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Polysulfate Ligands

Bis(tetrasulfato)palladate, $[Pd(S_4O_{13})_2]^{2-}$**

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The technical process of sulfuric acid production involves disulfuric acid, $H_2S_2O_7$, as an important intermediate. This acid is the condensation product of two molecules of H_2SO_4 and its structure has been determined, surprisingly late, only in 1991.[1] Although it is well established that further condensation is possible leading to polysulfuric acids of the general formula $H(SO_3)_nOH$, none of these acids has been properly characterized to date. The situation is only slightly better for the respective salts of polysulfuric acids. Our knowledge is basically restricted to disulfates which are best known for alkaline metals, some divalent metals, for example, cadmium, and selected main-group metals.[2] Concerning higher polysulfates, there were until recently only two reports, one on the trisulfate $(NO_2)_2[S_3O_{10}]$,[3] and one on the pentasulfate $K_2S_5O_{16}$.[4] As scrutiny of this fundamental class of compounds seemed to be mandatory we recently started a research program aiming at the preparation of polysulfates. It turned out that reactions with oleum containing variable amounts of SO_3 provide the best route for the preparation of disulfates, especially if they are carried out under harsh conditions, that is, at temperatures up to 250 °C in sealed glass ampoules. Following this route we have prepared a large number of unprecedented compounds, for example, the bis(disulfato)aurate $[Au(S_2O_7)_2]^{2-}$, the tris- and tetrakis(disulfato)silicates $[Si(S_2O_7)_3]^{2-}$ and $[Si(S_2O_7)_4]^{4-}$ in which the silicon has octahedral coordination,[5,6] and the palladium disulfate $Pd(S_2O_7)$ in which the octahedral Pd^{2+} coordination leads to the first example of a ferromagnetically ordering palladium(II) compound.[7] Nevertheless it must be stated that disulfates are the predominant phases from these type of reactions, and up to now we could obtain only one trisulfate, namely $Pb(S_3O_{10})$, from the reaction of $(NH_4)_2[PbCl_6]$ with SO_3-rich (65 %) oleum.[8] Aiming at the preparation of higher polysulfates we switched to neat SO_3 as reaction medium and could recently report on the elusive tetrasulfate anion, stabilized in the nitrylium salt $(NO_2)_2[S_4O_{13}]$.[9] As an important feature of the tetrasulfate anion, it has been found that there is a significant bond-length alteration within the S-O-S bridges of the anion, and in particular the respective distances for the terminal $\{SO_4\}$ tetrahedra are strongly affected (Table 1, right column). This finding is perfectly reproduced by theoretical investigations which furthermore predict an increase of the bond-lengths alterations with an increasing chain length of the anions. Energetically, the longer bond lengths cause a severe destabilization of the larger polyanions and even decomposition, for the reaction $[S_nO_{3n+1}]^{2-} \rightarrow [S_{n-1}O_{3n-2}]^{2-} + SO_3$ the value for ΔG is already positive for $n > 10$,[9] and even for $n > 6$ if the calculations take solvation effects into account.[10] Thus, the preparation of higher polysulfates will be an especially challenging task. One of our strategies, with respect to polysulfate stabilization, is to embed them into well-defined metal complexes.

Table 1: Bond lengths [pm] in the $(S_4O_{13})^{2-}$ groups in $K_2[Pd(S_4O_{13})_2]$ and $(NO_2)_2[S_4O_{13}]$. Entries in gray emphasize the bond length alterations within the S-O-S bridges.

	$K_2[Pd(S_4O_{13})_2]$	$(NO_2)_2[S_4O_{13}]$[a]
S1-O11	147.9[b]	142.0
S1-O12	141.6	142.3
S1-O13	142.2	141.6
S1-O121	170.4	176.6
	}14.2	}23.6
S2-O121	156.2	153.0
S2-O23	140.9	141.4
S2-O22	141.1	141.1
S2-O231	162.5	163.9
	}0.8	}3.0
S3-O231	161.7	160.9
S3-O32	140.7	141.3
S3-O33	141.3	142.0
S3-O341	156.0	153.4
	}15.9	}23.6
S4-O341	171.9	177.0
S4-O43	142.0	142.1
S4-O42	142.2	143.1
S4-O43	147.4[b]	143.1

[a] Average values for the four crystallographically different $(S_4O_{13})^{2-}$ groups in $(NO_2)_2[S_4O_{13}]$. [b] Oxygen atoms coordinated to Pd^{2+}.

For the first time, we were able to synthesize a complex containing polysulfate anions as ligands, namely the bis(tetrasulfato)palladate $[Pd(S_4O_{13})_2]^{2-}$. The compound has been obtained in form of its potassium salt, $K_2[Pd(S_4O_{13})_2]$, and allows the comparison of the bonded tetrasulfate anion with its "undisturbed" variant in $(NO_2)_2[S_4O_{13}]$. $K_2[Pd(S_4O_{13})_2]$ is synthesized quantitatively, by the reaction of the chloropalla-

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Supporting information for this article (measurement and refinement procedure, atom coordinates, bond lengths and angles, anisotropic displacement parameters, results of the DFT calculations, experimental and calculated IR and Raman vibration energies, and a photograph of $K_2[Pd(S_4O_{13})_2]$ crystals) is available on the WWW under http://dx.doi.org/10.1002/anie.201209346.

date $K_2[PdCl_4]$ with SO_3 at 120 °C in sealed glass tubes within 8 days, in form of very moisture sensitive yellow plate-shaped crystals (Figure S1 in the Supporting Information). The charge balance is achieved by K^+ ions. According to X-ray powder diffraction measurements (see the Experimental Section) $K_2[Pd(S_4O_{13})_2]$ is formed as the single phase. In the $[Pd(S_4O_{13})_2]^{2-}$ complex, the Pd^{2+} ion is coordinated by two symmetry-equivalent chelating $S_4O_{13}{}^{2-}$ groups which are bonded by the terminal tetrahedra of the polysulfate chain to the metal (Figure 1). The distances Pd–O in the resulting square-planar $\{PdO_4\}$ moiety are found at typical values of about 201 pm and also the angles O-Pd-O are only slightly influenced by the coordination mode with values of 87.9° and 92.1°. Within the $S_4O_{13}{}^{2-}$ groups the distances S–O for the terminal oxygen atoms (O12, O13, O22, O23, O32, O33, O42, O43) are found quite uniformly in the range from 140 to 142 pm while the oxygen atoms coordinated to Pd^{2+} show longer S–O bonds of 147.9 (O11) and 147.4 pm (O41). Remarkable differences between the S–O distances occur within the S-O-S bridges (Figure 1). The respective bridges to the terminal tetrahedra of the anion show values of 170.4, 156.2, and 171.9, 156 pm, while the inner bridge (S3-O231-S3) is almost symmetric, with bond lengths of about 162 pm. All of the observed distances within the complex $[Pd(S_4O_{13})_2]^{2-}$ ion are well reproduced by theoretical calculations using density functional theory (PBE0 level; cf. caption of Figure 1), although the theoretical values are slightly larger as it is frequently observed for calculations performed on negatively charged species. These calculations allowed also for a detailed assignment of the observed vibrational energies in the Raman und IR spectra (see Experimental Section and Supporting Information). In the crystal structure of $K_2[Pd(S_4O_{13})_2]$, the $[Pd(S_4O_{13})_2]^{2-}$ complexes are separated by K^+ ions which are in ninefold coordinated by oxygen atoms (Figure 2).

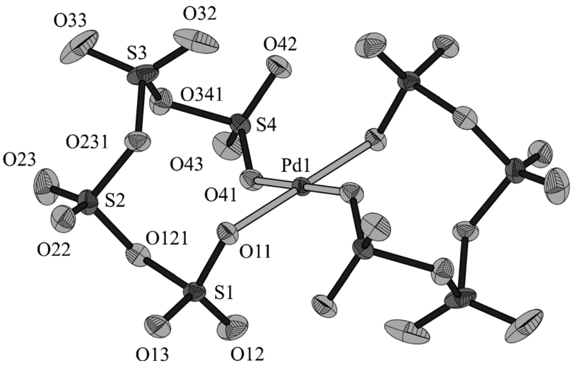

Figure 1. Structure and atom labeling of the $[Pd(S_4O_{13})]^{2-}$ anion in $K_2[Pd(S_4O_{13})]$. Both tetrasulfate groups are related by inversion symmetry at the Pd atom site. The thermal ellipsoids are set at 75 % probability . Selected bond lengths [pm] and angles [°] (calculated values for the $[Pd(S_4O_{13})]^{2-}$ ion in italics): Pd-O11 200.37(6)/*201.46*, Pd-O41 201.20(6)/*201.59*, S1-O11 147.67(7)/*149.59*, S1-O12 141.56(7)/*142.99*, S1-O13 142.04(7)/*142.99*, S1-O121 170.64(7)/*176.56*, S2-O121 156.16(7)/*156.03*, S2-O22 141.11(7)/*142.82*, S2-O23 140.63(8)/*142.68*, S2-O231 162.19(7)/*163.92*, S3-O231 161.15(7)/*163.79* S3-O32 140.61(10)/*142.50*, S3-O33 141.14(9)/*142.86*, S3-O341 155.86(7)/156.18, S4-O341 172.52(7)/*176.72*, S4-O42 141.77(7)/*143.08*, S4-O43 141.64(7)/*143.02*, S4-O41 147.34(7)/*149.05*; S1-O121-S2 122.65(4)/*126.88*, S2-O231-S3 125.85(5)/*126.96*, S3-O341-S4 122.82(4)/*128.17*. (Note: The theoretical calculations are performed without symmetry restrictions, that is, they give two values for each length and angle listed above. However, these are essentially identical in each case; the Supporting Information gives the full list).

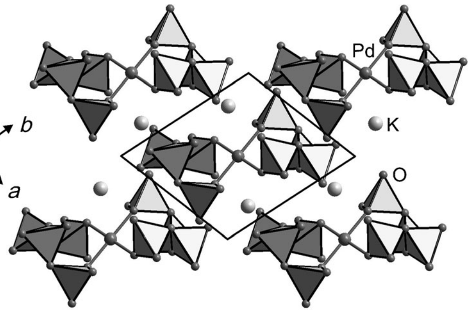

Figure 2. Crystal structure of $K_2[Pd(S_4O_{13})_2]$ viewed along the [001] direction.

The characterization of the bis(tetrasulfato)palladate anion $[Pd(S_4O_{13})_2]^{2-}$ allows the comparison of the structural parameters of the essentially undisturbed $S_4O_{13}{}^{2-}$ ions in $(NO_2)_2(S_4O_{13})$ and the coordinated analogues in $K_2[Pd(S_4O_{13})_2]$. The most interesting difference is the significantly decreasing asymmetry of the terminal S-O-S bridges in the palladium complex. While for the undisturbed $S_4O_{13}{}^{2-}$ ion in the nitrylium tetrasulfate the difference in the respective S–O bond lengths was found to be 23.6 pm this value decreases to 14.2 and 15.9 pm in the palladate (Table 1). We interpret this finding as a stabilization of the anion by formation of the complex, suggesting that the formation of complexes may in general be a suitable way to stabilize polysulfate anions, even for larger chain lengths. Both the preparation of large polysulfates and the investigation of the coordination chemistry of polysulfates are currently the focus of our research.

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 by liquid nitrogen prior to opening.

$K_2[Pd(S_4O_{13})_2]$: K_2PdCl_4 (0.055 g, obtained according to Ref. [11]), was loaded into a thick-walled glass ampoule (l = 250 mm, Ø = 20 mm, thickness of the tube wall = 2 mm). 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. While dropping the oleum onto the P_4O_{10}, the flask was heated to 150 °C and the SO_3 so produced was condensed into the liquid-nitrogen cooled ampoule connected to the third neck of the flask. 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 a period of 150 h. A large number of yellow crystals were obtained, and the yield was quantitative with respect to the initial palladium compound. The tetrasulfate crystals are extremely moisture sensitive, therefore the crystals have to be handled under strictly inert conditions.

X-ray Crystallography: In a glove box 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 (Ø = 0.1 mm) and immediately placed into a stream of cold N_2 ($-120\,^{\circ}C$) inside the diffractometer (κ-APEX II, Bruker, Karlsruhe, Germany). After unit cell determination, the reflection intensities were collected. $K_2[Pd(S_4O_{13})_2]$: yellow plates ($0.220 \times 0.220 \times 0.315$ mm^3), triclinic, P-1, $Z = 1$, $a = 732.25(2)$, $b = 859.56(2)$, $c = 903.13(2)$ pm, $\alpha = 73.266(1)$, $\beta = 88.684(1)$, $\gamma = 71.533(1)^{\circ}$, $V = 514.88(2)$ Å^3, $\rho = 2.764$ g cm^{-3}, $2\theta_{\mathrm{max.}} = 56.76^{\circ}$, $\lambda(\mathrm{Mo}_{K\alpha}) = 71.073$ pm, $T = 123$ K, 17869 reflections, 2586 unique reflections ($R_{\mathrm{int.}} = 0.0184$, $R_{\sigma} = 0.0103$), numerical absorption correction ($\mu = 22.45$ cm^{-1}, min./max. transmission = 0.06737/0.5721; programs X-RED 1.22 and X-SHAPE 1.06[13]), structure solution by direct methods, full-matrix-least-squares refinement (170 parameters) on $|F^2|$, (programs SHELXS-97 and SHELXL-97: G. M. Sheldrick[14]), $R_1 = 0.0150$, $wR_2 = 0.0390$ for 2557 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0152$, $wR_2 = 0.0391$ for all 2586 reflections, max./min. residual electron density = 0.406/−0.540 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-425249.

X-ray powder diffraction: The phase purity of $K_2[Pd(S_4O_{13})_2]$ was checked by X-ray powder diffraction on a sample prepared in a glass capillary (Ø = 0.2 mm) with the help of the powder diffractometer STOE STADIP using $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 154.06$ pm). The lattice parameters were refined as $a = 734.2(5)$, $b = 876.2(5)$, $c = 901.1(6)$ pm, $\alpha = 74.92(6)$, $\beta = 89.29(5)$, $\gamma = 71.08(4)^{\circ}$, $V = 527.8(8)$ Å^3.

Raman spectroscopy: The Raman spectrum of $K_2[Pd(S_4O_{13})_2]$ was measured (spectrometer FRA106, Bruker, Karlsruhe, Germany) on a number of selected crystals in a small glass tube. Important Raman intensities in cm^{-1} (exp./*calcd*): $\tilde{\nu}$ = 1458/*1462*, 1435/*1448*, 1419/*1426*, 1280/*1287*, 1233/*1243*, 1072/*1064*, 1042/*1035*, 888/*911*, 870/*881*, 783/*784*, 746/748, 665/*658*, 638/*626*, 598/*594*, 565/*543* cm^{-1}.

IR spectroscopy: Owing to its sensitivity a sample of $K_2[Pd(S_4O_{13})_2]$ 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} (exp./*calcd*): $\tilde{\nu}$ = 1456/*1464*, 1438/*1446*, 1390/*1429*, 1244/*1256*, 1228/*1239*, 1049/*1043*, 1027/*1027*, 857/*880*, 781/*784*, 742/745, 667/*658*, 636/*633*, 607/*593*, 565/*544* cm^{-1}.

Method of calculation: Throughout the study the Gaussian 03 program package was used.[12] A full geometry optimization of the $[Pd(S_4O_{13})_2]^{2-}$ 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. Using the optimized structure, infrared and Raman spectra were calculated.

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[1] W. Hönle, *Z. Kristallogr.* **1991**, *196*, 279–288.

[2] a) H. Lynton, M. R. Truter, *J. Chem. Soc.* **1960**, 5112–5118; b) M. A. Simonov, S. V. Shkovrov, S. I. Troyanov, *Kristallografiya* **1988**, *33*, 502–503; c) K. Ståhl, T. Balic-Zunic, F. da Silva, K. M. Eriksen, R. W. Berg, R. Fehrmann, *J. Solid State Chem.* **2005**, *178*, 1697–1704; d) F. W. B. Einstein, A. C. Wilis, *Acta Crystallogr. Sect. B* **1981**, *37*, 218–220; e) J. Douglade, R. Mercier, *Acta Crystallogr. Sect. B* **1979**, *35*, 1062–1067; f) I. D. Brown, D. B. Crump, R. J. Gillespie, *Inorg. Chem.* **1971**, *10*, 2319–2323; g) K. Ståhl, R. W. Berg, K. M. Eriksen, R. Fehrmann, *Acta Crystallogr. Sect. B* **2009**, *65*, 551–557; h) M. Jansen, R. Müller, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1055–1060; i) M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2000**, *626*, 621–622.

[3] a) J. W. Steeman, C. H. MacGillavry, *Acta Crystallogr.* **1954**, *7*, 402–404; b) K. Eriks, C. H. MacGillavry, *Acta Crystallogr.* **1954**, *7*, 430–434; c) D. W. J. Cruickshank, *Acta Crystallogr.* **1964**, *17*, 684–685.

[4] R. de Vries, F. C. Mijlhoff, *Acta Crystallogr. Sect. B* **1969**, *25*, 1696–1699.

[5] C. Logemann, M. S. Wickleder, *Inorg. Chem.* **2011**, *50*, 11111–11116.

[6] a) C. Logemann, J. Witt, D. Gunzelmann, J. Senker, M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2012**, *638*, 2053–2061; b) C. Logemann, K. Rieß, M. S. Wickleder, *Chem. Asian J.* **2012**, *7*, 2912–2920; c) C. Logemann, D. Gunzelmann, T. Klüner, J. Senker, M. S. Wickleder, *Chem. Eur. J.* **2012**, *18*, 15495–15503; d) C. Logemann, T. Klüner, M. S. Wickleder, *Chem. Eur. J.* **2011**, *17*, 758–760.

[7] J. Bruns, M. Eul, R. Pöttgen, M. S. Wickleder, *Angew. Chem.* **2012**, *124*, 2247–2250; *Angew. Chem. Int. Ed.* **2012**, *51*, 2204–2207.

[8] C. Logemann, T. Klüner, M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2012**, *638*, 758–762.

[9] C. Logemann, T. Klüner, M. S. Wickleder, *Angew. Chem.* **2012**, *124*, 5082–5085; *Angew. Chem. Int. Ed.* **2012**, *51*, 4997–5000.

[10] C. Logemann, M. Wieckhusen, T. Klüner, M. S. Wickleder, unpublished results.

[11] G. Brauer, *Handbuch der präparativen anorganischen Chemie*, F. Enke, Stuttgart, **1975**, 1729.

[12] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda,O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[13] *X-RED 1.22*, Stoe, Darmstadt, **2001**; *X-SHAPE 1.06*, Stoe, Darmstadt, **1999**

[14] SHELXS-97 and SHELXL-97: G. M. Sheldrick, *Programs for the solution and refinement of crystal structures*, Göttingen, **1997**.