

ASSOCIATED CONTENT

Supporting Information

Mixed-Valent Palladium(IV/II)-Oxoanion, $[\text{Pd}^{\text{IV}}\text{O}_6\text{Pd}^{\text{II}}_6((\text{CH}_3)_2\text{AsO}_2)_6]^{2-}$

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Analytical Techniques

Fourier Transform Infrared (FT-IR) spectral data were recorded on a Nicolet-Avatar 370 spectrometer in the range of 4000 - 400 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) was done using a TA Instruments Q600 device in the temperature range from room temperature to 500 $^{\circ}\text{C}$ utilizing a heating rate of 5 $^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere.

X-ray Photoelectron Spectroscopy

The as-prepared **Na-1** was dispersed in acetone and drop casted on a highly doped silicon wafer with a natural oxide layer. Once all the acetone was evaporated, the sample was introduced into an UHV chamber operated at a vacuum level of $\sim 10^{-9}$ mbar. The UHV chamber was equipped with a photoelectron spectrometer consisting of a hemispherical analyzer (Specs Phoebos 100) and a Mg/Al X-ray gun (Specs XR-50). For this experiment Mg K_{α} ($E = 1253.6$ eV) was used as a source of excitation and the analyzer was operated in fixed analyzer transmission mode with a pass energy of 30 eV. The measured XPS data was fitted with the CASA XPSTM software and the Shirley method was used to subtract the background.

ESI-mass spectrometry

High-resolution mass spectra were recorded using a Bruker Daltonics QTOF Impact HD mass spectrometer employing both negative and positive electrospray ionization modes. The QTOF Impact mass spectrometer (Bruker Daltonics) was fitted with an ESI source and external calibration was achieved with 10 mL of 0.1 M sodium formate solution. The instrument ion source and tubing were rinsed with methanol. The calibration was carried out using the enhanced quadratic calibration mode. All MS measurements were performed in both negative and positive ion modes. The samples were measured as direct infusions at a concentration of 100 $\mu\text{g/ml}$ in deionized water at a flow rate of 180 $\mu\text{l/min}$. The spectral simulations were carried out in Data Analysis 4.1 (Bruker Daltonics, Bremen).

Tandem mass spectrometry was carried out by isolating the precursor ion envelope with a width of 20 Da and applying a fragmentation energy of 2 eV.

Single Crystal X-Ray Diffraction

A single crystal of the title compound was mounted on a Hampton cryoloop (Hampton Research) using paratone-N oil and cooled under a stream of cold nitrogen (100 K). The data set was collected on a Bruker D8 SMART APEX II CCD diffractometer with kappa geometry (graphite monochromator, $\lambda_{\text{Mo } K_{\alpha}} = 0.71073$ Å) by using the APEX III software package.^{1a} The initial lattice parameters were determined by matrix scans. The reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT,^{1b} whereas multi-scan absorption corrections were performed using SADABS.^{1b} The space group

was identified based upon systematic absences and E-statistics, and the structures were solved using direct methods with the help of successive difference Fourier maps, and were refined using the APEX III software^{1a} and SHELXL-2018.^{1c} The H atoms of the dimethylarsinate methyl groups were placed in calculated positions and refined using a riding model, whereas non-hydrogen atoms were refined using anisotropic displacement parameters. The refinement was conducted by full-matrix least squares against $|F|$ using all data. The images of the crystal structure were generated by Diamond, version 3.2 (software copyright, Crystal Impact GbR) and PLATON.^{1d} Some of the lattice water molecules and counter cations were disordered and hence could not be located properly by XRD.^{1d} Single crystal data and structure refinement parameters are shown in Table S1. The cif file is provided free of charge by The Cambridge Crystallographic Data Centre (CCDC 2211787).

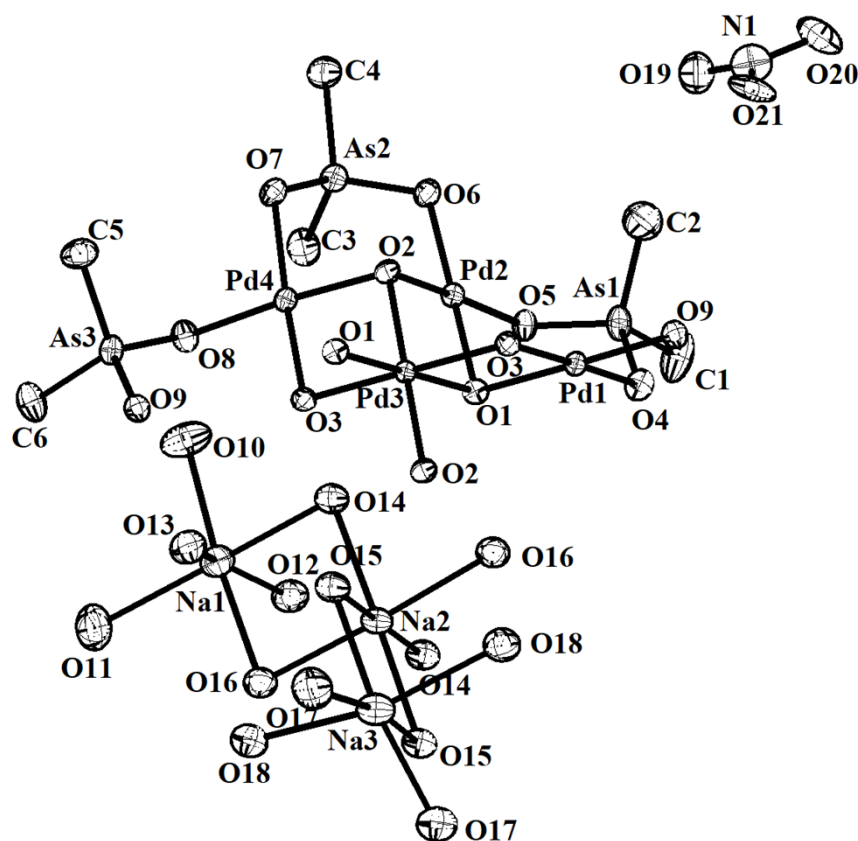


Figure S1. Ball and stick representation of the asymmetric unit of **Na-1** showing thermal ellipsoids (50%).

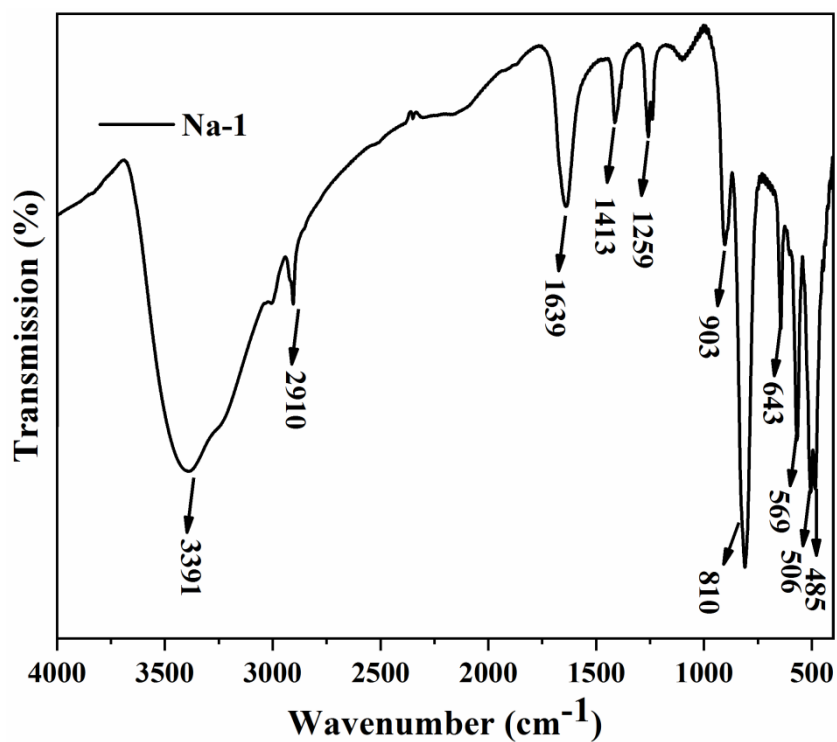


Figure S2. FT-IR spectrum of Na-1 from 400 - 4000 cm⁻¹ measured on a KBr pellet.

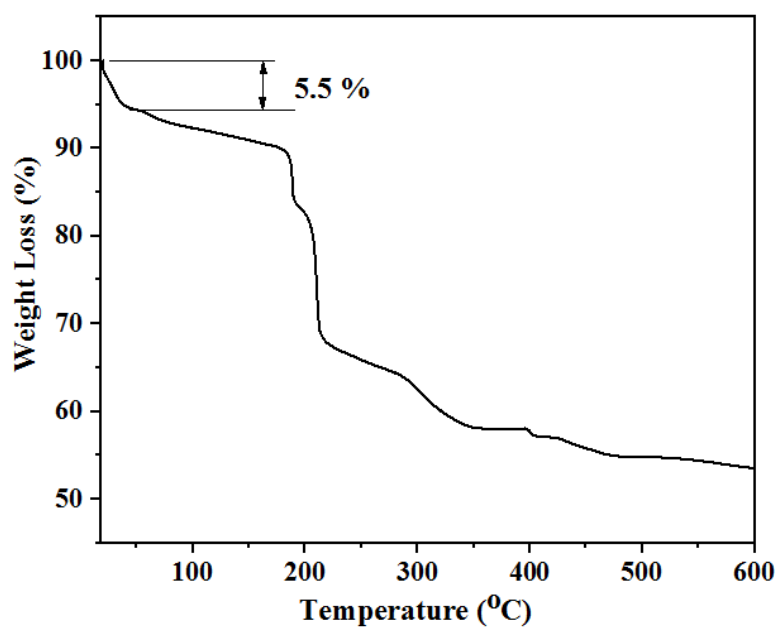


Figure S3. Thermogram of Na-1 from room temperature to 600 °C (measured under N₂ atmosphere).

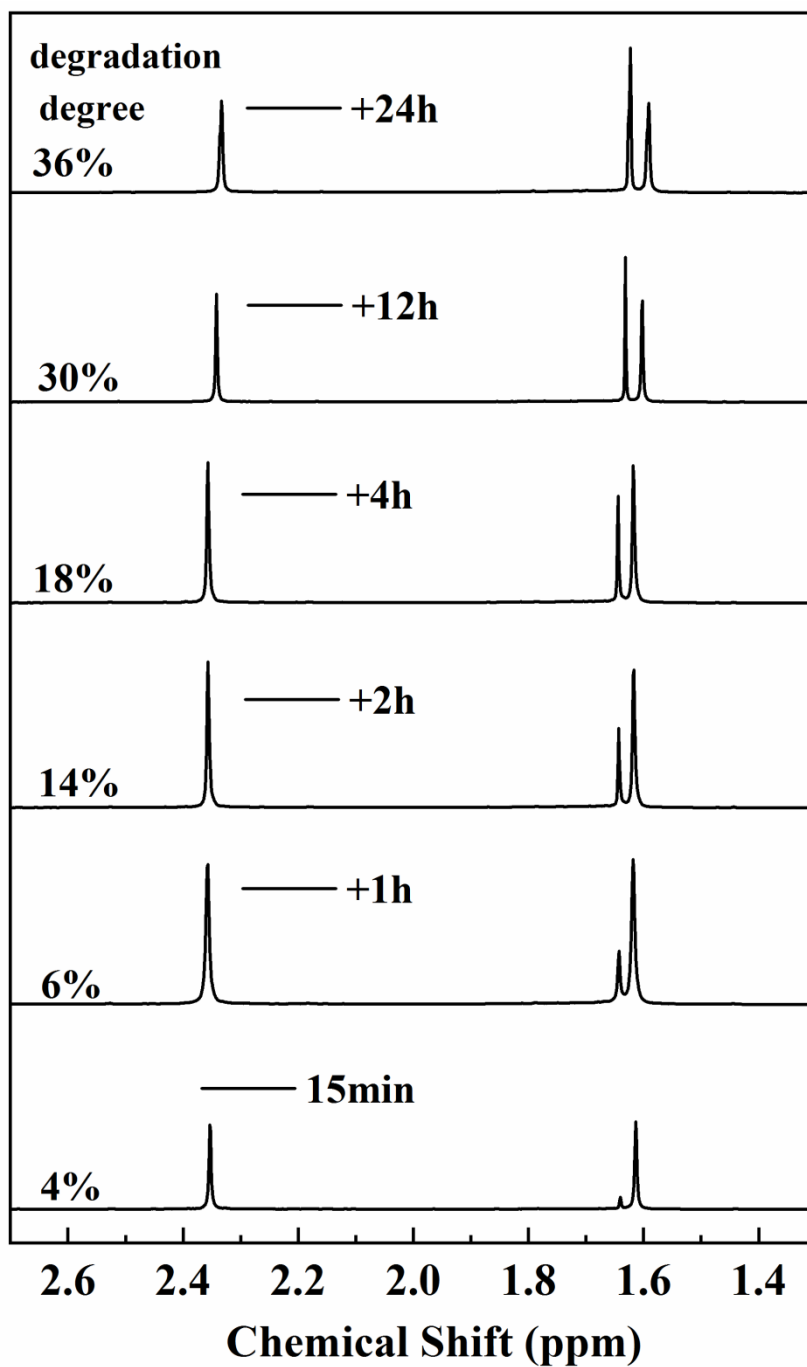


Figure S4. Time-dependent ¹H NMR spectra (measured at room temperature) of a solution prepared by dissolving 10 mg Na-1 in 0.5 mL H₂O/D₂O.

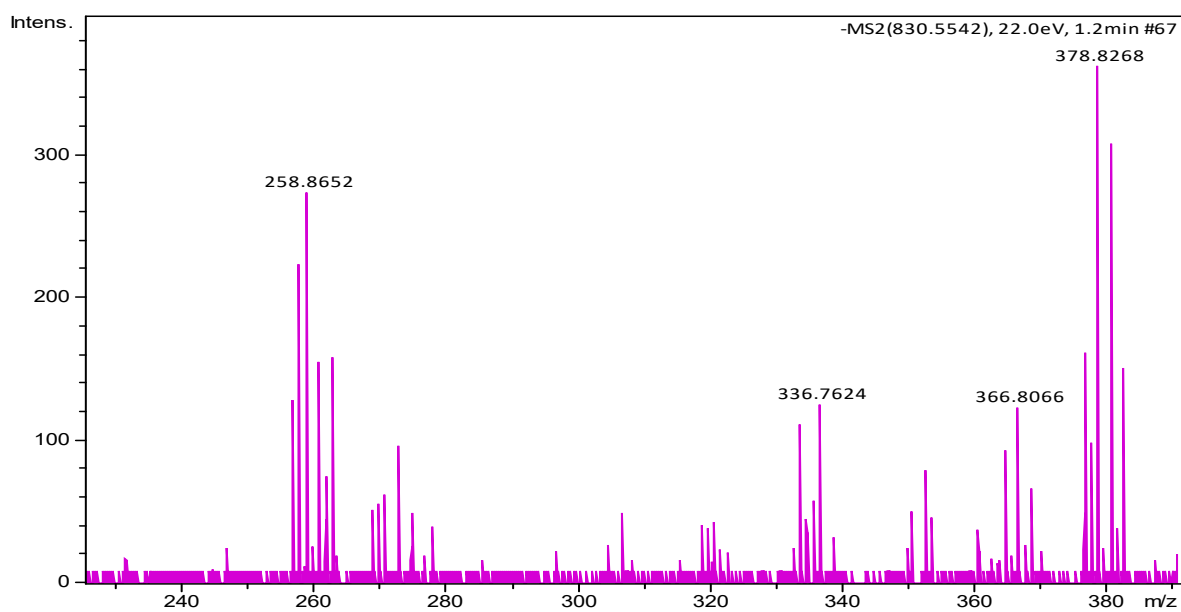
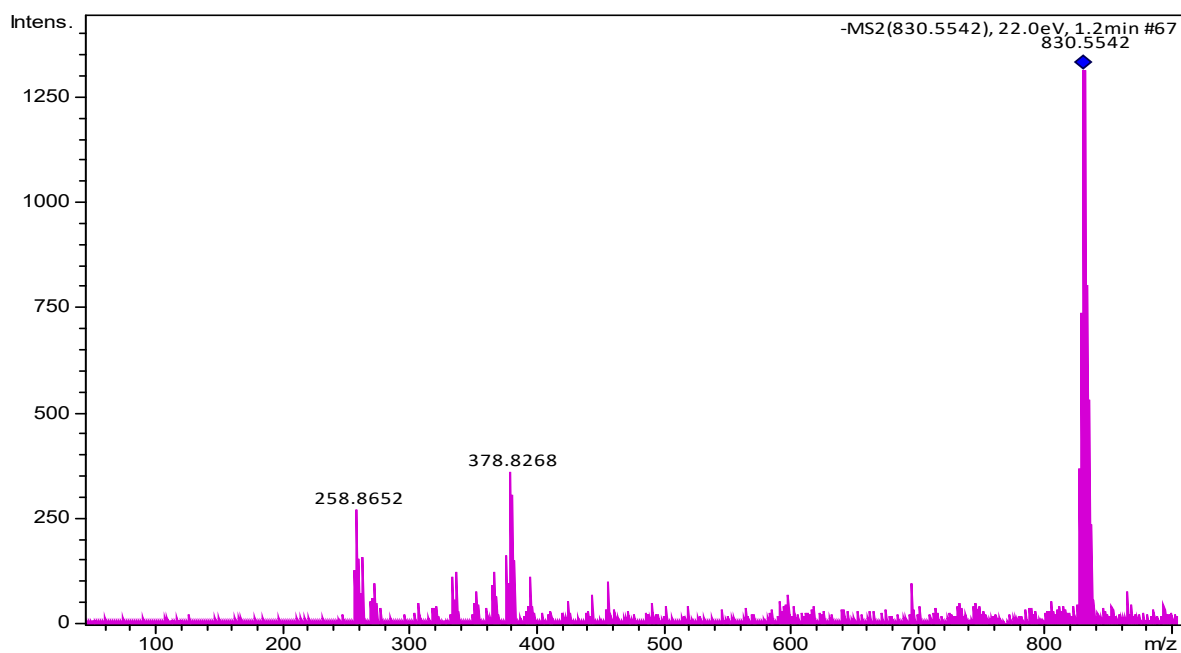


Figure S5. Tandem mass spectrum of $[\text{Pd}_7\text{O}_6((\text{CH}_3)_2\text{AsO}_2)_6]^{2-}$ in negative ion mode with the precursor ion at m/z 830 \pm 10. Full view (top panel) and expanded region (bottom panel).

Table S1. Single crystal data and structure refinement parameters of **Na-1**.

| Identification code | Na-1 |
|-----------------------------------|--|
| Empirical formula | H ₃₆ C ₁₂ N ₁ O _{45.5} Na ₄ As ₆ Pd ₇ (H ₆₁ C ₁₂ N ₂ O _{36.5} Na ₄ As ₆ Pd ₇)* |
| Formula weight | 2208.70 (2104.03)* |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Orthorhombic, <i>Pcca</i> |
| Unit cell dimensions | a = 26.7756(12) Å |
| | b = 13.3210(6) Å |
| | c = 19.6258(9) Å |
| Volume | 7000.1 (5) Å ³ |
| Z, Calculated density | 4, 2.096 mg/m ³ |
| Absorption coefficient | 4.684 mm ⁻¹ |
| F(000) | 4172 |
| Crystal size | 0.3 x 0.3 x 0.3 mm |
| Theta range for data collection | 3.406 to 26.373°. |
| Limiting indices | -33<=h<=33, -16<=k<=16, -24<=l<=24 |
| Reflections collected /unique | 111189 / 7159 [R(int) = 0.0416] |
| Completeness to theta =25.242 | 99.7% |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 7159 / 204 / 386 |
| Goodness-of-fit on F ² | 1.130 |
| Final R indices [I>2sigma(I)] | R ₁ ^[a] = 0.0446, wR ₂ ^[b] = 0.1238 |
| R indices (all data) | R ₁ = 0.0492, wR ₂ = 0.1269 |
| Largest diff. peak and hole | 2.119 and -0.792 e.Å ⁻³ |

$$^{[a]} R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^{[b]} wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

* In brackets is the actual formula unit and corresponding molar mass as obtained from elemental analysis on a bulk sample (representing the true composition of the material).

Table S2. Bond valence sum (BVS) values for selected atoms in **Na-1**.²

| Atom | BVS |
|------|-------|
| Pd1 | +2.26 |
| Pd2 | +2.27 |
| Pd3 | +4.47 |
| Pd4 | +2.28 |
| O1 | +1.97 |
| O2 | +1.97 |
| O3 | +1.95 |

Table S3. Selected bond lengths (Å) in **1**.

| atom1-atom2 | bond distance (Å) | atom1-atom2 | bond distance (Å) |
|--------------|-------------------|--------------|-------------------|
| Pd(1)-O(1) | 1.992(5) | Pd(3)-O(2) | 2.023(4) |
| Pd(1)-O(3)#1 | 2.006(4) | Pd(3)-O(1)#1 | 2.029(4) |
| Pd(1)-O(4) | 2.043(5) | Pd(3)-O(1) | 2.029(4) |
| Pd(1)-O(9)#1 | 2.052(5) | Pd(3)-O(3)#1 | 2.033(4) |
| Pd(2)-O(1) | 1.992(5) | Pd(3)-O(3) | 2.033(4) |
| Pd(2)-O(2) | 1.997(5) | Pd(4)-O(3) | 1.989(5) |
| Pd(2)-O(5) | 2.047(5) | Pd(4)-O(2) | 1.997(5) |
| Pd(2)-O(6) | 2.054(5) | Pd(4)-O(8) | 2.041(5) |
| Pd(3)-O(2)#1 | 2.023(4) | Pd(4)-O(7) | 2.054(5) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

References

1. a) APEX suite of crystallographic software, APEX 3, version 2015.5-2, Bruker AXS Inc., Madison, Wisconsin, USA, 2015; b) SAINT, Version 7.56a and SADABS Version 2008/1, Bruker AXS Inc., Madison, Wisconsin, USA, 2008; c) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8; d) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2010.
- 2 a) Brese, N. E.; O'Keeffe, M. Bond-valence parameters for solids. *Acta Cryst.* 1991, **B47**, 192-197; b) Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect. B* 1985, **41**, 244–247.