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$Pd(SeO_3)$, $Pd(SeO_4)$, and $Pd(Se_2O_5)$: The First Palladium Oxoselenates

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Depending on the reaction conditions, the reaction of elemental palladium with H_2SeO_4 in sealed glass tubes at 350 °C leads to red single crystals of $Pd(SeO_3)$ [$C2/m$, $Z = 4$, $a = 6.788(2)$, $b = 7.030(2)$, $c = 7.008(2)$ Å, $\beta = 118.09(3)°$] or to yellow-orange single crystals of $Pd(SeO_4)$ [$C2/c$, $Z = 4$, $a = 8.171(1)$, $b = 5.286(1)$, $c = 8.115(1)$ Å, $\beta = 94.54(1)°$]. Yellow-orange single crystals of $Pd(Se_2O_5)$ [$I2/a$, $Z = 4$, $a = 7.212(1)$, $b = 5.569(1)$, $c = 12.177(3)$ Å, $\beta = 106.84(2)°$] are obtained when SeO_3 is added to the reaction mixture. X-ray single-crystal diffraction shows that $Pd(SeO_3)$ consists of layers that are formed by square-planar coordinated Pd^{2+} ions and pyramidal SeO_3^{2-} groups. These layers are held together by weak interactions involving the lone electron pairs of the selenium atoms. The Se–O distances within the selenite ion are different (1.69 and 1.76 Å), in accordance with the different attachment of the oxygen atoms to the Pd^{2+} ions. The square-planar $[PdO_4]$ units in the crystal structure of $Pd(SeO_4)$ are linked by tetrahedral SeO_4^{2-} ions into a three-dimensional network. These anions act as monodentate ligands towards the Pd^{2+} ions, with Se–O distances of around 1.65 Å. The Pd^{2+} ions in the crystal structure of $Pd(Se_2O_5)$ are coordinated by two chelating diselenite ions. The $Se_2O_5^{2-}$ ions link the palladium ions into corrugated chains, which are held together by weak interactions only. The IR spectra of these compounds display the typical bands for oxoselenate anions.

Introduction

Despite the vital importance of platinum group metals in various fields, complete classes of compounds of these elements are almost essentially unexplored. This is particularly true for those compounds containing complex oxo anions. To some degree this is astonishing as these compounds play a crucial role in various applications: the separation of platinum metals involves reactions with sulfuric acid, for example, and the rhodium sulfate $Rh_2(SO_4)_3 \cdot 12H_2O$ is used as a homogeneous catalyst, although its structure is not known.[1] Such compounds might also be important as precursors for the preparation of metal nanoparticles by thermolysis.[2] The investigation, and especially the structure elucidations, of these compounds are often difficult because single crystals are hard to obtain. Recently, we started to investigate compounds of precious metals with complex oxo anions in a systematic way and were able to develop suitable preparative routes for compounds of the elements gold and platinum. We found that the oxidation of gold with concentrated selenic acid and of platinum with sulfuric acid leads to gold selenites and platinum sulfates, respectively.[3,4] Surprisingly, in the case of platinum only platinum(III) sulfates were obtained. The extension of this chemistry to further platinum group metals has now afforded the selenite $Pd(SeO_3)$ by oxidation of elemental palladium with H_2SeO_4. Furthermore, the selenate $Pd(SeO_4)$ has been obtained by using H_2SeO_4 in excess, and $Pd(Se_2O_5)$ is formed when SeO_3 is added to the reaction mixture. $Pd(SeO_3)$, $Pd(SeO_4)$, and $Pd(Se_2O_5)$ are the first binary oxoselenates of a platinum group metal. Only two other structurally characterized palladium compounds with complex oxo anions have been reported to date, namely $Pd(SO_4)$, which has been prepared in a single crystalline form,[5] and $Pd(NO_3)_2 \cdot 2H_2O$, which has been characterized by powder diffraction data.[6] IR data are presented for a number of perchlorate salts.[7]

Results and Discussion

Crystal Structures

$Pd(SeO_3)$ crystallizes in the monoclinic space group $C2/m$. In the crystal structure the Pd^{2+} ion is located at the special site $4e$ (site symmetry: C_i) and the selenium atom of the SeO_3^{2-} group is placed at the position $4i$ (site symmetry: C_s) of that space group (Table 1). The Pd^{2+} ion in square-planar coordination of four oxygen atoms ($2 \times O1$ and $2 \times O2$) from four monodentate selenite ions. The Pd–O distances are 2.01 and 2.02 Å, respectively, and a slight distortion of the square-planar coordination is found, with O1–Pd–O2 angles of 85.3° and 94.7° (Table 2). Two remarkably different distances are found within the SeO_3^{2-} group, namely 1.69 Å for Se–O1 and 1.76 Å for Se–O2. The differ-

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ence between these two can be attributed to the different coordination of the oxygen atoms by Pd^{2+} ions: O1 is bonded to only one palladium ion while O2 has two neighbors. In this way the SeO_3^{2-} ion is surrounded by four Pd^{2+} ions, and this linkage leads to electronically neutral $^2_\infty[Pd(SeO_3)_{4/4}]$ layers that are stacked in the [102] direction of the monoclinic unit cell. The square-planar $[PdO_4]$ units within these layers join two *trans* vertices to each other to yield infinite $^1_\infty[PdO(1)_{2/1}O(2)_{2/2}]^{4+}$ chains (Figure 1). The Pd^{2+}–Pd^{2+} distances are 3.52 Å within the chains and 3.39 Å between adjacent chains. The most remarkable feature of the crystal structure of $Pd(SeO_3)$ is that the neutral $^2_\infty[Pd(SeO_3)_{4/4}]$ layers are held together only by weak Van der Waals interactions with respect to the observed distances between the atoms of adjacent sheets (Figure 2). The selenium atoms of one layer and the oxygen atoms of the neighboring layer are separated by 3.15 Å, and the selenium atoms show a shortest distance of 3.70 Å from layer to layer. Thus, there is a large gap between the layers, which obviously contains the lone electron pairs of the selenium atoms. The layer type structure and the presence of only weak forces between the layers weakens the single crystals, which results in severe problems in finding a suitable single crystal for X-ray diffraction, as reflected by the rather high residual values (Table 4).

Table 1. Atomic positions and equivalent displacement parameters for $Pd(SeO_3)$, $Pd(SeO_4)$, and $Pd(Se_2O_5)$.[a]

Atom	Wyckoff	x/a	y/b	z/c	U_{eq}/Å^2
			$Pd(SeO_3)$		
Pd	4*e*	1/4	1/4	0	0.0123(8)
Se	4*i*	0.1658(5)	1/2	0.3527	0.0153(3)
O1	8*j*	0.268(2)	0.304(2)	0.290(2)	0.019(4)
O2	4*i*	0.894(4)	1/2	0.132(4)	0.018(3)
			$Pd(SeO_4)$		
Pd	4*c*	3/4	1/4	1/2	0.0048(2)
Se	4*e*	0	0.0684	1/4	0.0044(2)
O1	8*f*	0.9776(4)	0.2479(69	0.4144(4)	0.0092(7)
O2	8*f*	0.1679(3)	0.8943(6)	0.2788(4)	0.0094(6)
			$Pd(Se_2O_5)$		
Pd	4*a*	0	0	0	0.0100(3)
Se	8*f*	0.1819(2)	0.9114(1)	0.36149(8)	0.0091(3)
O1	4*e*	1/4	0.052(1)	1/2	0.020(2)
O2	8*f*	0.375(1)	0.730(1)	0.3699(7)	0.015(2)
O3	8*f*	0.001(1)	0.730(1)	0.3704(7)	0.013(2)

[a] $U_{eq} = 1/3[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$.

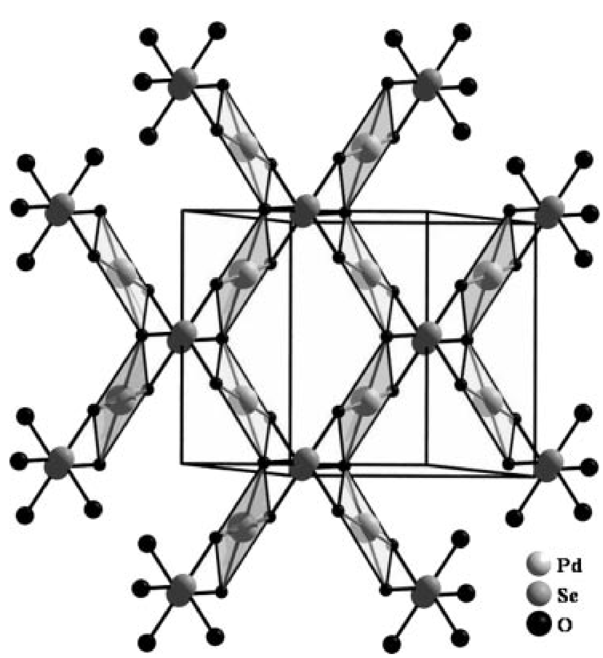

Figure 1. Linkage of the $[PdO_4]$ units according to $^1_\infty[PdO(1)_{2/1}$-$O(2)_{2/2}]^{4+}$. The metal ions lie in a square plane of oxygen atoms and are connected via *trans* vertices into chains.

$Pd(SeO_4)$ also crystallizes monoclinically with a face centered unit cell (space group *C*2/*c*) and is isotypic with the recently reported $Pd(SO_4)$.[5] The palladium atoms are surrounded in a square-planar manner by oxygen atoms, and the selenium atoms are tetrahedrally coordinated by oxygen atoms. Both the palladium and the selenium atoms are located on special sites (4*c* and 4*e*, respectively), which implies C_i symmetry for the $[PdO_4]$ units and C_2 symmetry for the SeO_4^{2-} anions (Table 1). The Pd–O distances are in the same range as found for $Pd(SeO_3)$ and show values of 2.04 (O1) and 2.02 Å (O2; Table 2). This is also in good agreement with the findings reported for $Pd(SO_4)$.[5] Similarly to $Pd(SeO_3)$, a distortion of the $[PdO_4]$ unit has to be taken into account, with O1–Pd–O2 angles of 87.0 and 93.0°,

Table 2. Selected bond distances [Å] and angles [°] in $Pd(SeO_3)$, $Pd(SeO_4)$, and $Pd(Se_2O_5)$.

$Pd(SeO_3)$			$Pd(SeO_4)$			$Pd(Se_2O_5)$		
Pd–O1	(2x)	2.02(1)	Pd–O1	(2x)	2.036(3)	Pd–O2	(2x)	2.035(8)
Pd–O2	(2x)	2.01(1)	Pd–O2	(2x)	2.015(3)	Pd–O3	(2x)	2.036(8)
O1–Pd–O1		180	O1–Pd–O1		180	O2–Pd–O2		180
O1–Pd–O2	(2x)	85.3(8)	O1–Pd–O2	(2x)	87.0(1)	O2–Pd–O3	(2x)	96.0(2)
O2–Pd–O1	(2x)	94.7(8)	O2–Pd–O1	(2x)	93.0(1)	O2–Pd–O1	(2x)	84.0(2)
O2–Pd–O2		180	O2–Pd–O2		180	O3–Pd–O3		180
Se–O1	(2x)	1.69(1)	Se–O1	(2x)	1.659(3)	Se–O1		1.793(3)
Se–O2		1.76(2)	Se–O2	(2x)	1.653(3)	Se–O2		1.69(1)
						Se–O3		1.678(9)
O1–Se–O1		109.1(9)	O1–Se–O1		110.3(2)	O1–Se–O3		101.9(3)
O1–Se–O2	(2x)	99.3(6)	O1–Se–O2	(2x)	106.8(1)	O1–Se–O2		101.8(3)
			O2–Se–O1	(2x)	110.4(2)	O2–Se–O3		106.2(3)
			O2–Se–O2		112.3(2)	Se–O1–Se		131.0(2)

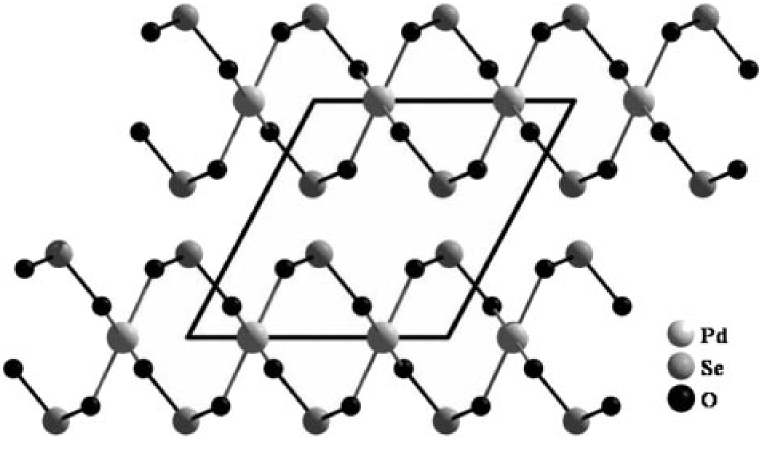

Figure 2. Stacking of electronically neutral $^2_\infty[Pd(SeO_3)_{4/4}]$ layers along the [102] direction of the unit cell.

respectively. The oxygen atoms of the $[PdO_4]$ groups ($2\times$O1, $2\times$O2) come from four monodentate SeO_4^{2-} ions. Each of the latter must be connected to four Pd^{2+} ions to achieve the composition $Pd(SeO_4)$. Thus, each of the oxygen atoms is connected to a Pd^{2+} ion, which leads to uniform Se–O distances of about 1.65 Å within the anions. Judging from the O–Se–O angles within the anion (106.8–112.3°) a slight deviation of the ideal tetrahedral symmetry is observed. The connectivity of Pd^{2+} and SeO_4^{2-} ions leads to a three-dimensional network, as expressed by the Niggli formula $^3_\infty[Pd(SeO_4)_{4/4}]$ (Figure 3). The crystal structure of $Pd(SeO_4)$ is related to that of PdSe if the complex SeO_4^{2-} ions are regarded as spheres.[8] The Se^{2-} ions in PdSe have the same coordination as the SeO_4^{2-} groups in $Pd(SeO_4)$.

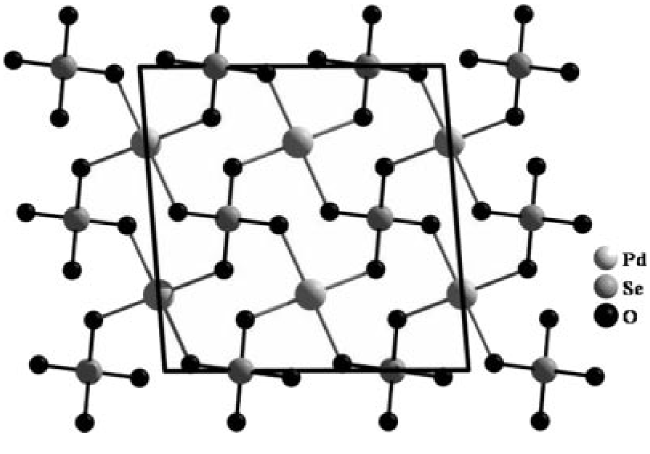

Figure 3. Perspective view of the crystal structure of $Pd(SeO_4)$ along the [010] direction of the unit cell.

The monoclinic structure of $Pd(Se_2O_5)$ ($I2/a$) contains the Pd^{2+} ion (Wyckoff site 4*e*; site symmetry: C_i) in a square-planar environment of oxygen atoms ($2\times$O2 and $2\times$O3) with the Pd–O distances being essentially equal at 2.03 Å. The deviation of the $[PdO_4]$ unit from ideal D_{4h} symmetry is again significant (Table 2). The four oxygen atoms belong to two $Se_2O_5^{2-}$ ions that act as chelating ligands (Figure 4). The distance between the bridging oxygen atom (O1) and the crystallographically equivalent selenium atoms is 1.793(3) Å, which matches the value that has been reported for other diselenites.[9] Furthermore, the Se–O1–Se angle of 131° lies within the range reported so far.[9] The oxygen atom O1 is located at the 4*e* site of space group

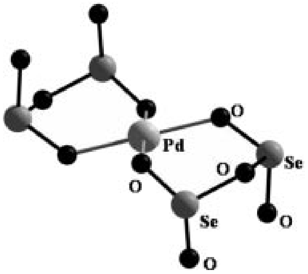

Figure 4.Coodination of the Pd^{2+} ion by two chelating $Se_2O_5^{2-}$ groups in the crystal structure of $Pd(Se_2O_5)$.

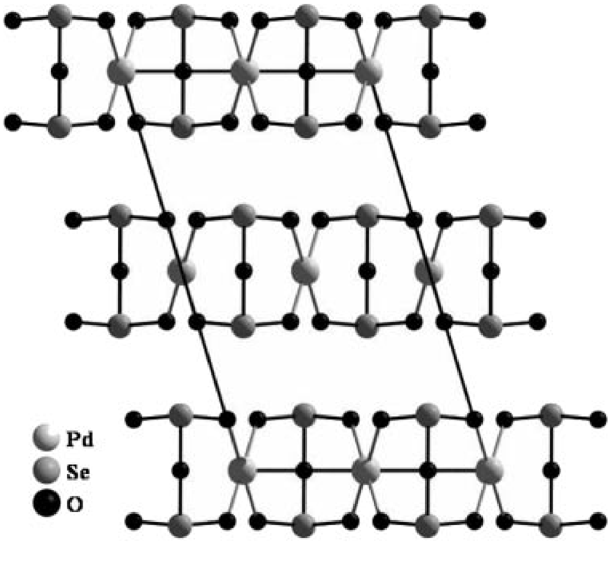

Figure 5. Perspective view of the crystal structure of $Pd(Se_2O_5)$ along the [010] direction of the unit cell.

$I2/a$, which yields C_2 symmetry for the $Se_2O_5^{2-}$ ion. According to the formulation $^1_\infty[Pd(Se_2O_5)_{2/2}]$, each $Se_2O_5^{2-}$ ion is coordinated to two Pd^{2+} ions, which leads to the formation of infinite chains (Figure 5). These chains are strongly corrugated, as shown in Figure 6, and are stacked in the [010] direction. The Pd–Pd distance between adjacent $[PdO_4]$ units is 3.60 Å. The $^1_\infty[Pd(Se_2O_5)_{2/2}]$ chains are only held together by weak interactions and therefore, similarly to $Pd(SeO_3)$, single crystals of $Pd(Se_2O_5)$ suitable for X-ray diffraction were hard to obtain.

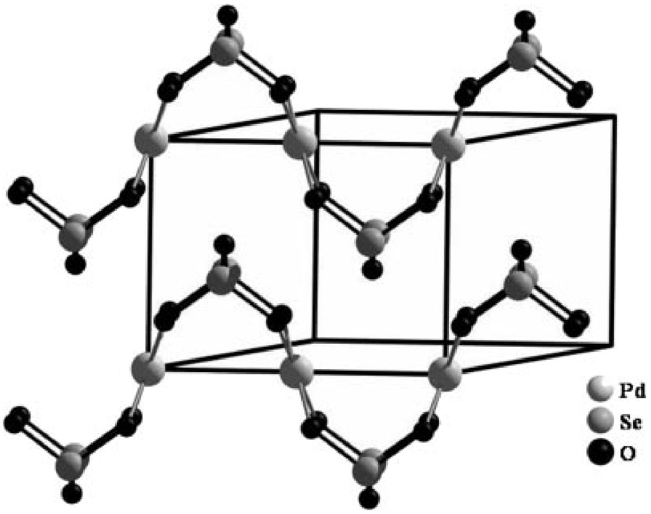

Figure 6. Stacking of the electronically neutral $^1_\infty[Pd(Se_2O_5)_{2/2}]$ chains in the crystal structure of $Pd(Se_2O_5)$.

Vibrational Spectroscopy

The symmetry of the SeO_3^{2-}, SeO_4^{2-}, and $Se_2O_5^{2-}$ ions is remarkably lower in the compounds under discussion than in the free anions. Thus, the anion in $Pd(SeO_3)$ has C_s symmetry, SeO_4^{2-} shows C_2 symmetry in $Pd(SeO_4)$, and C_2 symmetry is also found for the $Se_2O_5^{2-}$ ion in $Pd(Se_2O_5)$. A number of bands are observed in the IR spectra between 400 and 4000 cm^{-1}. These are summarized in Table 3 and their assignment is straightforward by comparison with literature data.[9,10]

Table 3. IR data [cm^{-1}] for $Pd(SeO_3)$, $Pd(SeO_4)$, and $Pd(Se_2O_5)$.[a]

Assignment	Wavenumber
	$Pd(SeO_3)$
ν_s (SeO_2)	863 (s), 829 (s)
δ_s (SeO_3)	530 (s), 413 (s)
ν_{as} (SeO_2)	744 (s), 700 (sh) 663 (s) 640 (s)
δ_{as} (SeO_3)	–[b]
	$Pd(SeO_4)$
ν_s (SeO_2)	823 (s), 910 (s), 709 (s), 739 (s)
δ_s (SeO_4)	–[b]
ν_{as} (SeO_2)	956 (s), 1160(w) 1247 (s)
δ_{as} (SeO_4)	422 (m), 470(m)
	$Pd(Se_2O_5)$
ν_s (SeO_2)	862 (s) 822 (s)
ν_{as} (SeO_2)	732 (m), 702 (sh) 664 (s)
ν_s (SeOSe)	473 (w)
ν_{as} (SeOSe)	525 (w)
δ_s (SeO_3)	410 (m)
δ_{as} (SeO_3)	–[b]

[a] s = strong, m = medium, sh = shoulder, w = weak. [b] Out of measuring range.

Conclusions

As an extension of our work on direct oxidation of precious metals by mineral acids, we have shown in this paper that elemetal palladium can be oxidized by selenic acid under solvothermal conditions, which leads to $Pd(SeO_3)$ or $Pd(SeO_4)$, depending on the metal/acid ratio. Furthermore, the diselenite $Pd(Se_2O_5)$ is obtained if SeO_3 is added to the reaction mixture. The compounds were characterized by single-crystal X-ray diffraction and IR spectroscopy.

Experimental Section

Synthesis: For the preparation of $Pd(SeO_3)$, 30 mg of palladium powder and 1 mL of H_2SeO_4, which was prepared from H_2O_2 and SeO_2 according to the literature procedure,[11] were sealed in a glass ampoule (length: 100 mm; width: 6 mm). This ampoule was heated to 350 °C for 72 h and then cooled slowly (3 °C/h). Plate-shaped and easily cleavable red crystals of $Pd(SeO_3)$ were recovered from the ampoule. Following the same procedure, lath-shaped yellow single crystals of $Pd(SeO_4)$ were obtained when only 15 mg of palladium powder was used in the reaction. Orange-yellow slightly needle shaped and cleavable single crystals of $Pd(Se_2O_5)$ were obtained upon treating 8 mg of palladium powder with 1 mL of H_2SeO_4 and 50 mg of SeO_3. This mixture was sealed in a glass ampoule, heated to 250 °C, and then slowly cooled (3 °C/h). The yields of the reactions were almost quantitative, and the samples were found to be single phase within the accuracy of X-ray powder diffraction.

Caution: All selenium-containing compounds are potentially poisonous. The glass ampoules are under considerable pressure after the reaction and should be handled with care and appropriate protection.

X-ray Crystallography: Crystals of $Pd(SeO_3)$, $Pd(SeO_4)$, or $Pd(Se_2O_5)$ were transferred into protecting oil and several specimens were glued on glass fibers and checked with the help of an image plate diffractometer (STOE IPDS). Reflection intensities for the best crystals were collected with the same diffractometer at 153 K. The crystal structures were solved by direct methods with the help of the program SHELXS97[12] assuming the space groups $C2/m$ $(PdSeO_3)$, $C2/c$ $(PdSeO_4)$, and $I2/a$ $Pd(Se_2O_5)$. The latter setting of space group no. 15 was chosen in order to obtain a smaller monoclinic angle. Full-matrix least-squares refinements on F^2 were performed for all compounds using SHELXL97.[12] All atoms were refined anisotropically after applying numerical absorption corrections.[13] Details of the data collection are given in Table 4. Crystallographic and structural data are summarized in Tables 1 and 2, respectively. The final residuals for $Pd(SeO_3)$ and $Pd(Se_2O_5)$ are significantly higher than those for $Pd(SeO_4)$ due to the structural features of the former two compounds (extremely fragile crystals). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen. These data

Table 4. Crystallographic data and structure determination parameters for Pd(SeO$_3$), Pd(SeO$_4$), and Pd(Se$_2$O$_5$).

	Pd(SeO$_3$)	Pd(SeO$_4$)	Pd(Se$_2$O$_5$)
a [Å]	6.788(2)	8.171(1)	7.212(1)
b [Å]	7.030(2)	5.286(1)	5.569(1)
c [Å]	7.008(2)	8.115(1)	12.177(3)
β [°]	118.09(3)	94.54(1)	106.84(2)
V [Å^3]	295.0(1)	349.37(9)	468.1(2)
Z	4	4	4
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/m$ (no. 12)	$C2/c$ (no. 15)	$I2/a$ (no. 15)
Measuring device	Stoe IPDS I		
Radiation	Mo-K_α (graphite monochromated, λ = 71.07 pm)		
T [K]	153	153	153
Theta range [°]	$3.3 < 2\theta < 52.3$	$3.3 < 2\theta < 52.1$	$3.3 < 2\theta < 52.1$
Index range	$-8 \leq h \leq 8$	$-10 \leq h \leq 10$	$-8 \leq h \leq 8$
	$-8 \leq k \leq 8$	$-6 \leq k \leq 6$	$-6 \leq k \leq 6$
	$-8 \leq l \leq 8$	$-9 \leq l \leq 9$	$-15 \leq l \leq 14$
Rotation angle [°]; ϕ increment [°]	$0 < \phi < 270$; 3	$0 < \phi < 240$; 1	$0 < \phi < 250.2$; 1.8
No. of exposures	90	160	139
Exposure time	7 min	6 min	6 min
Detector distance	70 mm	70 mm	70 mm
Data correction	Polarization and Lorentz factors		
Absorption correction	numerical		
μ [cm^{-1}]	184.1	155.7	194.35
Measured reflections	1537	1530	2313
Unique reflections	290	333	2313
with $I_o > 2\sigma(I)$	317	317	1445
No. of variables	29	23	25
R_{int}	0.0958	0.0379	0.0821
Structure determination	SHELXS-97 and SHELXL-97		
Scattering factors	International Tables, vol. C		
Extinction coefficient	0.002(2)	0.0016(4)	0.0006(4)
Goodness of fit	1.374	1.054	1.038
R_1/wR_2 [$I_o > 2\sigma(I)$]	0.0614/0.1496	0.0191/0.0401	0.0498/0.1343
R_1/wR_2 (all data)	0.0757/0.1717	0.0203/0.0402	0.0804/0.1520
Depository number	415955	416646	417900

can be obtained on quoting the depository number given in Table 4.

Vibrational Spectroscopy: The IR data were collected with a Vector 22 spectrometer (Bruker) in the range 400–4000 cm^{-1}. Some crystals of Pd(SeO$_3$) and Pd(Se$_2$O$_5$) were prepared in a KBr pellet while CsCl was used as mulling agent for Pd(SeO$_4$). The data obtained are given in Table 3.

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