ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

The Polyoxo-22-palladate(II), $[Na_2Pd^{II}_{22}O_{12}(As^{V}O_4)_{15}(As^{V}O_3OH)]^{25-}$

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I. General methods and materials.

The reagents were used as purchased without further purification. $Pd(NO_3)_2$ was donated by Johnson Matthey Plc. Elemental analysis was performed by Service Central d'Analyze, Solaize, France. The crystal water content was determined by thermogravimetric analysis (TGA) on a TA Instruments Q 600 device in 100 μL alumina pans, under a 100 mL/min N_2 flow and with a heating rate of 5 ºC min^{-1}. Infrared spectra were recorded on KBr disks using a Nicolet-Avatar 370 spectrometer.

II. X-ray Crystallography.

Crystal data for the **Na-1** structure was collected on a Bruker Kappa X8 APEX CCD single-crystal diffractometer equipped with a sealed Mo tube and graphite monochromator (λ = 0.71073 Å). The crystal was mounted on a Hampton cryoloop with light oil to prevent water loss. The SHELX software package (Bruker) was used to solve and refine the structure.[1] Absorption corrections were applied empirically using the SADABS program.[2] The structure was solved by direct methods and refined by the full-matrix least-squares method minimization of ($\Sigma w(F_0 - F_c)^2$) with anisotropic thermal parameters for heavy (Pd, As, Na) atoms. The hydrogen atoms of the crystal water molecules were not located. The relative site occupancy factors for the disordered positions of sodium countercations and oxygen atoms of crystallization waters were refined in an isotropic approximation and then fixed at the obtained values and refined normally.

The number of crystallization water molecules found by X-ray investigation was slightly higher than that determined by elemental and thermogravimetric analyses (67 *vs* 60 and 59, respectively). This fact could be easily explained by partial loss of crystal waters when drying the samples for the bulk material analyses while the single crystal for the XRD measurements was taken directly from the mother liquid and then frozen under nitrogen flow on the diffractometer. For the overall consistency the exact numbers of the crystal water molecules in **Na-1** determined by elemental analysis and TGA on the bulk crystalline material (ca. 60) were used throughout the paper and in the CIF file.

The high value for R_{int} on merging the data compared to R_{sigma} (0.1561 *cf.* 0.1001) together with several violations of systematic absences are indicative of the crystals of **Na-1** having at least one "friend", especially as structure solution and refinement in lower symmetry space groups (*P*1) did not yield an improved model. As we were unable to discern any pattern in the list of reflections for which $F_{obs} \gg F_{calc}$, we were not able to systematically remove composite reflections. Additional crystallographic data are summarized in Table S1.

III. Bond valence sum calculations

Bond valence sum (BVS) calculations[3,4] confirm the oxidation states of +2 ,+5 and +1 for the Pd, As and Na centers in **1**, respectively. The BVS values for the terminal oxygen atoms associated with the arsenic(V) centers (see Table S2) of the first and second structural types (see main text for details) suggest a presence of a proton which is disordered over these positions. The monoprotonation of polyanion **1** is in agreement with elemental analysis data for **Na-1** as well as with the number of Na^+ countercations located in the **Na-1** structure.

Table S1. Crystal data and structure refinement for **Na-1**

Empirical formula	$H_{121}As_{16}Na_{27}O_{136}Pd_{22}$
Formula weight, g/mol	6458.22
Crystal system	Triclinic
Space group	*P*-1
a, Å	15.342(3)
b, Å	22.377(4)
c, Å	24.311(5)
α, °	78.932(11)
β, °	86.739(10)
γ, °	86.527(10)
Volume, Å^3	8167(3)
Z	2
D_{calc}, g/cm^3	2.626
Absorption coefficient, mm^{-1}	5.757
F(000)	6092
Crystal size, mm	0.03 × 0.10 × 0.13
Theta range for data collection, °	1.55 – 24.11
Completeness to Θ_{max}, %	93.1
Index ranges	$-17 \le h \le 17$, $-25 \le k \le 25$, $-27 \le l \le 27$
Reflections collected	191435
Independent reflections	24186
R_{int}	0.1561
Observed ($I > 2\sigma(I)$)	15609
Absorption correction	Semi-empirical from equivalents
T_{min} / T_{max}	0.6216 / 0.8417
Data / restraints / parameters	24186 / 60 / 1228
Goodness-of-fit on F^2	1.064
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	R_1 = 0.0769, wR_2 = 0.1914
R_1,[a] wR_2[b] (all data)	R_1 = 0.1263, wR_2 = 0.2263
Largest diff. peak and hole, e. Å^{-3}	4.343 and –1.946

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. BVS values for the oxygen atoms of **1** in the crystal structure of **Na-1**

μ_4-O (Na, 3 Pd)	BVS	μ_4-O (Na, 2 Pd, As-III)	BVS	μ_2-O (Pd, , As-I/ As-III)	BVS
O1	2.03	O11T	1.32	O3D0	1.81
O2	2.06	O13T	1.28	O3D1	1.96
O3	2.07	O14T	1.56	O3A3	1.92
O5	2.05	O15T	1.30	O3A4	1.94
O6	2.06	O_t (As-II)	BVS	O4A1	1.66
O7	2.05			O4D1	1.86
O9	2.01	O8T1	1.38	O4D2	1.93
O10	2.09	O8T2	1.23	O4A4	1.76
O11	2.10	O16T	1.33	O5A2	1.81
O13	2.08	O16H	1.30	O5A5	1.73
O14	2.04	μ_2-O (Pd, As-I/ As-III)	BVS	O5A6	1.70
O15	2.05			O5A7	1.67
μ_4-O (Na, 2 Pd, As-III)	BVS	O0A2	1.85	O5A9	1.73
		O0A3	1.85	O6A3	1.64
O4	2.25	O0A6	1.80	O6A4	1.69
O8	2.31	O0A9	1.75	O6A6	1.65
O12	2.21	O1A0	1.69	O6A7	1.65
O16	2.31	O1A1	1.61	O7A4	1.77
O_t (As-I)	BVS	O1A2	1.70	O7A7	1.85
		O1A3	2.01	O7A8	1.74
O1T	1.24	O1A4	1.86	O8A1	1.83
O2T	1.25	O1A7	1.73	O8A5	1.72
O3T	1.23	O2A0	1.77	O8A6	1.72
O5T	1.35	O2A1	1.79	O8A8	1.88
O6T	1.34	O2A2	1.82	O9A1	1.71
O7T	1.34	O2A3	1.81	O9A3	1.64
O9T	1.26	O2A5	1.71	O9A5	1.67
O10T	1.26	O2A9	1.73	O9A6	1.81

IV. Thermogravimetric analysis for Na-1 from room temperature to 1000 °C under N_2 atmosphere.

The TGA curve of **Na-1** (Figure S1) exhibits a sharp weight loss in the temperature range from 25 to 205 °C corresponding to the release of about 51 water molecules of crystallization per formula unit (14.22 % calculated *vs* 14.15 % observed). It is followed by a smooth weight loss continued till ~500 °C that could be attributed to the release of more tightly bound (to Na^+ countercations) water molecules (total weight loss 16.5 %, 16.7 % calculated for the loss of 60 H_2O molecules per formula unit). After that the weight remains unchanged till 720 °C. The total weight loss observed at 1000 °C is 21.0 %.

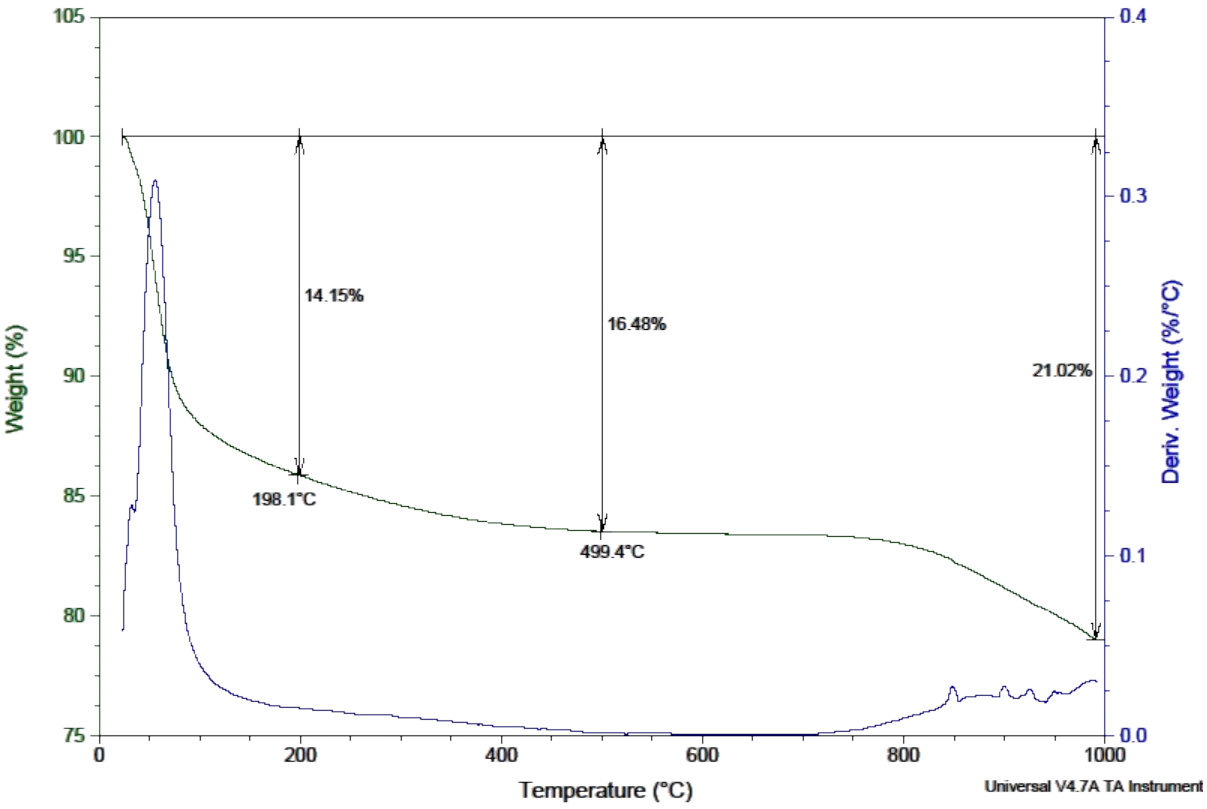

Figure S1. TG (dark-green) and DSC (blue) curves for **Na-1**.

V. FT-IR spectrum of Na-1.

The IR spectrum of **Na-1** (Figure S2, red) is very similar to that of Na-$Pd_{13}As_8$ (Figure S2, blue) besides different intensity of some of the vibration bands as well as the absence of a vibration mode at 662 cm^{-1}. The bands at 866 and 769 cm^{-1} correspond to vibrations of As–O bonds of the arsenate groups in **1** while the bands at 662 and 536 cm^{-1} belong to vibrations of Pd–O bonds.

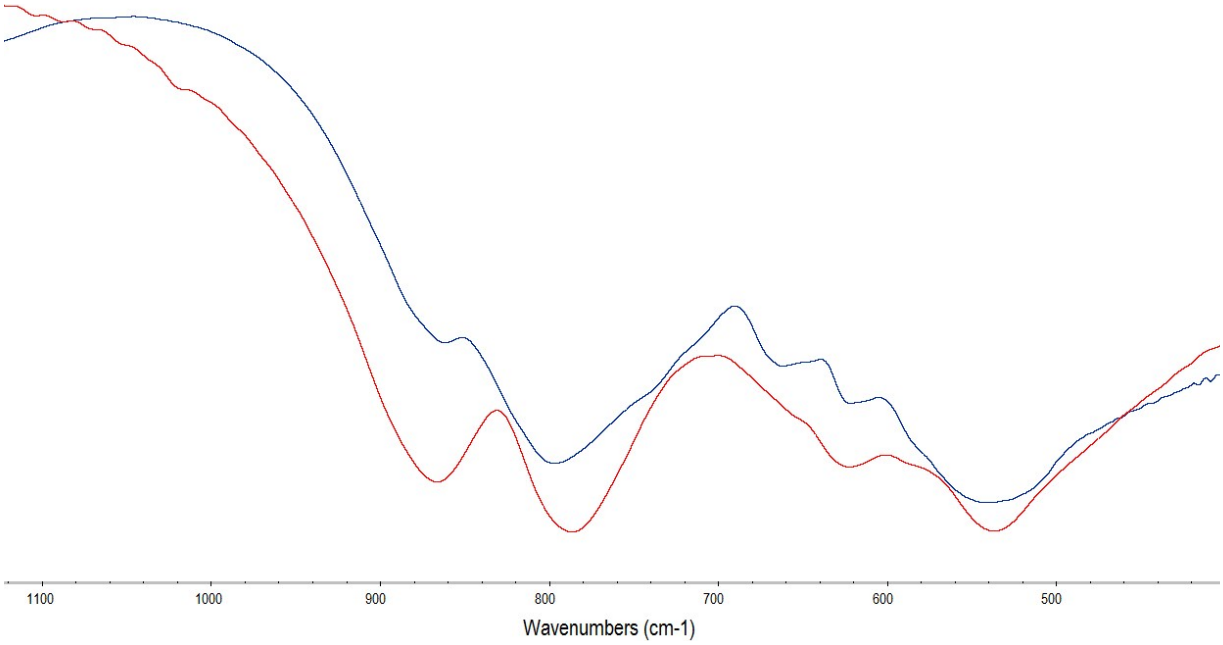

Figure S2. FT-IR spectrum of **Na-1** (red) in comparison with the FT-IR spectrum of Na-$Pd_{13}As_8$ (blue).

VI. Theoretical studies

a) Computational details

Amsterdam density functional code (ADF2013)[5] was used to perform the calculations. We used Slater basis sets of different quality and with large frozen cores (FC) for the different type of atoms. Triple-zeta basis sets with one polarization function (TZP) were used for Pd (frozen [Kr]) and As ([Ar]3d^{10}frozen), and double-zeta basis sets with one polarization function (DZP) were used for O ([He]frozen) and Na ([Ne] frozen).[6] Scalar relativistic corrections were taken into account within the zero-order regular approximation (ZORA).[7] Solvent effects were modeled by using the conductor-like screening model (COSMO) with the parameters for water (ε = 78.39; solvent radius = 1.93 Å).[8] The calculations were performed using the GGA Becke exchange[9] and Perdew 86 correlation[10] (BP) functional. Calculations of the first excitation by time-dependent DFT[11] of **1** and **2** were performed at the same theoretical level.

b) Molecular models, structural and electronic properties

The DFT-optimized structures of $[Na_2Pd_{22}As_{16}O_{76}]^{26-}$ (**1**) and $[Pd_{13}As_8O_{40}]^{14-}$ (**2**) are depicted in Figure S3. The symmetry of the polyanions, C_{2h} for **1** and D_{2h} for **2**, was considered in the calculations.

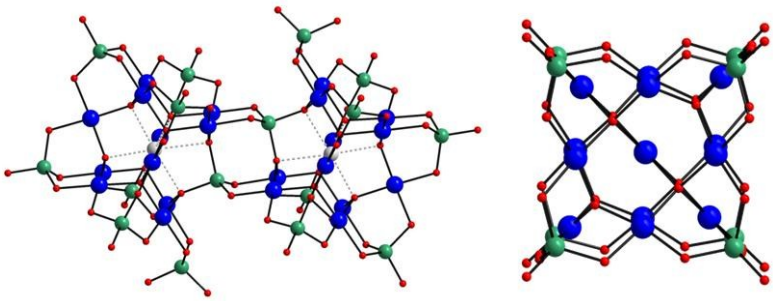

Figure S3. Ball and stick representation of the bare polyanion models **1** (left) and **2** (right). Color code: Pd blue, O red, As green, Na grey.

Table S3. Characteristic bond lengths and distances in the structures of **1** and **2** as optimized at the BP/ZORA-scalar/TZP-FC/COSMO theoretical level, and as determined experimentally by single crystal X-ray diffraction.

Approach		Bond lengths [pm]			
	Model	Na-O	As-O_t	As-Ob	Pd-O
Theory	1	239.8-264.5	175.4-177.3	178.17-188.7	201.44-210.69
Experiment[12]		228.4 -263.3	165.6-169.1	167.7-174.5	195.3-208.5
Theory	2		169.73-171.74	174.30-178.68	199.14-210.68
Experiment[12]			165.3-176.4	169.4-172.0	195.5-209.0

Table S4. DFT calculated energies of the HOMO (E_{HOMO}), the LUMO (E_{LUMO}) and the gap energy $\Delta E_{HOMO\text{-}LUMO}$ for **1** and **2**.

Structure	Theoretical level:BP/ZORA-scalar/TZP-FC/COSMO		
	E_{HOMO} [eV]	E_{LUMO} [eV]	$\Delta E_{HOMO\text{-}LUMO}$[eV]
1	-4.05	-3.21	0.83
2	-4.27	-3.26	1.01

Qualitative TD-DFT calculations revealed that the first allowed excitation for **1** and **2** corresponds to transitions between the frontier orbitals with a mixed character, involving *d-d* (Pd→Pd) and metal-to-ligand (Pd→O) transitions (Table S5 and Table S6).

Table S5. The TD-DFT calculated energies of the first excitation, the corresponding oscillator strength, *f*, and the nature of the dominant transition for **1** and **2**.

Structure	Theoretical level: BP/ZORA-scalar/TZP-FC/COSMO		
	Energy [eV]	Real ***f***	Transition [%]
1	0.84	$1.3 \cdot 10^{-3}$	HOMO → LUMO (99.6 %)
2	1.06	$1.6 \cdot 10^{-3}$	HOMO-1 → LUMO (89.9 %)

Table S6. Charge density distribution over different atoms of the molecular orbitals participating in the dominant transitionsin **1** and **2**.

Theoretical level: BP/ZORA-scalar/TZP-FC/COSMO							
1	Charge distribution			**2**	Charge distribution		
	Pd [%]	O [%]	As [%]		Pd [%]	O [%]	As [%]
HOMO	54.3	24.4	0.0	HOMO-1	73.2	22.8	0.0
LUMO	36.8	36.0	11.6	LUMO	60.0	31.9	1.0
$\Delta_{LUMO\text{-}HOMO}$	-17.5	11.5	11.6	$\Delta_{LUMO\text{-}HOMO\text{-}1}$	-13.1	9.1	1.0

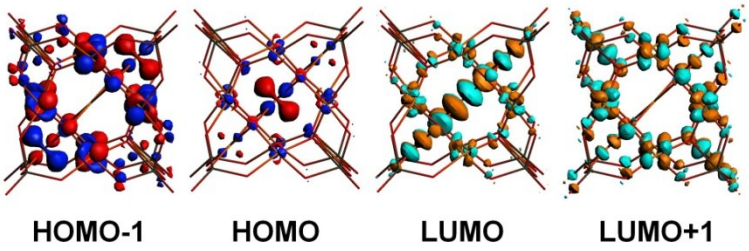

Figure S4. Distribution of the frontier orbitals in **2** plotted over a wireframe representation of the structure of **2**.

Table S7. Mulliken charge populations on the terminal and the μ_2-, μ_3- and μ_4-bridging oxygen atoms in **1** and **2**, as calculated at theBP/ZORA-scalar/TZP-FC/COSMO theoretical level.

Mullikencharge populations		
	1	**2**
O_t	-1.01 to -1.05	-0.99 to -1.02
μ_2-O	-0.84 to -0.93	-0.91 to -0.93
μ_4-O	-1.01 to -1.07	-1.08 to -1.10
μ_3-O		-1.11

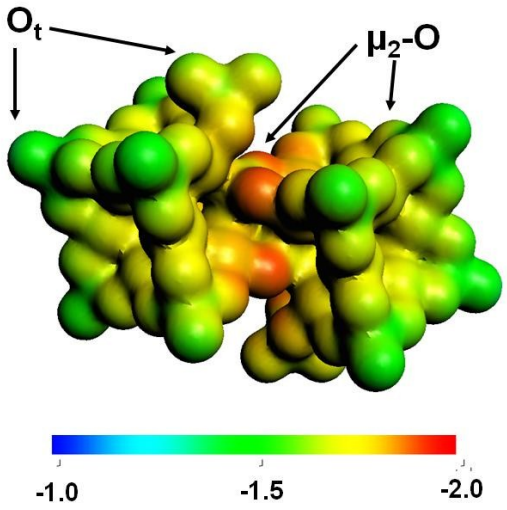

Figure S5. Molecular electrostatic potential plotted over a density isosurface of **1**. The red regions feature most negative (most basic) potentials. The position of the terminal oxo (O_t) and the bridging μ_2-O atoms is indicated.

c) Fragmentation pathways for 1 assuming heterolytic Pd-O bond dissociation

Two fragmentation pathways have been considered:

- **Pathway 1:** Fragmentation of **1** into two identical subunits :

$$[Na_2Pd_{22}As_{16}O_{76}]^{26-} \rightarrow 2\ [NaPd_{11}As_8O_{38}]^{13-} \qquad \text{Eq. S1}$$

- **Pathway 2:** Simultaneous loss of two μ_2-{AsO_4} groups:

$$[Na_2Pd_{22}As_{16}O_{76}]^{26-} \rightarrow [Na_2Pd_{22}As_{14}O_{68}]^{20-} + 2\ [AsO_4]^{3-} \qquad \text{Eq. S2}$$

These two pathways are illustrated in Figure S6. In both cases, four Pd-O bonds are broken simultaneously.

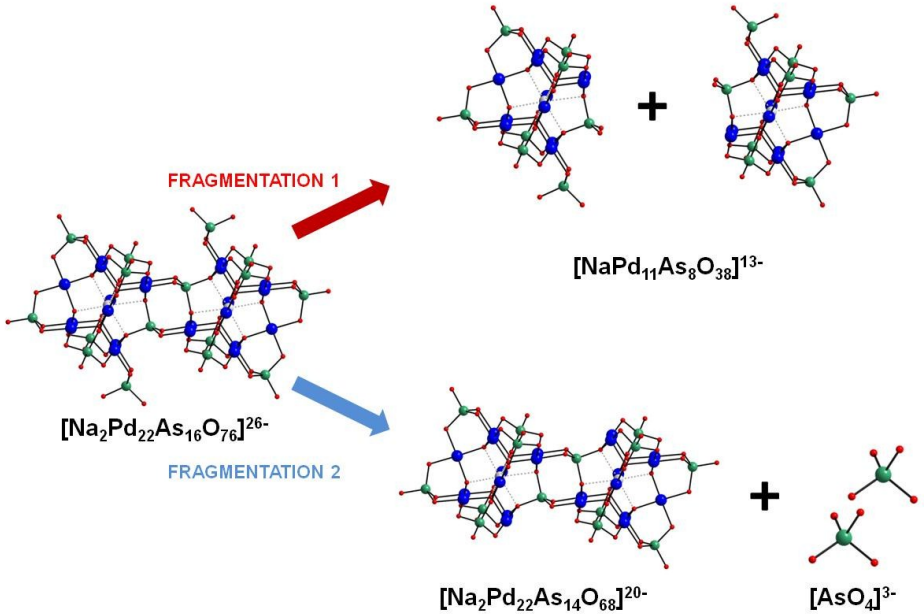

Figure S6. The two pathways for fragmentation of **1** considered in this study. Color code: Pd blue, O red, As green, Na grey.

Table S8. Calculated bonding energies, E_b, of polyanion**1** and the species obtained as a result of fragmentation of **1**, and energies of fragmentation ΔE corresponding to the assumed fragmentation pathways (see Eqs. 1 and 2, and Figure. S6).

Theoretical level: BP/ZORA-scalar/TZP-FC/COSMO/	
Model	$\boldsymbol{E}_b$[kcal·mol^{-1}]
$[Na_2Pd_{22}As_{16}O_{76}]^{26-}$	-16159.50
$[Na_2Pd_{22}As_{14}O_{68}]^{20-}$	-14275.02
$[NaPd_{11}As_8O_{38}]^{13-}$	-8074.85
$[AsO_4]^{3-}$	-929.04
Pathway	$\boldsymbol{\Delta E}$[kcal·mol^{-1}]
1	9.84
2	26.44

d) Optimized Cartesian coordinates [in Å]

Polyanion 1 (C_{2h})

Atom	X	Y	Z (Å)
Pd	3.74494870	2.91392887	-1.77209020
O	2.98050934	2.04495909	0.00000000
O	4.79816754	1.18839090	-2.01020848
O	2.62727979	4.65398257	-1.51291482
O	4.47840355	3.79146651	-3.49686879
Pd	3.74494870	2.91392887	1.77209020
As	1.24359172	1.40993325	0.00000000
Pd	4.16773295	-0.07213082	-3.47895961
Pd	6.82254839	1.35606647	-1.75115538
As	2.96752662	5.62644140	0.00000000
As	5.59101690	2.73739136	-4.48612361
O	4.79816754	1.18839090	2.01020848
O	2.62727979	4.65398257	1.51291482
O	4.47840355	3.79146651	3.49686879
O	1.61195018	-0.43608000	0.00000000
O	0.49786654	1.89692396	-1.54316298
O	0.49786654	1.89692396	1.54316298
O	3.56177588	-1.33711808	-1.99869366
O	3.52569662	-1.34336526	-5.03832903
O	4.77888563	1.20479597	-5.03316016
O	6.59486702	0.33016460	0.00000000
O	7.12041315	2.37459723	-3.57102917
O	8.90189938	1.56677758	-1.50779405
O	1.73889795	6.90512811	0.00000000
O	4.59694086	6.30915523	0.00000000
O	6.02504764	3.65183493	-5.92053134
Pd	4.16773295	-0.07213082	3.47895961
Pd	6.82254839	1.35606647	1.75115538
As	5.59101690	2.73739136	4.48612361
Pd	1.56676935	-1.57010050	-1.78172756
Pd	1.56676935	-1.57010050	1.78172756
Pd	-1.56676935	1.57010050	-1.78172756
Pd	-1.56676935	1.57010050	1.78172756
Pd	4.69133140	-3.02889816	-1.74373447
As	2.86109314	-2.94216626	-4.49190069
Pd	7.30553512	-1.58511752	0.00000000
As	9.57938372	0.80568512	0.00000000
O	3.56177588	-1.33711808	1.99869366
O	4.77888563	1.20479597	5.03316016
O	3.52569662	-1.34336526	5.03832903
O	7.12041315	2.37459723	3.57102917
O	8.90189938	1.56677758	1.50779405
O	6.02504764	3.65183493	5.92053134
O	1.35390203	-2.72920318	-3.48332291
O	-0.49786654	-1.89692396	-1.54316298
O	-0.49786654	-1.89692396	1.54316298
O	1.35390203	-2.72920318	3.48332291
O	-1.61195018	0.43608000	0.00000000

O	-3.56177588	1.33711808	-1.99869366
O	-1.35390203	2.72920318	-3.48332291
O	-3.56177588	1.33711808	1.99869366
O	-1.35390203	2.72920318	3.48332291
O	5.35467404	-2.20899579	0.00000000
O	4.09939177	-3.89883003	-3.56792676
O	5.82325308	-4.78032553	-1.50957857
O	2.40820906	-3.86546895	-5.91303963
O	9.32104514	-0.99582130	0.00000000
O	8.09449333	-3.53910859	0.00000000
O	11.31398937	1.09012122	0.00000000
Pd	4.69133140	-3.02889816	1.74373447
As	2.86109314	-2.94216626	4.49190069
As	-1.24359172	-1.40993325	0.00000000
Pd	-4.16773295	0.07213082	-3.47895961
Pd	-4.69133140	3.02889816	-1.74373447
As	-2.86109314	2.94216626	-4.49190069
Pd	-4.16773295	0.07213082	3.47895961
Pd	-4.69133140	3.02889816	1.74373447
As	-2.86109314	2.94216626	4.49190069
As	6.83785446	-4.85290850	0.00000000
O	5.82325308	-4.78032553	1.50957857
O	4.09939177	-3.89883003	3.56792676
O	2.40820906	-3.86546895	5.91303963
O	-2.98050934	-2.04495909	0.00000000
O	-4.79816754	-1.18839090	-2.01020848
O	-4.77888563	-1.20479597	-5.03316016
O	-3.52569662	1.34336526	-5.03832903
O	-5.35467404	2.20899579	0.00000000
O	-5.82325308	4.78032553	-1.50957857
O	-4.09939177	3.89883003	-3.56792676
O	-2.40820906	3.86546895	-5.91303963
O	-4.79816754	-1.18839090	2.01020848
O	-3.52569662	1.34336526	5.03832903
O	-4.77888563	-1.20479597	5.03316016
O	-4.09939177	3.89883003	3.56792676
O	-5.82325308	4.78032553	1.50957857
O	-2.40820906	3.86546895	5.91303963
O	7.67055279	-6.39950273	0.00000000
Pd	-3.74494870	-2.91392887	1.77209020
Pd	-3.74494870	-2.91392887	-1.77209020
Pd	-6.82254839	-1.35606647	-1.75115538
As	-5.59101690	-2.73739136	-4.48612361
Pd	-7.30553512	1.58511752	0.00000000
As	-6.83785446	4.85290850	0.00000000
Pd	-6.82254839	-1.35606647	1.75115538
As	-5.59101690	-2.73739136	4.48612361
O	-2.62727979	-4.65398257	1.51291482
O	-4.47840355	-3.79146651	3.49686879
O	-2.62727979	-4.65398257	-1.51291482
O	-4.47840355	-3.79146651	-3.49686879

O	-6.59486702	-0.33016460	0.00000000
O	-7.12041315	-2.37459723	-3.57102917
O	-8.90189938	-1.56677758	-1.50779405
O	-6.02504764	-3.65183493	-5.92053134
O	-9.32104514	0.99582130	0.00000000
O	-8.09449333	3.53910859	0.00000000
O	-7.67055279	6.39950273	0.00000000
O	-7.12041315	-2.37459723	3.57102917
O	-8.90189938	-1.56677758	1.50779405
O	-6.02504764	-3.65183493	5.92053134
As	-2.96752662	-5.62644140	0.00000000
As	-9.57938372	-0.80568512	0.00000000
O	-1.73889795	-6.90512811	0.00000000
O	-4.59694086	-6.30915523	0.00000000
O	-11.31398937	-1.09012122	0.00000000
Na	4.23532736	-0.09639789	0.00000000
Na	-4.23532736	0.09639789	0.00000000

Polyanion 2 (D_{2h})

Atom	X	Y	Z (Å)
Pd	1.68491609	-2.41071127	1.75133312
O	1.62733563	-1.33802614	0.00000000
Pd	-1.68491609	2.41071127	-1.75133312
Pd	-1.68491609	-2.41071127	1.75133312
O	-1.52776411	3.50067363	3.46927559
As	4.41631834	-3.00486305	0.00000000
O	1.52776411	-3.50067363	-3.46927559
O	-1.62733563	1.33802614	0.00000000
O	-1.52776411	-3.50067363	-3.46927559
O	-0.00000000	1.47541077	5.08621174
O	-0.00000000	1.61570052	-2.45616693
Pd	-0.00000000	0.00000000	3.68158964
O	-0.00000000	1.61570052	2.45616693
As	-4.41631834	3.00486305	0.00000000
O	-0.00000000	-1.47541077	-5.08621174
Pd	-1.68491609	2.41071127	1.75133312
O	-0.00000000	1.47541077	-5.08621174
O	4.77745383	-1.29970669	0.00000000
O	-4.77745383	1.29970669	0.00000000
Pd	-3.16841161	0.00000000	0.00000000
O	3.47438973	3.41522836	-1.41847227
As	4.41631834	3.00486305	0.00000000
O	4.77745383	1.29970669	0.00000000
Pd	1.68491609	2.41071127	-1.75133312
O	3.47438973	-3.41522836	1.41847227
As	-4.41631834	-3.00486305	0.00000000
O	-4.77745383	-1.29970669	0.00000000
Pd	3.16841161	0.00000000	0.00000000
As	-0.00000000	3.07559445	4.29104686
Pd	-1.68491609	-2.41071127	-1.75133312
As	-0.00000000	-3.07559445	-4.29104686
O	-3.47438973	3.41522836	-1.41847227
O	-3.47438973	-3.41522836	1.41847227
As	-0.00000000	-3.07559445	4.29104686
O	3.47438973	3.41522836	1.41847227
O	-0.00000000	-1.47541077	5.08621174
Pd	-0.00000000	0.00000000	-3.68158964
O	-0.00000000	-4.15888894	5.62364297
Pd	1.68491609	-2.41071127	-1.75133312
O	1.52776411	-3.50067363	3.46927559
O	-3.47438973	-3.41522836	-1.41847227
O	-1.52776411	3.50067363	-3.46927559
O	-5.86268599	-3.89307573	0.00000000
O	-3.47438973	3.41522836	1.41847227
O	1.52776411	3.50067363	3.46927559
O	-0.00000000	4.15888894	5.62364297
O	-1.52776411	-3.50067363	3.46927559
O	-0.00000000	-1.61570052	2.45616693
As	-0.00000000	3.07559445	-4.29104686
O	-0.00000000	-1.61570052	-2.45616693

O	1.62733563	1.33802614	0.00000000
Pd	-0.00000000	0.00000000	0.00000000
O	1.52776411	3.50067363	-3.46927559
O	5.86268599	-3.89307573	0.00000000
O	-5.86268599	3.89307573	0.00000000
O	-0.00000000	-4.15888894	-5.62364297
O	5.86268599	3.89307573	0.00000000
Pd	1.68491609	2.41071127	1.75133312
O	-1.62733563	-1.33802614	0.00000000
O	3.47438973	-3.41522836	-1.41847227
O	-0.00000000	4.15888894	-5.62364297

$[Na_2Pd_{22}As_{14}O_{68}]^{20-}(C_{2h})$

Atom	X	Y	Z (Å)
Pd	3.67612291	2.69775923	-1.82807557
O	2.88233945	2.03936695	-0.00000000
O	4.80897425	1.06389321	-2.00897609
O	-5.94251472	-3.61134917	5.94768683
O	4.34711007	3.62010854	-3.52569807
Pd	3.67612291	2.69775923	1.82807557
As	1.17556078	1.34407728	-0.00000000
Pd	4.17696775	-0.15922755	-3.48747436
Pd	6.79399442	1.38013111	-1.74713879
O	-11.25085876	-1.25538793	-0.00000000
As	5.55008834	2.66974500	-4.52700975
O	4.80897425	1.06389321	2.00897609
Na	4.22138660	-0.18123204	-0.00000000
O	4.34711007	3.62010854	3.52569807
O	1.54352123	-0.49466767	-0.00000000
O	0.47995870	1.92047468	-1.53893797
O	0.47995870	1.92047468	1.53893797
O	3.56982928	-1.40746332	-2.00233884
O	3.59951058	-1.44965216	-5.00059369
O	4.81039506	1.09560806	-5.03917992
O	6.58993120	0.36382819	-0.00000000
O	7.05686226	2.39879267	-3.55705676
O	8.82549309	1.64753147	-1.50509823
Na	-4.22138660	0.18123204	-0.00000000
As	-9.53286630	-0.90563171	-0.00000000
O	5.94251472	3.61134917	-5.94768683
Pd	4.17696775	-0.15922755	3.48747436
Pd	6.79399442	1.38013111	1.74713879
As	5.55008834	2.66974500	4.52700975
Pd	1.58710947	-1.62726547	-1.78704349
Pd	1.58710947	-1.62726547	1.78704349
Pd	-1.58710947	1.62726547	-1.78704349
Pd	-1.58710947	1.62726547	1.78704349
Pd	4.73787519	-3.06579372	-1.72417786
As	2.90919288	-3.04078804	-4.45137250
Pd	7.32264585	-1.53770508	-0.00000000
As	9.53286630	0.90563171	-0.00000000
O	3.56982928	-1.40746332	2.00233884
O	4.81039506	1.09560806	5.03917992
O	3.59951058	-1.44965216	5.00059369
O	7.05686226	2.39879267	3.55705676
O	8.82549309	1.64753147	1.50509823
O	5.94251472	3.61134917	5.94768683
O	1.39576554	-2.79466987	-3.46245687
O	-0.47995870	-1.92047468	-1.53893797
O	-0.47995870	-1.92047468	1.53893797
O	1.39576554	-2.79466987	3.46245687
O	-1.54352123	0.49466767	-0.00000000
O	-3.56982928	1.40746332	-2.00233884
O	-1.39576554	2.79466987	-3.46245687

O	-3.56982928	1.40746332	2.00233884
O	-1.39576554	2.79466987	3.46245687
O	5.40367343	-2.22710504	-0.00000000
O	4.13096971	-3.97898519	-3.50399072
O	5.91595016	-4.76255757	-1.49889750
O	2.45918213	-3.96053891	-5.87116115
O	9.30867944	-0.89228372	-0.00000000
O	8.14930715	-3.45113061	-0.00000000
O	11.25085876	1.25538793	-0.00000000
Pd	4.73787519	-3.06579372	1.72417786
As	2.90919288	-3.04078804	4.45137250
As	-1.17556078	-1.34407728	-0.00000000
Pd	-4.17696775	0.15922755	-3.48747436
Pd	-4.73787519	3.06579372	-1.72417786
As	-2.90919288	3.04078804	-4.45137250
Pd	-4.17696775	0.15922755	3.48747436
Pd	-4.73787519	3.06579372	1.72417786
As	-2.90919288	3.04078804	4.45137250
As	6.94318279	-4.80825067	-0.00000000
O	5.91595016	-4.76255757	1.49889750
O	4.13096971	-3.97898519	3.50399072
O	2.45918213	-3.96053891	5.87116115
O	-2.88233945	-2.03936695	-0.00000000
O	-4.80897425	-1.06389321	-2.00897609
O	-4.81039506	-1.09560806	-5.03917992
O	-3.59951058	1.44965216	-5.00059369
O	-5.40367343	2.22710504	-0.00000000
O	-5.91595016	4.76255757	-1.49889750
O	-4.13096971	3.97898519	-3.50399072
O	-2.45918213	3.96053891	-5.87116115
O	-4.80897425	-1.06389321	2.00897609
O	-3.59951058	1.44965216	5.00059369
O	-4.81039506	-1.09560806	5.03917992
O	-4.13096971	3.97898519	3.50399072
O	-5.91595016	4.76255757	1.49889750
O	-2.45918213	3.96053891	5.87116115
O	7.82770992	-6.32413613	-0.00000000
Pd	-3.67612291	-2.69775923	1.82807557
Pd	-3.67612291	-2.69775923	-1.82807557
Pd	-6.79399442	-1.38013111	-1.74713879
As	-5.55008834	-2.66974500	-4.52700975
Pd	-7.32264585	1.53770508	-0.00000000
As	-6.94318279	4.80825067	-0.00000000
Pd	-6.79399442	-1.38013111	1.74713879
As	-5.55008834	-2.66974500	4.52700975
O	-7.05686226	-2.39879267	3.55705676
O	-4.34711007	-3.62010854	3.52569807
O	-8.82549309	-1.64753147	1.50509823
O	-4.34711007	-3.62010854	-3.52569807
O	-6.58993120	-0.36382819	-0.00000000
O	-7.05686226	-2.39879267	-3.55705676

O	-8.82549309	-1.64753147	-1.50509823
O	-5.94251472	-3.61134917	-5.94768683
O	-9.30867944	0.89228372	-0.00000000
O	-8.14930715	3.45113061	-0.00000000
O	-7.82770992	6.32413613	-0.00000000

$[NaPd_{11}As_8O_{38}]^{13-}(C_s)$

Atom	X	Y	Z (Å)
O	-1.29636183	-4.99481020	-0.58751580
O	1.22335905	-5.02330152	0.70264548
O	2.14779178	-0.00000000	-1.10417057
O	4.68556040	-1.50792354	-1.49271848
O	3.78550923	-3.54839296	0.22738094
O	3.71301341	-5.91552599	1.90865623
O	-1.29637540	2.01332303	-0.59504775
O	1.22335905	5.02330152	0.70264548
O	-1.29636183	4.99481020	-0.58751580
O	3.78550923	3.54839296	0.22738094
O	4.68556040	1.50792354	-1.49271848
O	3.71301341	5.91552599	1.90865623
Na	-0.04013754	0.00000000	-0.06210763
Pd	-2.98782538	1.75040528	0.48801722
Pd	-2.98782538	-1.75040528	0.48801722
Pd	-1.43315381	-1.73888874	-2.61340922
As	-2.84114589	-4.43966422	-1.37981576
Pd	1.53151597	-0.00000000	-3.04910277
As	4.77813174	-0.00000000	-2.50985856
Pd	-1.43315381	1.73888874	-2.61340922
As	-2.84114589	4.43966422	-1.37981576
O	-4.69631736	1.50510076	1.64211604
O	-3.87199529	3.46198577	-0.24165941
O	-4.69631736	-1.50510076	1.64211604
O	-3.87199529	-3.46198577	-0.24165941
O	-0.39648098	-0.00000000	-2.40591975
O	-2.48926518	-3.51999293	-2.90228157
O	-1.60437678	-1.50240801	-4.67930192
O	-3.75574813	-5.87634828	-1.80127594
O	0.96942964	-0.00000000	-5.05198630
O	3.49267504	-0.00000000	-3.78556642
Pd	1.37213033	-1.77573068	2.58062444
Pd	1.37213033	1.77573068	2.58062444
O	-2.11080758	0.00000000	1.26017984
O	-1.29637540	-2.01332303	-0.59504775
O	6.34846928	-0.00000000	-3.29289446
O	-2.48926518	3.51999293	-2.90228157
O	-1.60437678	1.50240801	-4.67930192
O	-3.75574813	5.87634828	-1.80127594
As	-5.70464512	0.00000000	1.39583899
As	-0.82559388	-0.00000000	-5.34326498
O	-6.85476429	0.00000000	2.74652755
O	-6.54075045	0.00000000	-0.16029410
As	-1.54999090	0.00000000	3.04632083
O	-1.90202002	-1.47529747	3.89738784
O	-1.90202002	1.47529747	3.89738784
Pd	-0.04255225	-3.47419678	0.04527829
O	0.33973423	0.00000000	2.77631713
O	1.20129563	-1.97922884	0.59790198
O	2.49958057	-3.46612367	2.89085188

O	1.20129563	1.97922884	0.59790198
O	2.49958057	3.46612367	2.89085188
Pd	2.93795603	-1.73769936	-0.41343506
As	2.80414344	-4.50193727	1.41745605
Pd	-0.04255225	3.47419678	0.04527829
Pd	2.93795603	1.73769936	-0.41343506
O	-1.06999457	-0.00000000	-7.08405634
As	2.80414344	4.50193727	1.41745605

$(AsO_4)^{3-}$ (T_d)

Atom	X	Y	Z (Å)
As	0.00000000	0.00000000	0.00000000
O	1.03720704	-1.03720704	1.03720704
O	1.03720704	1.03720704	-1.03720704
O	-1.03720704	1.03720704	1.03720704
O	-1.03720704	-1.03720704	-1.03720704

e) Calculated IR spectrum of polyanion 1.

The calculated infrared spectrum of **1** (Figure S7) shows good qualitative agreement with the experimental spectrum (Figure S3). The calculated IR underestimates the position of the stretching modes, which is most probably a result of neglecting the counter cations surrounding the highly negative polyanion in the crystal structure. Interpretation of the four characteristic modes is provided in Table S9.

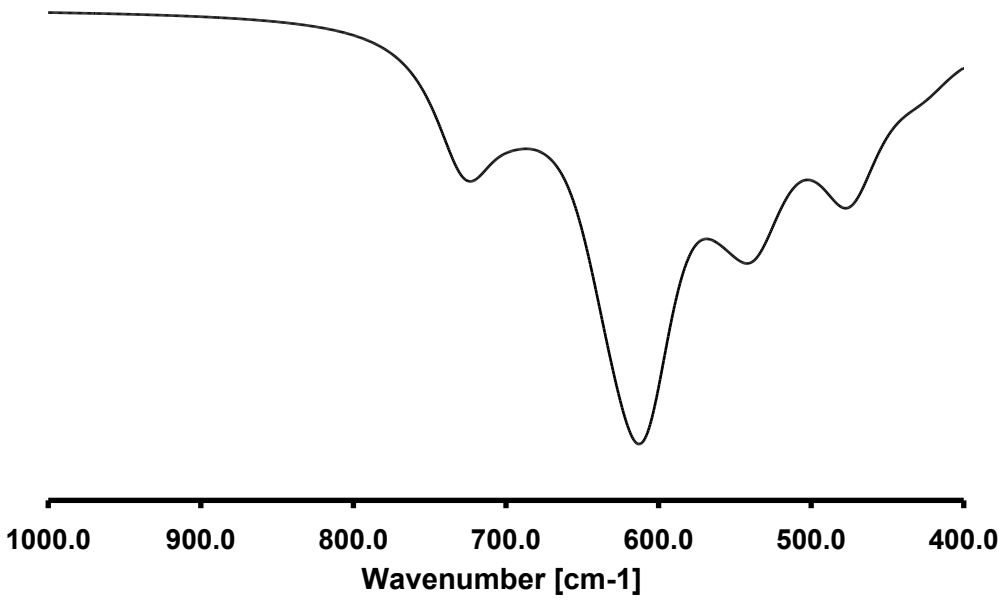

Figure S7: Calculated spectrum of bare **1** on BP/ZORA-Scalar/TZP/COSMO/FC level and convoluted with a factor of 50 cm^{-1}.

Table S9: Approximate assignment of the characteristic normal modes and the respective wavenumbers as calculated (BP/ZORA-Scalar/TZP/COSMO/FC) for bare **1**.

Mode	Experimental [cm^{-1}]	Calculated [cm^{-1}]	Assignment
1	871	732	$\nu(As–O_t)$
2	790	619	$\nu(As–O_{Pd})$
3	627	552	$\nu(Pd–O_{As})$
4	543	483	$\nu(As–O_{Pd})$

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