acted as a tridentate ligand and it can be regarded as being deprotonated one proton to satisfy the whole molecular charge balance. The Pd1–Br1 and Pd2–Br2 bond lengths are 2.440(2)

and 2.435(2) Å, which are in a range of common bond distances for similar Pd(II) complexes.[13] The Pd1–N2 (1.933(1) Å) and Pd2–N5 (1.931(1) Å) bond lengths are slightly shorter than those of the two outer nitrogen atoms (2.033(1) Å/2.030(1) Å; 2.037(1) Å/2.034(1) Å). Due to the deprotonation effect of the central pyridine ring, the two neighboring aromatic C–C bonds (1.440(2)–1.443(2) Å) are slightly longer than the other four (1.348(2)–1.382(2) Å), which should be mainly ascribed to the electron delocalization around C8 and C23 atoms.

In the crystal packing, the component ions are linked into a three-dimensional network by a combination of O–H···O, C–H···O, C–H···Br and $\pi\cdots\pi$ stacking interactions. In more details, these two methanol molecules are respectively anchored to the host Pd(II) coordination unit by means of O–H···O hydrogen bonds ($d_{O1\cdots O3}$ = 2.733(2) Å, $d_{O2\cdots O4}$ = 2.704(2) Å). The atomic distances $d_{H14\cdots Br1(1-x,\,2-y,\,2-z)}$ = 2.984(2) Å and $d_{H29\cdots Br2(1-x,\,-y,\,1-z)}$ = 2.968(2) Å are slightly shorter than the sum of their van der Waal's radii, 3.05 Å, indicating weak intermolecular forces between the symmetrically related molecules and forming dimers between molecules of these same type. Further, these dimers are linked into two-dimensional layer structure parallel to the (-2-12) plane by C–H···O interactions (C12–H12···O2 and C27–H27···O1). Finally, those neighboring two-dimensional (-2-12) layer structures are linked into the whole three-dimensional structure via two weak $\pi\cdots\pi$ interactions. For instances, the centroid-to-centroid distances between symmetry-related pyridine rings (N1-related-pyridie/N6-related-pyridine (x, 1 + y, z)) and (N3-related-pyridine/N4-related-pyridine (1 + x, y – 1, z)) are 3.557(2) and 3.731(2) Å by a calculation using *PLATON*,[14] showing a moderate $\pi\cdots\pi$ interaction.

Acknowledgments: This work was financially supported by Kashi University.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Kashi University.

Conflict of interest: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX 3* and *SAINT* V8.40B; Bruker AXS Inc.: Madison, WI, USA. 2003.
2. Sheldrick, G. M. *SHELXTL* Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.
3. Sheldrick, G. M. Crystal Refinement with *SHELX*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Sheldrick, G. M. A Short History of *SHELX*. *Acta Crystallogr.* **2008**, *A64*, 112–122.
5. Brandenburg, K. *DIAMOND*; Crystal Impact GbR: Bonn Germany, 2006.
6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *A42*, 339–341.
7. Ramakrishnan, A.; Kuppan, M.; Agarwal, A.; Sivin, V. Advances in the Biological Studies of Metal–Terpyridine Complexes: An Overview from 2012 to 2022. *Coord. Chem. Rev.* **2023**, *496*, 215380.
8. Tian, X.; Zhang, Q.; Zhang, M.; Uvdal, K.; Wang, Q.; Chen, J.; Du, W.; Huang, B.; Wu, J.; Tian, Y. Probe for Simultaneous Membrane and Nucleus Labeling in Living Cells and In Vivo Bioimaging Using a Two-Photon Absorption Water-Soluble Zn(II) Terpyridine Complex with a Reduced π-conjugation System. *Chem. Sci.* **2016**, *8*, 142–149.
9. Manikandamathavan, V. M.; Thangaraj, M.; Weyhermuller, T.; Parameswari, R. P.; Punitha, V.; Narasimha Murthy, N.; Unni Nair, B. Novel Mononuclear Cu (II) Terpyridine Complexes: Impact of Fused Ring Thiophene and Thiazole Head Groups towards DNA/BSA Interaction, Cleavage and Antiproliferative Activity on HepG2 and Triple Negative CAL-51 Cell Line. *Eur. J. Med. Chem.* **2007**, *135*, 434–446.
10. Wang, K. Y.; Weber, M.; Chung, T. S. P.; Zheng, J.; Yan, W.; Wu, W.; Jiang, H. B_2pin_2 Mediated Palladium–Catalyzed Diacetoxylation of Aryl Alkenes with O_2 as Oxygen Source and Sole Oxidant. *Org. Lett.* **2018**, *20*, 5090–5093.
11. Maskus, M.; Abruna, H. D. Synthesis and Characterization of Redox–Active Metal Complexes Sequentially Self-Assembled onto Gold Electrodes via a New Thiol–Terpyridine Ligand. *Langmuir* **1996**, *12*, 4455–4462.
12. Ha, K. Redetermination of Crystal Structure of [bis(pyridin-2-ylmethyl) Amine-κ^3 *N*, *N′*, *N″*]Chloridopalladium(II) Chloride Monohydrate. *Z. Kristallogr. N. Cryst. Struct.* **2023**. *228*, 467–469.
13. Broring, M.; Brandt, C. D. One Compound, Two Structures: Synthesis, Structures and Reactivity of a Novel (Tripyrrinato)Palladium(II) Trifluoracetate Complex $TrpyPdOAc_f$. *J. Chem. Soc., Dalton Trans.* **2002**, 1391–1395. https://doi.org/10.1039/B109510M.
14. Spek, A. L. Structure Validation in Chemical Crystallography. *Acta Crystallogr.* **2009**, *D65*, 148–155.