Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Self-Assembly of Polyoxoselenitopalladate Nanostars $[Pd_{15}(\mu_3\text{-}SeO_3)_{10}(\mu_3\text{-}O)_{10}Na]^{9-}$ and their Supramolecular Pairing in the Solid State

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Characterization of $Na_{14}(H_3O)_6[Pd_{15}(\mu_3\text{-}SeO_3)_{10}(\mu_3\text{-}O)_{10}Na]_2(SeO_3)\cdot 27H_2O$ (1)

1. Material and methods: All manipulations were carried out at room temperature in the air; $Pd(CH_3COO)_2$ and Na_2SeO_3 were purchased and used as received (Aldrich). The H elemental analyse was carried out by using a Carlo Erba EA1108 microanalyzer, Pd, Se, and Na were determined by using a Jobin Yvon Ultima 2 ICP-OES spectrophotometer. Thermogravimetry analysis was carried out on a Perkin-Elmer TGA7 Thermal analyzer in flowing N_2 with a heating rate of 5 °C min^{-1}. FTIR spectra (4000-400 cm^{-1}) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond crystal). A LTQ-FT Orbitrap mass spectrometer (Thermo Electron GmbH, Bremen, Germany) equipped with a nano electrospray ionization (ESI) probe operating in negative-ion mode was used. Full-scan accurate mass spectra (mass range 500-2000 Da) were obtained at high resolution (50000 FWHM). The ESI source conditions were: source voltage 1.5 kV, heated capillary temperature 100°C, capillary voltage -5V and tube lens -100V.

2. Structure determination: Data for the structure of **1** were collected at 293 K on a Bruker SMART 1000 CCD single-crystal diffractometer[S1] equipped with a sealed Mo tube and graphite monochromator (λ= 0.71073 Å). Crystals were mounted on a glass fiber and fixed with a glue. The crystals were needle-like. The SMART program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[S2] and SADABS[S3] to yield the reflection data file.
The structure of **1** was solved by direct methods and refined by full-matrix least-squares against F_o^2 using the SHELXTL program package.[S4] All atoms were refined anisotropically. The hydrogen atoms of the crystal waters and hydronium ions were not localized.

Table S1. Bond Valence Sum (v.u.) calculation for $[Pd_{15}(\mu_3\text{-}SeO_3)_{10}(\mu_3\text{-}O)_{10}Na]^{9-}$.

Atoms	BVS	Assigned Oxidation State	Atoms	BVS	Assigned Oxidation State
Pd1	1.86	+2	O9	1.66	-2
Pd2	1.86	+2	O10	1.75	-2
Pd3	1.82	+2	O11	1.74	-2
Pd4	1.83	+2	O12	1.75	-2
Pd5	1.83	+2	O13	1.79	-2
Pd6	1.85	+2	O14	1.70	-2
Pd7	1.84	+2	O15	1.75	-2
Pd8	1.82	+2	O16	1.85	-2
Pd9	1.80	+2	O17	1.71	-2
Pd10	1.85	+2	O18	1.76	-2
Pd11	1.90	+2	O19	1.61	-2
Pd12	1.84	+2	O20	1.75	-2
Pd13	1.82	+2	O21	1.66	-2
Pd14	1.84	+2	O22	1.73	-2
Pd15	1.87	+2	O23	1.75	-2
Se1	4.27	+4	O24	1.76	-2
Se2	3.95	+4	O25	1.68	-2
Se3	3.99	+4	O26	1.76	-2
Se4	4.20	+4	O27	1.77	-2
Se5	4.23	+4	O28	1.77	-2
Se6	4.27	+4	O29	1.77	-2
Se7	4.04	+4	O30	1.70	-2
Se8	4.18	+4	O31	1.76	-2
Se9	4.14	+4	O32	1.76	-2
Se10	4.15	+4	O33	1.82	-2
O1	1.73	-2	O34	1.87	-2
O2	1.72	-2	O35	1.86	-2
O3	1.82	-2	O36	1.77	-2
O4	1.74	-2	O37	1.66	-2
O5	1.72	-2	O38	1.81	-2
O6	1.64	-2	O39	1.88	-2
O7	1.69	-2	O40	1.75	-2
O8	1.77	-2			

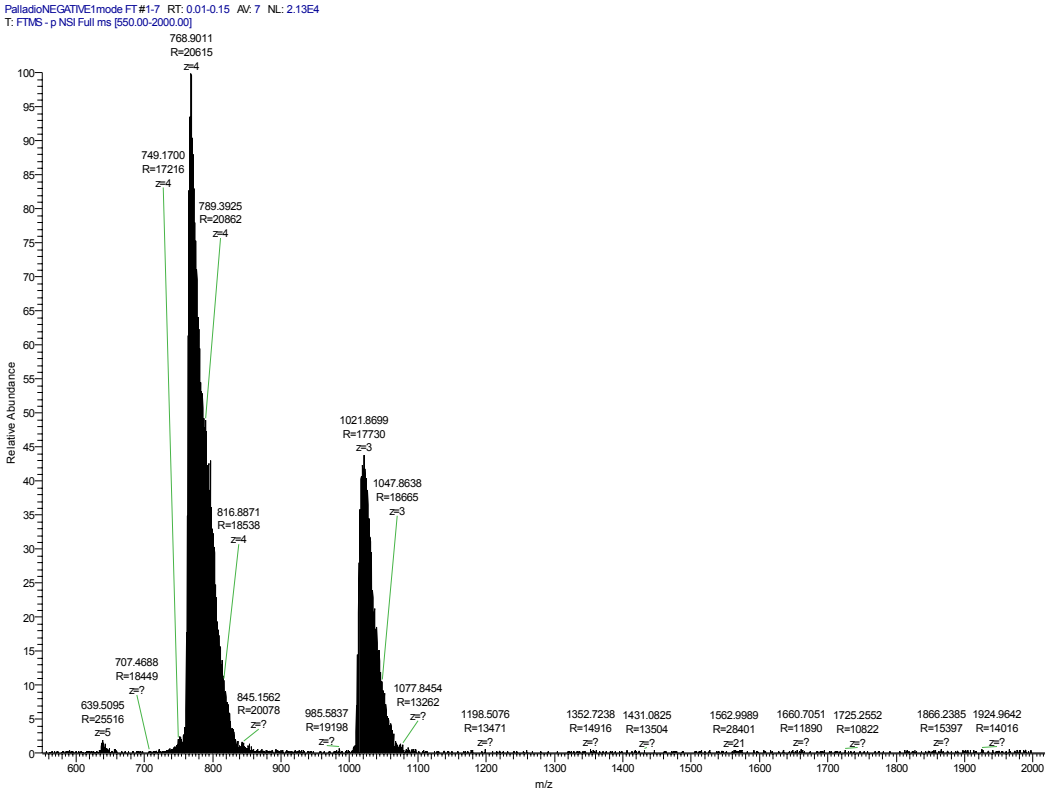

Figure S1. Negative ESI-LTQ-FT spectrum of $Na_{14}(H_3O)_6[Pd_{15}(SeO_3)_{10}(O)_{10}Na]_2(SeO_3)\cdot 27H_2O$ dissolved in H_2O.

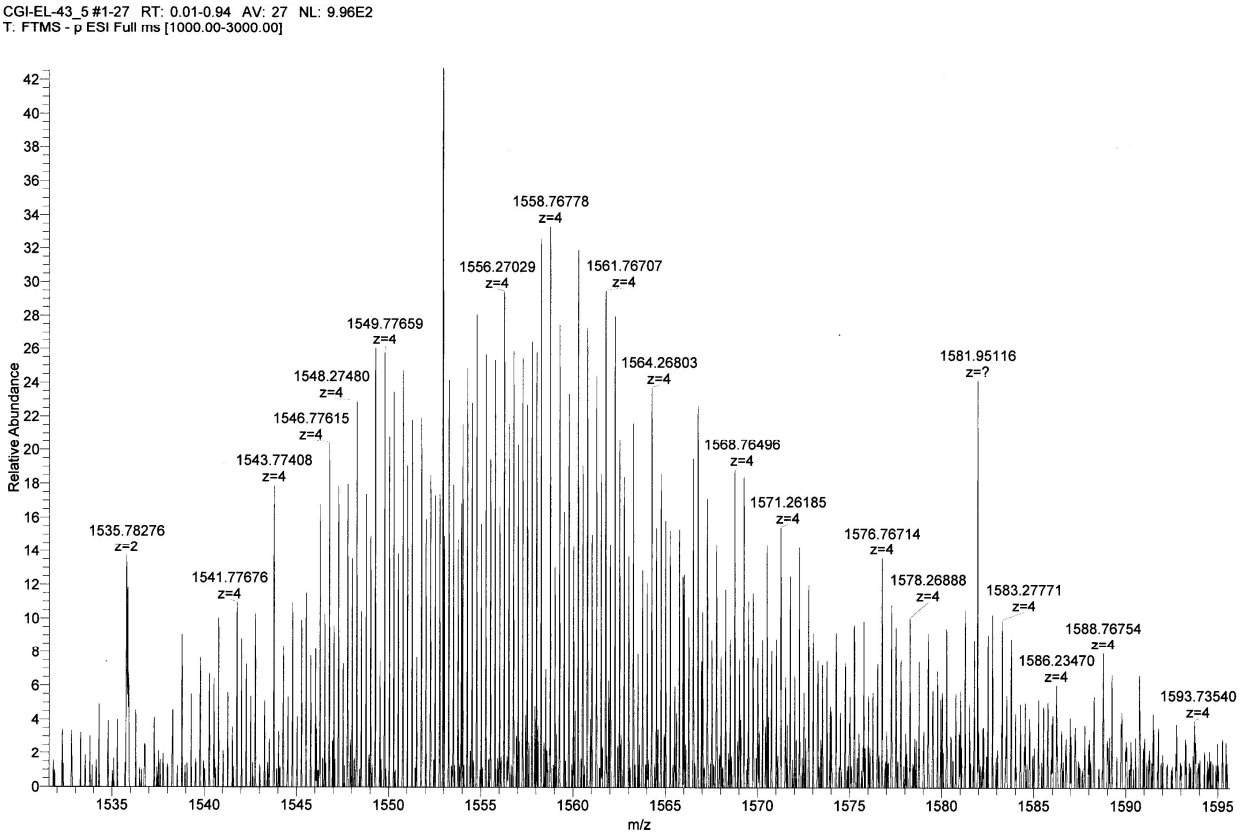

Figure S2. Spectrum suggesting the supramolecular interaction in water solution of **1** detected by ESI-LTQ-FT (Negative mode, 1500-1600 m/z). The spectrum was recorded under soft condition with respect to Figure S1.

Table S2. ICP-OES operating conditions and wavelengths examined.

Power generator	1000 W
Plasma Gas (Ar) Flow rate	12 L/min
Auxiliary Flow rate	0
Nebulization Pressure	3 bar
Nebulization Flow rate	0.50 L/min
Pump speed	20 rpm
Wavelength (nm)	Pd 324.270, Se 196.026, Na 588.995

Table S3. % of Pd, Se and Na in **1** (standard deviations are given in parentheses).

	%	σ
Pd	44.6	0.3
Se	23.1	0.4
Na	4.9	0.1

S1 *SMART Software Users Guide*, *Version 5.1*; Bruker Analytical X-ray Systems: Madison, WI, 1999.

S2 *SAINT Software Users Guide, Version 6.0*; Bruker Analytical X-ray Systems: Madison, WI, 1999.

S3 Sheldrick, G. M. SADABS; Bruker Analytical X-ray Systems, Madison, WI, 1999.

S4 Sheldrick, G. M. SHELXTL, Version 5.10; Bruker Analytical X-ray Systems, Madison, WI, 1999.