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Serendipitous formation and characterization of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$

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Abstract: A potassium tetranitratopalladate(II) with the composition $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ was synthesized by a simple solvothermal process in a glass ampoule. The new compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with the lattice parameters $a=1017.15(4)$, $b=892.94(3)$, $c=880.55(3)$ Å, and $\beta=98.13(1)^\circ$ ($Z=2$). The crystal structure of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ reveals isolated complex $[Pd(NO_3)_4]^{2-}$ anions, which are surrounded by eight potassium cations and four HNO_3 molecules. The complex anions and the cations are associated in layers which are separated by HNO_3 molecules. $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ can thus be regarded as a HNO_3 intercalation variant of β - $K_2[Pd(NO_3)_4]$. The characterization is based on single-crystal X-ray and powder X-ray diffraction.

Keywords: nitric acid; palladium; potassium; tetranitratopalladate.

1 Introduction

Synthesis and characterization of new binary and ternary borates is an intensively investigated field of research. Through different reaction conditions not only BO_3 but also BO_4 groups can be formed [1]. Thus, the structural diversity is immense and properties like second harmonic generation are accessible, especially for compounds with different anionic substructures. Further promising candidates are heteroleptic compounds with different anionic species like $Sn_3[B_3O_7]F$ [2] and $Pb_3B_6O_{11}F_2$ [3]. With the synthesis of $K_3Na[B_6O_9(OH)_3]NO_3$ [4], $Lu_2B_2O_5(NO_3)_2 \cdot 2H_2O$ [5], and $Pr[B_5O_8(OH)(H_2O)_{0.87}]NO_3 \cdot 2H_2O$ [6], we contributed

first results on the synthesis of borate nitrates. These compounds were obtained from a low acidic medium, essentially *via* hydrothermal synthesis. To avoid the implementation of water, we now investigated reactions of suitable metal precursors and borate species with fuming nitric acid (N_2O_4 in HNO_3), in which N_2O_4 will capture remaining molecules of water under formation of a HNO_3 - HNO_2 mixture.

A serendipitous result of the reaction between elemental palladium, $K_2B_4O_7 \cdot 4H_2O$, and fuming nitric acid is the formation of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$. Tetranitratopalladates are well known and comprise several compounds like α - $K_2[Pd(NO_3)_4]$ [7], which is similar to $K_2[Pt(NO_3)_4] \cdot \frac{1}{2}H_2O$ [8]. α - $K_2[Pd(NO_3)_4]$ was already published by Elding, Norén, and Oskarsson in 1986. In both compounds, the four squarely coordinated nitrate groups were found to be situated on the same side of the coordination plane (Fig. 1, left).

In the year 2000, the sodium tetranitratopalladate $Na_2[Pd(NO_3)_4]$ [9] was synthesized, and in 2005, the compounds $Rb_2[Pd(NO_3)_4]$ [10] and $Cs_2[Pd(NO_3)_4]$ [10] were discovered. All three structures consist of $[Pd(NO_3)_4]^{2-}$ anions with monodentate nitrate groups turned in pairs in one direction, just like in β - $K_2[Pd(NO_3)_4]$ [11], which was synthesized in 2009. A comparison of the complex anions in α - $K_2[Pd(NO_3)_4]$ (left) and β - $K_2[Pd(NO_3)_4]$ (right) is shown in Fig. 1. The tetranitratopalladate system has now been complemented by the synthesis of the novel compound $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ described in the following.

2 Experimental section

2.1 Synthesis

The reaction was performed in an evacuated, torch sealed borosilicate glass ampoule ($l=300$ mm, $\varnothing=16$ mm, thickness of the tube wall=1.8 mm). A mixture of 50 mg (0.47 mmol) Pd and 100 mg (0.33 mmol) $K_2B_4O_7 \cdot 4H_2O$ in 1 mL fuming nitric acid was heated up to a temperature of 353 K and kept there for 24 h. Afterwards, the ampoule was cooled with a rate of 6 K h^{-1} down to room temperature. Red platelets were obtained on the ampoule wall. The mother liquor was separated from the crystals by decantation, the

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Fig. 1: Comparison of the complex anions $[Pd(NO_3)_4]^{2-}$ in α - $K_2[Pd(NO_3)_4]$ (left) and β - $K_2[Pd(NO_3)_4]$ (right). In α - $K_2[Pd(NO_3)_4]$, the nitrate groups are coordinated on one side of the coordination plane, whereas in β - $K_2[Pd(NO_3)_4]$ the nitrate groups are turned in pairs.

acid containing side was cooled with liquid nitrogen and after cracking of the ampoule, several crystals were transferred directly into inert oil. The remaining bulk material was dried under reduced pressure in a Schlenk flask and transferred into the glovebox for further treatment. The handling was carried out strictly under inert conditions, as the compound appears to be sensitive to moisture.

2.2 X-ray structure determination

A STOE Stadi P diffractometer with curved Ge(111)-monochromatized $MoK\alpha_1$ radiation ($\lambda = 0.7093 \text{ \AA}$) was used to characterize a polycrystalline sample by X-ray powder diffraction. Diffraction intensities were measured with a Mythen2 1 K detector (Dectris, Switzerland) microstrip detector with 1280 strips.

The Rietveld refinements were accomplished with the software package DIFFRACPLUS-TOPAS® 4.2 (Bruker AXS GmbH, Karlsruhe, Germany) [12] based on single-crystal data for β - $K_2[Pd(NO_3)_4]$ [11] (collection code: 166766) and β - HBO_2 [13] (collection code: 34640) from the ICSD [14–16]. The reflection shapes were modelled using modified Thompson-Cox-Hastings pseudo-Voigt profiles [17, 18]. Instrumental contributions on reflection profiles were corrected from the refinement of a standard (LaB_6) [19]. The background was fitted with Chebyshev polynomials up to the 6th order [20].

Under a polarisation microscope, a suitable single crystal of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ with a diameter of 30 μm

was fixed on the tip of a MicroMount™ (MiTeGen, LLC, Ithaca, NY, USA) and immediately placed into a stream of cold N_2 inside the diffractometer. The intensity data was collected with a Bruker D8 Quest diffractometer (Bruker, Karlsruhe, Germany) equipped with a Photon 100 detector system and an Incoatec microfocus source generator (multi-layered optic, monochromatized $MoK\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The collection strategy, concerning the ω and φ scans, was optimized using the APEX 3 [21] program package. Thus, a complete data set up to high angles with high redundancies was received. For data processing and data reduction, the program SAINT [22] was employed. Thereafter, multi-scan absorption corrections were applied with the program SADABS [23].

In the course of the structure solution and parameter refinement with anisotropic displacement parameters for all non-hydrogen atoms with the SHELXS/L-17 [24–27] software suite, the monoclinic space group $P2_1/c$ was found to be correct. The hydrogen atom H7 was refined isotropically, while employing a bond restraint of $0.84(2) \text{ \AA}$ using the DFIX command.

Relevant details of the data collection and evaluation are listed in Table 1, the atomic coordinates and the

Table 1: Crystal data and structure refinement of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ (standard deviations in parentheses).

Empirical formula	$K_2[Pd(NO_3)_4] \cdot 2HNO_3$
Molar mass, $g\text{mol}^{-1}$	558.68
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Single-crystal diffractometer	Bruker D8 Quest Photon 100
Radiation; wavelength, $\text{\AA}$	$MoK\alpha$; $\lambda = 0.71073$
a , $\text{\AA}$	10.1715(4)
b , $\text{\AA}$	8.9294(3)
c , $\text{\AA}$	8.8055(3)
β , deg	98.13(1)
V , $\text{\AA}^3$	791.73(5)
Formula units per cell, Z	2
Calculated density, $g\text{cm}^{-3}$	2.34
Crystal size, mm^3	$0.05 \times 0.05 \times 0.05$
Temperature, K	213(2)
Absorption coefficient, mm^{-1}	1.8
$F(000)$, e	544
2θ range, deg	6.1–75.0
Range in hkl	$\pm 17, \pm 15, \pm 15$
Total no. of reflections	53342
Independent reflections/ R_{int}	4162/0.0474
Data/restraints/parameters	4162/1/138
Absorption correction	Multi-scan (Bruker SADABS 2016/2)
Final $R1/wR2$ [$I > 2\sigma(I)$]	0.0334/0.0766
Final $R1/wR2$ (all data)	0.0531/0.0820
Goodness-of-fit on F_o^2	1.061
Largest diff. peak/hole, $e\text{\AA}^{-3}$	0.98/–1.28

isotropic displacement parameters in Table 2, and the anisotropic displacement parameters in Table 3. Interatomic distances and bond angles are shown in Table 4 and the hydrogen bond data in Table 5.

Table 2: Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} ($\text{\AA}^2$) for $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ (space group $P2_1/c$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pd1	1/2	1/2	1/2	0.01676(5)
K1	0.7079(2)	0.06281(8)	0.6449(2)	0.0405(4)
K2	0.7638(9)	0.0555(7)	0.5909(9)	0.121(2)
O1	0.3180(2)	0.4251(2)	0.5267(2)	0.0277(3)
O2	0.1773(2)	0.2423(2)	0.4866(3)	0.0483(5)
O3	0.3592(2)	0.2337(2)	0.3863(2)	0.0387(4)
O4	0.5818(2)	0.3378(2)	0.6396(2)	0.0259(3)
O5	0.5786(2)	0.4923(2)	0.8317(2)	0.0358(3)
O6	0.6698(2)	0.2737(2)	0.8664(2)	0.0340(3)
O7	0.0719(2)	0.4393(3)	0.6630(3)	0.0486(5)
O8	0.9092(2)	0.2801(3)	0.6397(4)	0.0738(8)
O9	0.9018(3)	0.4768(3)	0.7782(5)	0.080(1)
N1	0.2861(2)	0.2960(2)	0.4637(2)	0.0300(3)
N2	0.6107(2)	0.3706(2)	0.7844(2)	0.0238(3)
N3	0.9519(2)	0.3945(3)	0.6972(3)	0.0461(5)
H7	0.101(4)	0.370(4)	0.609(4)	0.07(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses). All atoms are on the Wyckoff position 4e, except palladium, which is on the Wyckoff position 2b. All sites are fully occupied with the exception of K1 exhibiting a s.o.f. of 0.72 and K2 with a s.o.f. of 0.28.

Table 3: Anisotropic displacement parameters ($\text{\AA}^2$) of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ (space group $P2_1/c$) with standard deviations in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	0.02185(8)	0.01332(7)	0.01527(7)	0.00013(6)	0.00313(5)	−0.00148(7)
K1	0.0531(6)	0.0218(3)	0.0427(5)	−0.0001(3)	−0.0067(3)	−0.0011(3)
K2	0.144(5)	0.101(4)	0.128(5)	0.014(4)	0.052(5)	0.016(4)
O1	0.0274(6)	0.0202(6)	0.0371(7)	−0.0050(5)	0.0100(6)	−0.0059(5)
O2	0.0396(9)	0.0407(10)	0.0673(13)	−0.0089(9)	0.0165(9)	−0.0226(8)
O3	0.0432(9)	0.0251(7)	0.0501(10)	−0.0123(7)	0.0147(8)	−0.0072(7)
O4	0.0386(8)	0.0205(6)	0.0178(5)	0.0019(5)	0.0019(5)	0.0050(5)
O5	0.0523(10)	0.0312(7)	0.0237(6)	−0.0046(6)	0.0043(6)	0.0046(7)
O6	0.0399(8)	0.0361(8)	0.0248(7)	0.0115(6)	0.0011(6)	0.0050(7)
O7	0.0344(9)	0.0584(13)	0.0545(12)	−0.0122(11)	0.0110(8)	−0.0187(9)
O8	0.0472(13)	0.0578(14)	0.119(2)	−0.0187(15)	0.0217(14)	−0.0255(11)
O9	0.0636(17)	0.0754(19)	0.110(3)	−0.0270(17)	0.0451(18)	−0.0115(14)
N1	0.0324(9)	0.0213(7)	0.0366(9)	−0.0013(6)	0.0060(7)	−0.0074(6)
N2	0.0267(7)	0.0261(7)	0.0191(6)	0.0035(5)	0.0053(5)	0.0002(6)
N3	0.0294(10)	0.0487(13)	0.0607(15)	0.0020(11)	0.0078(10)	−0.0076(9)

Table 4: Selected interatomic distances ($\text{\AA}$) and selected bond angles (deg) in $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ (standard deviations in parentheses).

Atoms	Distance	Atoms	Bond angle
Pd1–O4	2.003(2)	O4–Pd–O1	89.83(6)
Pd1–O4 ^a	2.003(2)	O4–Pd–O1	90.17(6)
Pd1–O1	2.013(2)		∅ = 90
Pd1–O1 ^a	2.013(2)		
	∅ = 2.01		
N2–O4	1.301(2)	O3–N1–O2	122.8(2)
N2–O5	1.225(2)	O3–N1–O1	120.7(2)
N2–O6	1.228(2)	O2–N1–O1	116.5(2)
	∅ = 1.25		∅ = 120
N1–O1	1.301(2)	O5–N2–O6	123.9(2)
N1–O2	1.247(2)	O5–N2–O4	119.9(2)
N1–O3	1.213(3)	O6–N2–O4	116.2(2)
	∅ = 1.25		∅ = 120
N3–O7	1.358(3)	O9–N3–O8	128.5(3)
N3–O8	1.194(3)	O9–N3–O7	115.3(3)
N3–O9	1.188(4)	O8–N3–O7	116.2(3)
	∅ = 1.25		∅ = 120

^aSymmetry operation: 1 – *x*, 1 – *y*, 1 – *z*.

Table 5: The hydrogen bond paramters ($\text{\AA}$, deg) in $K_2[Pd(NO_3)_4] \cdot 2HNO_3$.

H Bond	D–H	H...A	D...A	D–H...A
O7–H7...O2	0.86(4)	1.82(4)	2.670(4)	1.72(4)

CCDC 1897204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

3.1 Crystal structure

According to the single-crystal diffraction data, $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with the cell parameters $a = 10.1715(4)$, $b = 8.9294(3)$, $c = 8.8055(3)$ Å, and $\beta = 98.13(1)^\circ$. The $[Pd(NO_3)_4]^{2-}$ anion consists of a central palladium atom, which is coordinated monodentately in a square planar fashion by four NO_3 groups, as is depicted in Fig. 2 (left) in comparison to the similar $[Pd(NO_3)_4]^{2-}$ anion found in β - $K_2[Pd(NO_3)_4]$ (right). The mean Pd–O bond length in $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ is 2.01 Å and, as the palladium atom is situated on a centre of inversion, only two crystallographically independent nitrate groups are distinguishable. The deviation of the O–Pd–O angle from the theoretical value for a perfect square planar coordination is 0.17° . The nitrate groups are nearly planar, deviating only $0.2(2)^\circ$ for the nitrate group of N1 and $0.3(2)^\circ$ for the nitrate group of N2 from planarity. The terminal N–O distances with 1.213(3) to 1.247(2) Å are noticeably shorter than the palladium coordinating O–N distances possessing values of 1.301(2) Å each. The O–N–O bond angles vary from $116.2(2)$ to $123.9(2)^\circ$ and are in good accordance with the theoretical value of 120° for a trigonal planar structure.

Each $[Pd(NO_3)_4]^{2-}$ anion is surrounded by eight potassium cations with Pd $\cdots$ K distances of 4.053(2) to 5.800(1) Å, which is in good agreement with Pd $\cdots$ K distances of 4.3905(4) to 5.5658(4) Å found for β - $K_2[Pd(NO_3)_4]$ [11]. The two crystallographically different potassium sites are not fully occupied. The K1 position reveals a site occupancy factor (s.o.f.) of 0.72 and the K2 site a s.o.f. of 0.28. The

initial results were obtained by refining the potassium positions with a free variable. Determining the same positions freely results in similar values of K1 s.o.f. 0.70 and K2 s.o.f. 0.15. The potassium cation K1 is surrounded by ten oxygen atoms, with K–O distances ranging from 2.738(2) to 3.242(2) Å. The potassium cation K2 is surrounded by nine oxygen atoms, with K–O distances ranging from 2.493(8) to 3.354(9) Å. Both potassium sites are depicted in Fig. 3. The potassium cations are surrounded by NO_3^- anions and HNO_3 molecules. The distance between the two potassium sites is 0.794(9) Å.

The $[Pd(NO_3)_4]^{2-}$ anion is surrounded by four HNO_3 molecules. The array allows for hydrogen bonds between hydrogen atoms H7 and the oxygen atoms O2 with an H7 $\cdots$ O2 distance of 1.82(4) Å and an O7–H7 $\cdots$ O2 bond angle of $172(4)^\circ$ (see Fig. 4 and for crystallographic details Table 5). The hydrogen atom was fixed at a bond length of 0.84(2) Å to the oxygen atom O7 using the DFIX command. The HNO_3 molecule is nearly planar with a O9–O8–O7–H7 torsion angle of $4(3)^\circ$ and exhibits two shorter and one longer N–O distances with 1.188(4), 1.194(3), and 1.358(3) Å, respectively. The hydrogen atom is bonded to the oxygen atom belonging to the elongated N–O bond. The O–N–O bond angles comprise two smaller and one larger angle with $115.3(3)$, $116.2(3)$, and $128.5(3)^\circ$.

The general packing motif for the complex anion is determined by two alternating orientations for the square-planar complex anion with a change of $74.73(4)^\circ$, as is shown in Fig. 5. $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ can be regarded as a HNO_3 intercalation variant of β - $K_2[Pd(NO_3)_4]$. The $[Pd(NO_3)_4]^{2-}$ anion in β - $K_2[Pd(NO_3)_4]$ is surrounded by potassium cations and further complex anions. In $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ on the other hand, the complex

Fig. 2: The $[Pd(NO_3)_4]^{2-}$ anion in $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ (left) is built up from a central palladium atom, which is coordinated in a monodentate fashion by four NO_3^- anions. It is very similar to the anion in β - $K_2[Pd(NO_3)_4]$ (right).

Fig. 3: Each potassium site is surrounded by NO_3^- anions. Left: The K1 site is surrounded by six NO_3^- anions and one HNO_3 molecule. Right: The K2 site is surrounded by four NO_3^- anions and two HNO_3 molecules.

Fig. 4: The moderately strong hydrogen bond $O7-H7 \cdots O2$ is shown as a fragmented line [28].

anion is surrounded by disordered potassium cations and HNO_3 molecules along the a axis. Both compounds are very similar with the main difference being the intercalation of HNO_3 groups.

3.2 Powder diffraction data

In a glovebox, the bulk material was ground to a powder in an agate mortar and transferred to a glass capillary ($\varnothing = 0.3$ mm). Figure 6 shows the experimentally obtained powder diffraction data (black; top) in comparison to the data simulated from the single-crystal diffraction data (red; bottom). It is obvious that the diffraction patterns do not match. Upon further

Fig. 5: Left: $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ featuring layers along the bc plane and stacks along the a axis. It can be regarded as a HNO_3 intercalation variant of β - $K_2[Pd(NO_3)_4]$ (right). The different potassium sites are shown in purple. The less occupied K2 site is emphasized in form of transparent spheres.

Fig. 6: Observed powder pattern (MoK α_1 radiation, $\lambda = 0.7093 \text{ \AA}$) (top), compared to the theoretical powder pattern of $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ calculated from the single-crystal data (bottom).

Fig. 7: Rietveld refinement of the powder X-ray diffraction data. The observed powder pattern can be attributed to $\beta\text{-K}_2[Pd(NO_3)_4]$ and $\beta\text{-HBO}_2$.

investigation it became clear that the sample already decomposed, probably caused by vacuum treatment, which was necessary for the transfer into the glovebox. The powder pattern can be identified as a mixture of $\beta\text{-K}_2[Pd(NO_3)_4]$ and $\beta\text{-HBO}_2$ [13], which formed as a side product of the reaction. The Rietveld refinement of the decomposition products is shown in Fig. 7. The experimental data are shown in black, the best fit profile in red, and the difference curve in blue.

4 Conclusion

A new potassium tetranitratopalladate with the composition $K_2[Pd(NO_3)_4] \cdot 2HNO_3$ was synthesized *via* solvothermal synthesis in a torch-sealed glass ampoule. The structure is composed of $[Pd(NO_3)_4]^{2-}$ anions and potassium cations, similar to $\beta\text{-K}_2[Pd(NO_3)_4]$. However, HNO_3 molecules reside between the layer-like arrangement of $[Pd(NO_3)_4]^{2-}$ anions and potassium cations along the *bc* plane.

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