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Selenium Oxoanion Compounds of Palladium(II)

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Three new palladium compounds, $PdSeO_3$, $PdSe_2O_5$, and $Na_2Pd(SeO_4)_2$, containing selenium oxoanions of both Se(IV) and Se(VI) have been prepared under mild hydrothermal conditions. $PdSe_2O_5$ and $Na_2Pd(SeO_4)_2$ both possess one-dimensional structures. Within the structure of $PdSe_2O_5$, [PdO_4] square planar building blocks are joined together through diselenite, $Se_2O_5^{2-}$, anions, and form a zigzag chain along the *c* axis. In $Na_2Pd(SeO_4)_2$, [PdO_4] units are connected by two selenate, SeO_4^{2-}, anions, and extend along the *a* axis to form a $[Pd(SeO_4)_2]^{2-}$ chain. Na^+ cations reside in the space between the $[Pd(SeO_4)_2]^{2-}$ chains and act as counter cations. Unlike above two compounds, $PdSeO_3$ exhibits a layered structure. In the structure of $PdSeO_3$, [PdO_4] units are connected to each other by corner-sharing and form a zigzag chain along the *b* axis. The chains are further joined together by tridentate selenite, SeO_3^{2-}, anions to form layers in the [*ab*] plane that stack along the *c* axis. Crystallographic data: (193 K; Mo Kα, $\lambda = 0.71073$ Å): $PdSeO_3$, monoclinic, space group $P2_1/m$, $a = 3.8884(5)$ Å, $b = 6.4170(8)$ Å, $c = 6.1051(7)$ Å, $\beta = 96.413(2)°$, $V = 151.38(3)$ Å^3, $Z = 2$; $PdSe_2O_5$, monoclinic, space group $C2/c$, $a = 12.198(2)$ Å, $b = 5.5500(8)$ Å, $c = 7.200(1)$ Å, $\beta = 107.900(2)°$, $V = 463.8(1)$ Å^3, $Z = 4$; $Na_2Pd(SeO_4)_2$, triclinic, space group $P\bar{1}$, $a = 4.9349(11)$ Å, $b = 5.9981(13)$ Å, $c = 7.1512$ (15) Å, $\alpha = 73.894(4)°$, $\beta = 86.124(4)°$, $\gamma = 70.834(4)°$, $V = 192.03(7)$ Å^3, $Z = 1$.

Introduction

The aqueous and solid-state chemistry of selenium are extraordinarily rich, yielding a variety of Se(IV) and Se(VI) species that include H_2SeO_3, $HSeO_3^-$, SeO_3^{2-}, $Se_2O_5^{2-}$, and SeO_4^{2-}.[1,2] One of the primary interests in Se(IV) compounds is discerning the role that the lone-pair of electrons on the Se(IV) centers plays in the local and extended structures of these compounds. There are three major themes recognized for the effects of the lone-pair of electrons that are in addition to its local stereochemical activity. The first of these is dimensional reduction. Take for example the uranyl selenite system, the majority of uranyl-containing compounds are two-dimensional;[3] however, $Ca[UO_2(SeO_3)_2]$ and $Sr[UO_2(SeO_3)_2]\cdot 2H_2O$ are both one-dimensional.[4] The second effect is the formation of channels and cavities within extended networks to house the lone-pair of electrons. Cavity and channel formation is recognized in β-$AgNpO_2(SeO_3)$,[5] $M_2(SeO_3)_3\cdot 3H_2O$ (M = Al,[6] Ga,[7] Cr[8]), $In(OH)(SeO_3)$.[9] $Tb_3O_2Cl(SeO_3)_2$,[10] $Tb_5O_4Cl_3(SeO_3)_2$,[10] and $Tb_2Se_2O_7$.[11] The third major effect is the formation of noncentrosymmetric structures as occurs in $A_2(MoO_3)_3SeO_3$ (A = Rb, Cs, Tl, NH_4),[12] $Cs(VO_2)_3(SeO_3)_2$,[13] and Na_2MoSeO_6.[14]

Diselenite compounds containing the $Se_2O_5^{2-}$ anion are becoming increasingly common in Se(IV) oxoanion chem-

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istry, and are known with f-block metals, e.g., in $UO_2Se_2O_5$,[15] with alkaline-earth metals in $AESe_2O_5$ (AE = Mg,[16] Ca,[17] Sr,[18] Ba[19]), and with d-block metals, e.g., in $MnSe_2O_5$,[20] and $[H_2pip][Cu_2(Se_2O_5)_3]$.[21] MSe_2O_5 (M = Pb, Cd, Mn) and $Cr_2(Se_2O_5)_3$ are also known and have been characterized by vibrational spectroscopy.[22] The ammonium salt of diselenite, $(NH_4)_2Se_2O_5$, has been studied by neutron diffraction and shown to undergo a phase transition at 312 K.[23-25] Despite the presence of two lone-pairs of electrons on the diselenite anion, most compounds are centrosymmetric; notable exceptions include $LiFe(Se_2O_5)_2$,[26] $Nb_2Se_4O_{13}$,[27] $Nd_2(Se_2O_5)_3\cdot H_2SeO_3\cdot 2H_2O$,[28] and $In_2(Se_2O_5)_3$.[29] Small second-harmonic generation responses have been observed for the frequency-doubling of 1064 nm light by $In_2(Se_2O_5)_3$.[29] Magnetic ordering has been observed in diselenite compounds, e.g., in $M_2(Se_2O_5)_3$ (M = Cr,[30] Mn,[31] Fe[30]). Mixed selenite/diselenite compounds have also been reported and include $Ca_2(HSeO_3)_2(Se_2O_5)$,[1,32] $Ca_2(SeO_3)(Se_2O_5)$,[19] $Au_2(SeO_3)_2(Se_2O_5)$,[33] $M(HSeO_3)(Se_2O_5)$ (M = Fe,[34] Cr[35]), $Sm_2(SeO_3)(Se_2O_5)_2$,[36] $La(Se_2O_5)(HSeO_3)(H_2O)\cdot H_2O$,[37] and $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$.[38]

While it is generally and correctly predicted that selenate compounds containing SeO_4^{2-} would possess similar structures with that of sulfates, the fact is that selenates have proven to be far richer with examples of nanotubules being observed in the uranyl selenates, $(C_4H_{12}N)_{14}[(UO_2)_{10}(SeO_4)_{17}(H_2O)]$[39] and $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$.[40] In this work we provide example of new Pd(II) compounds containing selenite, diselenite, and selenate anions with the synthesis, structures, and characterization of $PdSeO_3$, $PdSe_2O_5$, and $Na_2Pd(SeO_4)_2$.

Experimental Section

$Pd(NO_3)_2$ (99.9%, Alfa-Aesar), Na_2SeO_4 (99.8%, Alfa-Aesar), and KNO_3 (99.9%, Alfa-Aesar) were used as received without further purification. Concentrated H_2SeO_4 solution was prepared by evaporating 40% H_2SeO_4 (Alfa-Aesar) at ~200 °C. Distilled and Millipore-filtered water with resistance of 18.2 MΩ·cm was used in all reactions. SEM/EDX analyses were performed using a JEOL JSM-7000F. Sodium, palladium, and selenium standards were used to calibrate the results, and the EDX ratios are within 3% of the ratios determined from single-crystal X-ray diffraction experiments.

$PdSeO_3$ was prepared by loading $Pd(NO_3)_2$ (101.0 mg, 0.438 mmol), KNO_3 (88.6 mg, 0.876 mmol), 0.2 mL of concentrated H_2SeO_4, and 0.5 mL of water in a 23-mL PTFE-lined autoclave. The autoclave was sealed and heated at 200 °C in a box furnace. After 4 days, the furnace was cooled to room temperature at a rate of 9 °C/h. The reaction product contained a single phase of dark orange crystals immersed in a pale yellow mother liquor. The product was washed with water and methanol and allowed to dry. Yield: 84 mg (82% based on Pd). EDX analysis provided a Pd/Se ratio of 1:1 (47:53).

$PdSe_2O_5$ was prepared by loading $Pd(NO_3)_2$ (183.0 mg, 0.794 mmol), KNO_3 (160.6 mg, 1.588 mmol), 0.4 mL of concentrated H_2SeO_4, and 0.5 mL of water in a 23-mL PTFE-lined autoclave. The autoclave was sealed and heated at 200 °C in a box furnace. After 4 days, the furnace was cooled to room temperature at a rate of 9 °C/h. The reaction product contained a single phase of orange crystals immersed in a colorless mother liquor. The product was washed with water and methanol and allowed to dry. Yield: 183 mg (66.9% based on Pd). EDX analysis provided a Pd/Se ratio of 1:2 (34:66).

$Na_2Pd(SeO_4)_2$ was prepared by loading $Pd(NO_3)_2$ (116.5 mg, 0.506 mmol), Na_2SeO_4 (191.2 mg, 1.012 mmol), 0.3 mL of concentrated H_2SeO_4, and 0.5 mL of water in a 23-mL PTFE-lined autoclave. The autoclave was sealed and heated at 200 °C in a box furnace. After 4 days, the furnace was cooled to room temperature at a rate of 9 °C/h. The reaction product consist of yellow crystals of $Na_2Pd(SeO_4)_2$ as major product and orange crystals of $PdSe_2O_5$ as minor product. The product was washed with water and methanol and allowed to dry. Yield: 120 mg (54.3% based on Pd). EDX analysis provided a Na/Pd/Se ratio of 2:1:2 (42:19:39).

Crystallographic Studies. Single crystals of $PdSeO_3$, $PdSe_2O_5$, and $Na_2Pd(SeO_4)_2$ with dimensions of 0.035 mm × 0.033 mm × 0.010 mm, 0.092 mm × 0.089 mm × 0.023 mm, and 0.110 mm × 0.039 mm × 0.020 mm were selected and mounted on glass fibers with epoxy and aligned on a Bruker SMART APEX CCD X-ray diffractometer with a digital camera. Intensity measurements were performed using graphite-monochromated Mo Kα radiation from a sealed tube with a monocapillary collimator. The intensities and positions of reflections of a sphere were collected by a combination of three sets of exposure frames. Each set had a different φ angle for the crystal, and each exposure covered a range of 0.3° in ω. A total of 1800 frames was collected with an exposure time per frame of 30 s for $PdSeO_3$, 10 s for $PdSe_2O_5$, and 20 s for $Na_2Pd(SeO_4)_2$.

Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. A numerical absorption correction was applied on the basis of the indexed crystal faces followed by a semiempirical absorption correction using SAD-

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Table 1. Crystallographic Data for $PdSeO_3$, $PdSe_2O_5$, and $Na_2Pd(SeO_4)_2$

formula	$PdSeO_3$	$PdSe_2O_5$	$Na_2Pd(SeO_4)_2$
formula mass	233.36	344.32	438.3
color and habit	orange, plate	orange, prism	yellow, block
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/m$ (No. 11)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	3.8884(5)	12.198(2)	4.9349(11)
b (Å)	6.4170(8)	5.5500(8)	5.9981(13)
c (Å)	6.1051(7)	7.200(1)	7.1512(15)
α (deg)	90	90	73.894(4)
β (deg)	96.413(2)	107.900(2)	86.124(4)
γ (deg)	90	90	70.834(4)
V (Å^3)	151.38(3)	463.8(1)	192.03(7)
Z	2	4	1
T (K)	193	193	193
λ (Å)	0.71073	0.71073	0.71073
max 2θ (deg)	56.54	56.58	56.60
ρ_{calcd} (g cm^{-3})	5.120	4.931	3.790
μ(Mo Kα) (cm^{-1})	179.25	196.1	120.15
$R(F)^a$ for $F_o^2 > 2\sigma(F_o^2)$	0.0190	0.0234	0.0241
$R_w(F_o^2)^b$	0.0476	0.0596	0.0656

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$.

ABS.[41] The program suite SHELXTL (v 5.1) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL).[42] The final refinements included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Some crystallographic details are listed in Table 1. Further details of the crystal structure investigations may be obtained from the Supporting Information.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were collected with a Rigaku Miniflex powder X-ray diffractometer using Cu Kα (λ = 1.54056 Å) radiation. The collected patterns were compared with that calculated from single-crystal data using ATOMS.[43]

Vibrational Spectroscopy. The IR spectra of three title compounds were taken from a sample in KBr with the spectrometer Shimadzu IR Prestige-21 in the wavenumber range of 4000−400 cm^{-1}.

Thermal Analysis. For the investigation of the thermal behavior, 12 mg of the title compounds were heated (3 °C/min) up to 600 °C under a nitrogen flow using a TA differential scanning calorimeter (DSC) Instruments Model 2920. The residue compositions were checked by powder X-ray diffraction.

Results and Discussion

Synthesis of $PdSeO_3$, $PdSe_2O_5$, and $Na_2Pd(SeO_4)_2$. Both of $PdSeO_3$ and $PdSe_2O_5$ were synthesized by reacting $Pd(NO_3)_2$, KNO_3, and concentrated H_2SeO_4 under mild hydrothermal condition. In these two reactions, some of the SeO_4^{2-} was reduced to SeO_3^{2-} as occurs in the preparations of $Th(SeO_3)(SeO_4)$[44] and $Ag_4(Mo_2O_5)(SeO_4)_2(SeO_3)$.[45] The relatively strong oxidizing power of selenate ($E°$ = 1.151 V) might be sufficient to oxidize water under hydrothermal conditions. In the preparation of $PdSe_2O_5$, the concentration of H_2SeO_4 was double that in the synthesis of $PdSeO_3$. At higher concentrations of H_2SeO_4, the formation of $PdSe_2O_5$, instead of $PdSeO_3$, was more favorable, which is consistent with previously reported results.[38] The role of KNO_3 in these reactions is not clear, but the attempts to make these two compounds in the absence of KNO_3 failed. In the synthesis of $Na_2Pd(SeO_4)_2$, the addition of Na_2SeO_4 to the reaction mixture allowed for the isolation of a selenate compound. There were also small amounts of $PdSe_2O_5$ found as a byproduct.

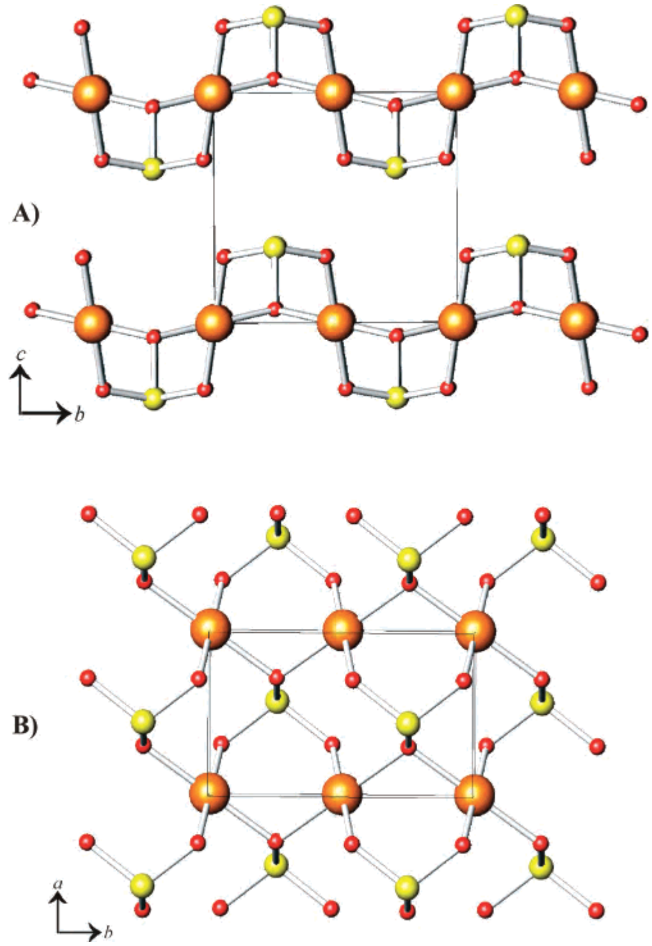

Figure 1. (a) View of the structure of $PdSeO_3$ showing [PdO_4] units joined together through corner-sharing to form a chain that extends down the b axis. The palladium chains are further connected by tridentate SeO_3^{2-} anions. (b) A depiction of the neutral layers in $PdSeO_3$.

Crystal Structure of $PdSeO_3$. The structure of $PdSeO_3$ contains a crystallographically unique Pd(II) center in a classical four coordinate environment with a square planar geometry. The Pd atom resides on the origin (inversion center), and is bound to four oxygen atoms from four selenite anions. The Pd−O bond distances within the [PdO_4] unit are 2.021(2) and 2.008(2) Å, and the O−Pd−O angles are 88.95(11)° and 91.05(11)°, which are close to an idealized geometry. Two [PdO_4] units are joined together through corner-sharing to form a chain that extends down the b axis. The palladium chains are further connected by tridentate SeO_3^{2-} anions and form a layered structure, as shown in Figure 1. There are two crystallographically unique oxygen

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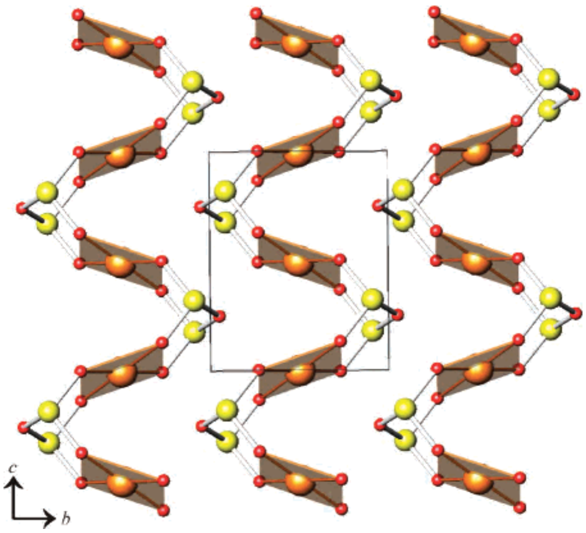

Figure 2. Illustration of the one-dimensional chains formed from [PdO_4] units and $Se_2O_5^{2-}$ anions in the structure of $PdSe_2O_5$.

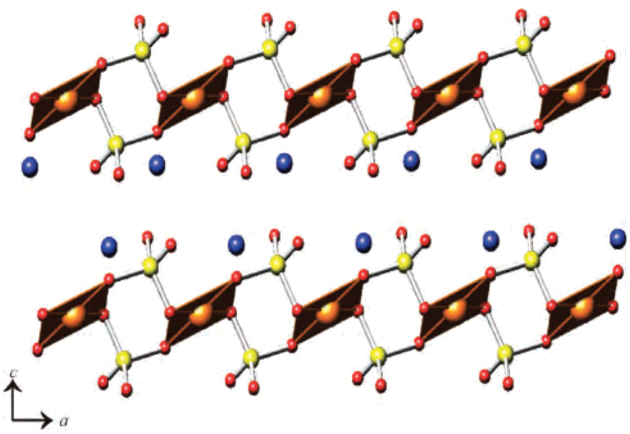

Figure 3. View of the one-dimensional [$Pd(SeO_4)_2]^{2-}$ chains in $Na_2Pd(SeO_4)_2$.

atoms within the selenite anions. O(1) is connected to two Pd atoms with Se−O bond distance of 1.785(1) Å, while O(2) is connected to one Pd atom with a Se−O bond distance of 1.689(2) Å. The bridging tridentate SeO_3^{2-} anion has bond angles ranging from 97.0(1)° to 105.4(2)°. The palladium selenite layers further stack along the *c* axis, as is shown in Figure 1A. The calculated bond valence sums (BVS) for Pd(1) and Se(1) are 2.193 and 3.855, respectively.[46,47] Selected bond distances are given in Table 2.

Crystal Structure of $PdSe_2O_5$. In the structure of $PdSe_2O_5$, Pd(II) ions also have a square planar four-coordinate environment. The Pd atoms sit on a mirror plane and are bound to four oxygen atoms from two $Se_2O_5^{2-}$ anions. The Pd−O bond distances within the [PdO_4] unit are 2.017(3) and 2.018(3) Å, which are nearly equal. The O−Pd−O angles show significant deviations from 90° with the lowest and highest values being 84.3(1)° and 95.7(1)°. Each [PdO_4] unit is connected to two other [PdO_4] units through two $Se_2O_5^{2-}$ anions and forms a chain, as is shown in Figure 2. The chains extend along the *c* axis. In the bridging $Se_2O_5^{2-}$ anions, each selenium atom has two oxygen atoms bound to two [PdO_4] squares. The bond distances of Se(1)−O(1) and Se(1)−O(2) are 1.685(3) and 1.672(3) Å, respectively. The remaining oxygen atom O(3) is bound to two selenium atoms as a bridge with a Se−O bond distance of 1.788(2) Å. The BVS values for Pd(1) and Se(1) are 2.174 and 3.926, respectively.[46,47] Selected bond distances are given in Table 3.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $PdSeO_3$

Bond Distances (Å)			
Pd(1)−O(1) × 2	2.021(2)	Se(1)−O(1)	1.785(3)
Pd(1)−O(2) × 2	2.008(2)	Se(1)−O(2)	1.689(2)
Angles (deg)			
O(1)−Pd(1)−O(1′)	180	O(1)−Se(1)−O(2)	97.01(10)
O(1)−Pd(1)−O(2)	91.05(11)	O(1)−Se(1)−O(2′)	97.01(10)
O(1)−Pd(1)−O(2′)	88.95(11)	O(2)−Se(1)−O(2′)	105.37(16)
O(1′)−Pd(1)−O(2)	88.95(11)		
O(1′)−Pd(1)−O(2′)	91.05(11)		
O(2)−Pd(1)−O(2′)	180		

Table 3. Selected Bond Distances (Å) and Angles (deg) for $PdSe_2O_5$

Bond Distances (Å)			
Pd(1)−O(1) × 2	2.018(3)	Se(1)−O(1)	1.685(3)
Pd(1)−O(2) × 2	2.017(3)	Se(1)−O(2)	1.672(3)
		Se(1)−O(3)	1.788(2)
Angles (deg)			
O(1)−Pd(1)−O(1′)	180	O(1)−Se(1)−O(2)	105.8(2)
O(1)−Pd(1)−O(2)	84.3(1)	O(1)−Se(1)−O(3)	101.2(1)
O(1)−Pd(1)−O(2′)	95.7(1)	O(2)−Se(1)−O(3)	102.1(1)
O(1′)−Pd(1)−O(2)	95.7(1)		
O(1′)−Pd(1)−O(2′)	84.3(1)		
O(2)−Pd(1)−O(2′)	180		

Crystal Structure of $Na_2Pd(SeO_4)_2$. Similar to $PdSe_2O_5$, the title compound exhibits a one-dimensional chain structure. The Pd atoms in the structure reside on a center of inversion and are coordinated by four oxygen atoms in a square planar geometry. The bond distances within the [PdO_4] unit are 2.014(2) and 2.019(2) Å. The O−Pd−O angles are 85.48(8)° and 94.52(8)°. [PdO_4] units connect with two neighboring [PdO_4] units through two bidentate SeO_4^{2-} anions to form one-dimensional chains, as is shown in Figure 3. The chains extend along the *a* axis. In the SeO_4^{2-} anions, the bond distances of the selenium atom to bridging oxygen atoms are 1.675(2) and 1.673(2) Å, while those for the terminated oxygen atoms are 1.617(2) and 1.616(2) Å. There is only one crystallographically unique Na^+ cation in this structure. Na(1) has a six-coordinate environment with Na−O bond distances ranging from 2.342(2) to 2.762(3) Å. The BVS values for Na(1), Pd(1), and Se(1) are 1.094, 2.181, and 5.902, respectively.[46,47] Selected bond distances are given in Table 4.

Vibrational Spectroscopy. The infrared spectra of these three palladium compounds consist of two primary regions. Several weak bands centered at 560 cm^{-1} in these three IR spectra can be assigned to the distortions of the [PdO_4] square plane.[48,49] In the IR spectrum of $PdSeO_3$, five sharp bands

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $Na_2Pd(SeO_4)_2$

Bond Distances (Å)			
Pd(1)−O(1) × 2	2.014(2)	Se(1)−O(1)	1.675(2)
Pd(1)−O(2) × 2	2.019(2)	Se(1)−O(2)	1.673(2)
		Se(1)−O(3)	1.616(2)
		Se(1)−O(4)	1.617(2)
Angles (deg)			
O(1)−Pd(1)−O(1′)	180	O(1)−Se(1)−O(2)	105.2(1)
O(1)−Pd(1)−O(2)	94.52(8)	O(1)−Se(1)−O(3)	111.2(1)
O(1)−Pd(1)−O(2′)	85.48(8)	O(1)−Se(1)−O(4)	109.4(1)
O(1′)−Pd(1)−O(2)	85.48(8)	O(2)−Se(1)−O(3)	104.5(1)
O(1′)−Pd(1)−O(2′)	94.52(8)	O(2)−Se(1)−O(4)	112.6(1)
O(2)−Pd(1)−O(2′)	180	O(3)−Se(1)−O(4)	113.7(1)

at 807, 730, 672, 621, and 591 cm^{-1} are attributable to the vibrational modes of SeO_3^{2-}.[50] Four sharp bands occur at 828, 786, 722, and 675 cm^{-1} in the IR spectrum of $PdSe_2O_5$ are due to the stretching vibrations of Se−O bonds within the $Se_2O_5^{2-}$ anions.[22,29] The vibration bands of SeO_4^{2-} in $Na_2Pd(SeO_4)_2$ are found at 882, 869, 861, 846, and 832 cm^{-1}, and match well with the previously reported vibrational data for selenate.[51]

Thermal Analysis. The thermal behavior of selenites and selenates is of interest because there are multiple mechanisms of decomposition including loss of oxygen by selenate and decomposition of the selenate and selenite anions to yield SeO_2.[50,52] $PdSeO_3$ and $PdSe_2O_5$ exhibit similar thermal properties. Both of them show a broad endothermic peak in the temperature ranges of 350−560 °C in their DSC thermograms. The composition of the final residue for the above two compounds is pure PdO, which is identified by powder X-ray diffraction. While in the DSC thermogram of $Na_2Pd(SeO_4)_2$, there are two endothermic peaks centered at 310 and 450 °C, respectively. The small and sharp endothermic peak occurs at 310 °C is due to the loss of O_2 during the decomposition of SeO_4^{2-} to SeO_3^{2-}. The second strong and broad endothermic peak in the temperature range of 360−550 °C is attributated to the loss SeO_2 from SeO_3^{2-}, which is similar to the thermal behavior of $PdSeO_3$ and $PdSe_2O_5$. The composition of the final residue is identified as pure PdO by powder X-ray diffraction.

Conclusions

In this report we have detailed the syntheses, structures, vibrational spectroscopy, and thermal behavior of three new Pd(II) compounds containing oxoanions of selenium. What makes these compounds unusual is the presence of a square planar metal center, which has been previously known primarily from Au(III) compounds with different compositions and structures, e.g., $Au_2(SeO_3)_2(Se_2O_5)$[33] and $Au_2(SeO_3)_2(SeO_4)$.[53] Both of these aforementioned compounds are layered, whereas both $PdSe_2O_5$ and $Na_2Pd(SeO_4)_2$ are one-dimensional. The presence of the lone-pair of electrons on the Se(IV) centers may lead to the low-dimensional structures observed for $PdSeO_3$ and $PdSe_2O_5$. Both of these compounds are centrosymmetric despite the presence of the lone-pair of electrons.

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Supporting Information Available: X-ray crystallographic files in CIF format for $PdSeO_3$, $PdSe_2O_5$, and $Na_2Pd(SeO_4)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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