Pd^{4+} Complexes

International Edition: DOI: 10.1002/anie.201601767
German Edition: DOI: 10.1002/ange.201601767

Palladium(IV) in an Oxoanionic Environment: The XeF_2 Assisted Synthesis of $[Pd(S_2O_7)_3]^{2-}$

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Abstract: *For the first time tetravalent palladium is detected, coordinated exclusively by simple oxoanions. Stabilization was achieved by formation of the $[Pd(S_2O_7)_3]^{2-}$ complex in which three chelating disulfate groups surround the metal atom. The salt $K_2[Pd(S_2O_7)_3]$ could only be obtained if the reaction of $K_2[PdCl_6]$ and neat SO_3 was performed in the presence of XeF_2.*

It is undergraduate knowledge that the chemistry of palladium is strongly stamped by the oxidation sate +II. Higher oxidation states, especially +IV are accessible only under oxidizing conditions, and the formation of PdF_4 from palladium and elemental fluorine is an illustrative example.[1,2] Further stabilization of Pd^{IV} is achieved by formation of $[PdF_6]^{2-}$ complexes which exist for many counter cations.[3] A limited number of such complex anions is also known for other halides, and the palladates $A_2[PdX_6]$ (A = alkaline metal; X = Cl, Br, I) are stable compounds, even if the binary halides PdX_4 (X = Cl, Br, I) cannot be obtained.[4] Oxygen should also be a suitable oxidant for the preparation of tetravalent palladium compounds and, indeed, a number of complex oxides are known which have been obtained in most cases from high-pressure reactions.[5] Interestingly, according to recent investigations the binary oxide PdO_2, which was reported to be accessible at high oxygen pressure with a rutile type of structure,[6] is not stable under ambient conditions.[7] Two further remarkable examples showing Pd^{4+} ions in octahedral coordination environment of oxygen atoms are the highly charged complexes $[Pd_2(TeO_6)_2(HTeO_6)_2]^{14-}$ and $[Pd_2(IO_6)_2(HIO_6)_2]^{10-}$.[8] In both anions the palladium atoms are part of a framework consisting of six edge-connected octahedra. Therefore, tetravalent palladium in an environment of oxygen atoms is a quite rare phenomenon.

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201601767.

Thus, it is not surprising that the oxoanionic palladium compounds known so far are divalent.[9] Our group has conducted a lot of work on noble-metal compounds containing oxoanions but in case of palladium we were, up to now, also only able to prepare Pd^{II} compounds, even if strong oxidizers, such as N_2O_5, SO_3, and H_2SeO_4 were used in the reactions.[10] It is worth mentioning that also the divalent palladium compounds display fascinating structures and the disulfates $Pd[S_2O_7]$ and $Pd[HS_2O_7]_2$ which exhibit octahedral Pd^{II} coordination environments and ferromagnetic ordering are striking examples.[11] For the heavier palladium congener platinum the situation is completely different and no Pt^{II} species are known to date. Instead, reactions with H_2SO_4 and SO_3, respectively, led most often to Pt^{III} sulfates which are structurally typified by the presence of metal–metal-bonded $[Pt_2]$ dumbbells.[12] Under special conditions we were also able to prepare tetravalent platinum compounds, for example, the complex nitrate $(NO)_2[Pt(NO_3)_6]$ from reactions with N_2O_5 and the *tris*-disulfatoplatinate anion $[Pt(S_2O_7)_3]^{2-}$ which forms in SO_3-rich oleum.[13] In the structure of the $[Pt(S_2O_7)_3]^{2-}$ anion the platinum atom is octahedrally coordinated by three chelating $S_2O_7^{2-}$ groups. This structural motif seems to be highly favorable for the stabilization of tetravalent metals, because we have previously found $[M(S_2O_7)_3]^{2-}$ type complexes for the metals (M) germanium, tin, titanium, and even for silicon, representing a rarely seen example of octahedral Si^{IV} coordination with inorganic oxo-ligands.[14] With respect to these findings we argued that this type of complex should also be a suitable candidate for the stabilization of tetravalent palladium. According to our previous findings oxidation of elemental palladium or Pd^{II} by SO_3 cannot be expected. Thus, we chose $K_2[PdCl_6]$ as a starting material to provide the metal already in its tetravalent state, and a reaction according to $K_2[PdCl_6] + 9\,SO_3 \rightarrow K_2[Pd(S_2O_7)_3] + 3\,Cl_2 + 3\,SO_2$ should occur. Surprisingly, this reaction did not lead to the desired Pd^{IV} complex but reduction to divalent palladium was observed yielding the unique palladate $K_2[Pd(S_4O_{13})_2]$.[15] Because the variation of the reaction temperature did not improve the situation we decided to add XeF_2 to the reaction mixture to strengthen the oxidizing conditions during synthesis. Indeed this procedure was very successful and led nearly quantitatively to the desired compound, $K_2[Pd(S_2O_7)_3]$. This compound is one of the few examples of Pd^{IV} coordinated to oxygen atoms, and it is the first observation of tetravalent palladium in a simple oxoanionic salt.

$K_2[Pd(S_2O_7)_3]$ is obtained in the form of red-orange single crystals (Figure S1, see the Supporting Information). The reaction was carried out in evacuated, torch-sealed glass ampoules in a tube furnace with a maximum temperature of 120 °C and slow cooling (see Experimental Section). It is an

interesting question how the presence of XeF_2 suppresses the reduction of Pd^{IV}. It might be possible that XeF_2 reacts in a first step with SO_3 yielding bis(fluorosulfuryl)peroxide ($XeF_2 + 2SO_3 \rightarrow Xe + S_2O_6F_2$). The formation of this compound from elemental fluorine and SO_3 is well known and its capability for the synthesis of oxoanionic noble-metal compounds has been reported.[16] However, further investigations are needed for the elucidation of the reaction mechanism. The crystal structure of $K_2[Pd(S_2O_7)_3]$ is triclinic and shows inversion symmetry (space group $P\bar{1}$). That means that the compound is racemic because the octahedral coordination of a metal atom by three chelating ligands could lead to two enantiomorphs with Δ- and Λ-configuration. In all of the $[M(S_2O_7)_3]^{2-}$ type complexes we have described so far this racemic crystallization is observed. In $K_2[Pd(S_2O_7)_3]$ two crystallographically different $[Pd(S_2O_7]_3]^{2-}$ anions are found which are, however, almost identical (see Figure S2). One of the complexes is depicted in Figure 1 and shows the chelating attachment of the three $S_2O_7^{2-}$ groups to the Pd^{4+} ion. In both $[Pd(S_2O_7)_3]^{2-}$ complexes the Pd–O distances in the $[PdO_6]$ octahedra are found quite uniformly at 197 pm and also the angles O-Pd-O deviate only slightly from the ideal value of 90°. Within the $S_2O_7^{2-}$ anions the S–O distances for the terminal oxygen atoms are found at about 142 pm while the Pd^{4+} coordinated oxygen atoms show longer S–O distances ranging from 150.7(1) to 152.0(1) pm. The S–O bond lengths within the S-O-S bridges are longer with values between 162.5(1) and 164.4(1) pm. In the platinum complex $[Pt(S_2O_7)_3]^{2-}$ the bond lengths Pt–O are on average longer by about 1 pm compared to the findings for the palladium compound. Charge compensation for the $[Pd(S_2O_7)_3]^{2-}$ complexes is achieved by four crystallographically different K^+ ions which show coordination numbers between eight and ten if distances up to 350 pm are taken into account (Figure 2).

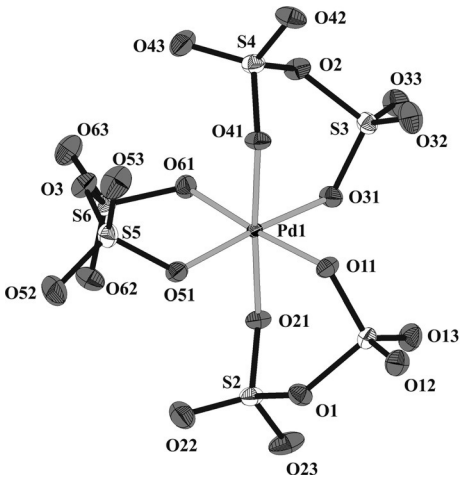

Figure 1. Structure and atom labelling of one of the two crystallographically independent $[Pd(S_2O_7)_3]^{2-}$ anions in $K_2[Pd(S_2O_7)_3]$ (the second one is almost identical, see Supporting Information). The thermal ellipsoids are set at 75% probability. Selected bond lengths in pm; *in italics*: calculated values based on a PBE0 functional using a cc-pVTZ basis for S and O and a cc-pVTZ-PP basis set for Pd. (full data are given in the supplement): Pd1-O11: 198.66(13)/*197.88*, Pd1-O21: 198.17(13)/*199.14*, Pd1-O31: 196.31(13)/*199.12*, Pd1-O41: 197.77(13)/*197.87*, Pd1-O51: 197.86(13)/*199.17*, Pd1-O61: 197.58(13)/*197.85*, S1-O11: 151.60(14)/*153.97*, S1-O12: 142.44(14)/*142.96*, S1-O13: 141.96-(14)/*143.52*, S1-O1: 163.00(14)/*163.97*, S2-O1: 164.31(14)/*165.21*, S2-O21: 151.64(14)/*153.30*, S2-O22: 141.29(16)/*143.60*, S2-O23: 142.34-(15)/*143.05*, S3-O31: 151.81(14)/*153.28*, S3-O32: 142.07(15)/*143.05*, S3-O33: 141.81(14)/*143.60*, S3-O2: 163.85(14)/*165.20*, S4-O2: 162.67-(13)/*163.96*, S4-O41: 152.01(14)/*153.96*, S4-O42: 141.74(15)/*143.52*, S4-O43: 142.96(15)/*142.95*, S5-O51: 150.72(14)/*153.28*, S5-O52: 142.92(16)/*143.05*, S5-O53: 141.72(15)/*143.60*, S5-O3: 163.33(14)/*165.21*, S6-O3: 163.24(14)/*163.95*, S6-O61: 151.89(14)/*153.97*, S6-O62: 141.80(15)/*142.95*, S6-O63: 141.68(15)/*143.52*.

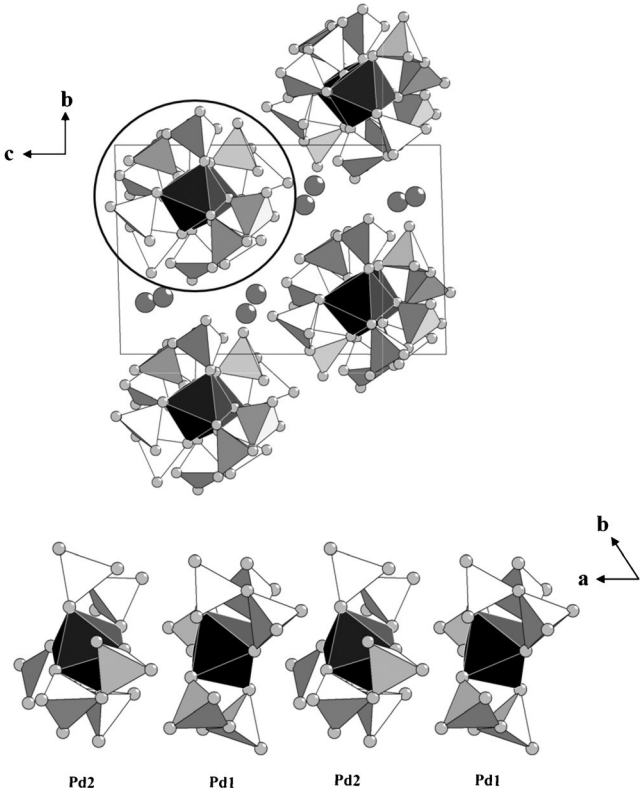

Figure 2. Crystal structure of $K_2[Pd(S_2O_7)_3]$ viewed along the [100] direction (top). In this direction the $[Pd(S_2O_7)_3]^{2-}$ complexes of Pd1 and Pd2 are stacked alternatingly. The stacking sequence is emphasized in the bottom panel.

The bonding parameters for the $[Pd(S_2O_7)_3]^{2-}$ anion are well reproduced by quantum chemical calculations on the PBE0 level using a cc-pVTZ basis for S and O and a cc-pVTZ-PP basis set for Pd, respectively (see legend of Figure 1).[17] From these calculations the Mulliken charge of the central palladium atom is found to be +0.67. Even if this value should not be misinterpreted as an absolute charge it is interesting to compare it with charges calculated for the other known $[M(S_2O_7)_3]^{2-}$ type complexes (see Table S6). These decrease within the sequence Sn (+1.28) > Ge (+0.97) > Si (+0.87) > Ti (+0.79) > Pt (+0.57), indicating increasing covalency in the M–O bonds of the $[MO_6]$ octahedra. The Mulliken charge for the palladium atom in $[Pd(S_2O_7)_3]^{2-}$ fits quite well between titanium and platinum into this row. From the quantum chemical calculations also the expected vibrational frequencies could be extracted so that an assignment of

the bands observed in both IR and Raman spectrum were possible (Figure S4, Table S9). As previously discussed for other $[M(S_2O_7)_3]^{2-}$ type complexes most of the normal modes are complex combination vibrations.[13,14]

The thermal decomposition of $K_2[Pd(S_2O_7)_3]$ is a three-step process (Figure S5, Table S10) and leads finally to a mixture of K_2SO_4 and elemental palladium. Note that the last step of the degradation can be clearly attributed to the decomposition of PdO.[10] Thus, this oxide forms as an intermediate, in line with the observation that PdO_2 is not a stable compound.[7]

Experimental Section

Caution: Oleum and SO_3 are strong oxidizers which need careful handling. During and even after the reaction the ampoule might be under remarkable pressure. It is mandatory to cool down the ampoule with liquid nitrogen prior to opening.

Synthesis of $K_2[Pd(S_2O_7)_3]$: K_2PdCl_6 (48 mg, 0.12 mmol; obtained according to Ref. [18]), was dried under reduced pressure in a desiccator over Sicapent for one week. Additionally, the dried K_2PdCl_6 was transferred to a glovebox and loaded into a thick-walled glass ampoule ($l = 250$ mm, $\phi = 20$ mm, thickness of the tube wall = 2 mm). XeF_2 (62 mg, 0.37 mmol; 99.5 %, abcr, Karlsruhe, Germany) were added. For the generation of SO_3, a 1000 mL three-necked flask was filled with P_4O_{10} (30 g; 97 %, Merck, Darmstadt, Germany) and a dropping funnel filled with oleum (30 mL; 65 % SO_3, puriss, Merck, Darmstadt, Germany) was connected. By heating to 150 °C, SO_3 was driven off and condensed into the ampoules by cooling the ampoules with liquid nitrogen. The ampoule was torch sealed, placed into a tube furnace and heated up to 120 °C. The temperature was maintained for two days and finally reduced to 25 °C over 100 hours. A large number of red-orange crystals were obtained, and the yield was almost quantitative with respect to the initial palladium compound. The obtained crystals are extremely moisture sensitive; therefore the crystals have to be handled under strictly inert conditions.

X-ray Crystallography: Some single crystals were transferred into inert oil (AB128333, ABCR, Karlsruhe, Germany). Under a cooling nitrogen stream a suitable crystal was mounted onto a glass needle ($\varnothing = 0.1$ mm) and immediately placed into a stream of cold N_2 (−173 °C) inside the diffractometer (κ-APEX II, Bruker, Karlsruhe, Germany). After unit cell determination, the reflection intensities were collected. $K_2[Pd(S_2O_7)_3]$: needle ($0.142 \times 0.088 \times 0.073$ mm), triclinic, $P\bar{1}$ (no. 2), $Z = 4$, $a = 1125.65(3)$ pm, $b = 1126.16(3)$ pm, $c = 1629.68(5)$ pm, $\alpha = 79.300(1)°$, $\beta = 70.177(1)°$, $\gamma = 61.402(1)°$, $V = 1705.67(9)$ Å^3, $\rho = 2.776$ g cm^{-3}, $2\theta_{max.} = 72.636°$, $\lambda(Mo_{K\alpha}) = 71.073$ pm, $T = 100$ K, 87474 reflections, 16512 unique reflections ($R_{int.} = 0.0406$, $R_\sigma = 0.0317$), numerical absorption correction ($\mu = 24.24$ cm^{-1}, min./max. transmission = 0.725/0.843, program SADABS-2012/1: Bruker, Madison, Wisconsin 2001), structure solution by direct methods, full-matrix-least-square refinement (541 parameters) on $|F^2|$, SHELX program),[19] $R1 = 0.0287$, $wR2 = 0.0608$ for 13744 reflections with $I > 2\sigma(I)$ and $R1 = 0.0399$, $wR2 = 0.0649$ for all 87474 reflections, max./min. residual electron density = 1.66/−1.04 e$^-$ Å^{-3}. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-429425.

Thermal analysis: The investigation of the thermal behavior was performed using a TGA/SDTA device (TGA/SDTA851e, Mettler-Toledo GmbH, Schwerzenbach, Switzerland). In a flow of dry nitrogen, about 15 mg of $K_2[Pd(S_2O_7)_3]$ was placed in a corundum crucible and heated at a rate of 10 K min^{-1} up to 1000 °C. The characteristic points were extracted from the DTG curve.

X-ray powder diffraction: The residual product of the thermal decomposition of $K_2[Pd(S_2O_7)_3]$ was investigated by X-ray powder diffraction using a flat sample holder with the help of the powder diffractometer STOE STADIP using $Cu_{K\alpha}$ radiation ($\lambda = 154.06$ pm). The obtained pattern was compared to simulations for elemental Pd and K_2SO_4.[20,21]

Raman spectroscopy: The Raman spectrum of $K_2[Pd(S_2O_7)_3]$ was measured (spectrometer FRA106, Bruker, Karlsruhe, Germany) on a number of selected crystals in a small glass tube. Important Raman intensities in cm^{-1} (exptl./*calcd*): 1408/*1420*, 1398/*1404*, 1377/*1397*, 1241/*1256*, 1212/*1216*, 1200, 1181, 1021/*1011*, 658/*667*, 610/*636*, 590/*583*, 576/*578*, 544/*543*, 447, 369, 361 338/*345*, 270, 260/*257*, 218, 188, 152/*148*. For a details see Figure S4 and Table S9.

IR spectroscopy: Owing to its sensitivity a sample of $K_2[Pd(S_2O_7)_3]$ was mounted in a glove box to the sample holder of a FTIR spectrometer (PlatinumATR, Tensor 27, Bruker) and immediately measured. Important IR intensities in cm^{-1} (exptl./*calcd*): 1439/*1427*, 1397/*1419*, 1363/*1397*, 1232/*1229*, 1211/*1216*, 1183/*1208*, 1060, 1015, 971/*972*, 908/*916*, 795/*773*, 756, 730/*727*, 659/*667*, 627/*636*, 575/*556*. For a details see Figure S4 and Table S9.

Method of calculation: Throughout the study the Gaussian09 program package was used.[22] A full geometry optimization of the $[Pd(S_2O_7)_3]^{2-}$ complex was performed using the PBE0 functional for exchange and correlation within density functional theory using a cc-pVTZ basis for S and O and a cc-pVTZ-PP basis set for Pd, respectively.[23] Using the optimized structure, infrared and Raman spectra were calculated.

Acknowledgments

Financial support of the Deutsche Forschungsgemeinschaft, and the Stiftung der Metallindustrie im Nord-Westen is gratefully acknowledged. We thank Dr. Marc Schmidtmann (University of Oldenburg) for the collection of the X-ray data. Furthermore we thank Regina Stötzel and Prof. Claudia Wickleder (both University of Siegen) for measuring the Raman spectrum. We are also grateful to Dr. Wolfgang Herrendorf (University of Giessen) for helpful discussions.

Keywords: density functional theory · disulfate · palladium · structure elucidation · vibrational spectroscopy

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 8121–8124
Angew. Chem. **2016**, *128*, 8253–8256

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Received: February 19, 2016
Published online: May 30, 2016

