Supplementary Information

$[Pd_2(\eta^4\text{-}P_7)_2]^{4-}$: a Pd_2 dimer sandwiched by two anionic nortricyclane-type polyphosphide

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1 Experimental Session

1.1 General

All steps of synthesis and sample preparation were carried out inside an argon-filled glove box (MBraun, $p(H_2O)$, $p(O_2) < 0.1$ ppm). Sodium (Na, rods, 99 %), $[Pd(PPh_3)_4]$ (99.9 %) and red phosphorus (P, powder, 98.5 %) were used without any further purification. DMF (99.8 %) were freshly distilled by CaH_2 prior to use, and stored in argon prior to use. THF (99.8 %) was distilled from sodium/benzophenone under argon and stored under argon. Crypt-222[1] (98 %) was dried in vacuo for at least 18 hours. The precursors Na_3P_7 was prepared according to a previously reported synthetic procedure from a mixture of the elements heated at 750 K for 3 days in sealed niobium containers.[2]

1.2 Synthesis of $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$

Na_3P_7 (60 mg, 0.200 mmol), crypt-222 (80 mg, 0.210 mmol) and $[Pd(PPh_3)_4]$ (242.58mg, 0.200 mmol) were dissolved in 3 ml DMF and stirred for 4 h to yield a dark brown solution. The resulting dark brown solution was filtered, then carefully layered by 3 ml THF. After 7 days, dark red crystals of $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$ were observed in the test tube in approximately 10% yield overall.

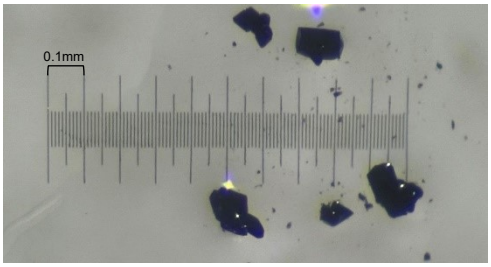

Figure S1. Crystal photographs of $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$ taken under a light microscope.

2 Single-Crystal X-Ray Crystallography (SCXRD)

2.1 Single-Crystal X-ray Diffraction

A metallic reddish red, block-shaped crystal was mounted on the goniometer. Data for $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$ were collected from a shock-cooled single crystal at 150.00 K on a Bruker D8 VENTURE Dual Wavelength with a PHOTON III CAPD detector. The diffractometer used MoK_α radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT V8.40B and a multi-scan absorption correction using was applied. The structure was solved by direct methods with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL 2018/3.[3][4] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with isotropic displacement parameters. Some of their coordinates were refined freely and some on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[5] CCDC 2493250 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[6]

Table S1. Crystal data and details of the structure determination of compound $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$.

Compound	**$[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$**
CCDC number	2493250
Empirical formula	$C_{72}H_{144}N_8Na_4O_{24}P_{14}Pd_2$
Formula weight	2244.28
Temperature [K]	150.00
Crystal system	triclinic
Space group (number)	$P\bar{1}$
a [Å]	13.1373(4)
b [Å]	13.3017(4)
c [Å]	16.1154(5)
α [°]	105.8900(10)
β [°]	91.8060(10)
γ [°]	112.9760(10)
Volume [Å^3]	2463.02(13)
Z	1
ρ_{calc} [gcm^{-3}]	1.513
μ [mm^{-1}]	0.681
F(000)	1170
Crystal size [mm^3]	0.2×0.3×0.5
Crystal colour	metallic reddish red
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.64 to 69.79 (0.62 Å)
Index ranges	$-21 \le h \le 18$ $-20 \le k \le 19$ $-25 \le l \le 24$
Reflections collected	199874
Independent reflections	19812 R_{int} = 0.0474 R_{sigma} = 0.0254
Completeness to θ = 25.242°	99.6 %
Data / Restraints / Parameters	19812 / 0 / 599
Absorption correction T_{min}/T_{max}	0.7830 / 0.8730 (multi-scan)

(method)	
Goodness-of-fit on F^2	1.073
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0278$ w$R_2 = 0.0740$
Final R indexes [all data]	$R_1 = 0.0368$ w$R_2 = 0.0817$
Largest peak/hole [eÅ^{-3}]	0.72/−0.90

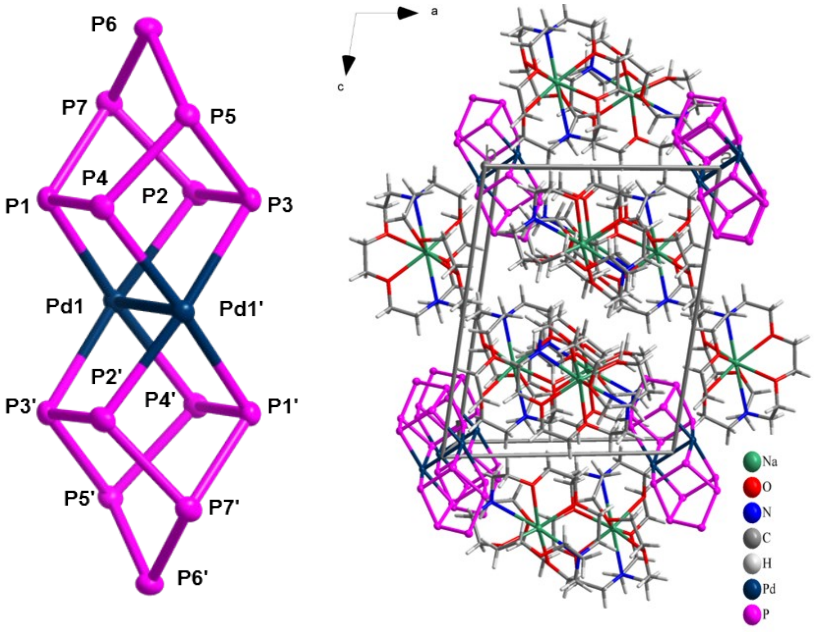

Figure S2. Molecular structure of the anion $[Pd_2P_{14}]^{4-}$ in compound $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$ (left) and unit cell view of $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$ (right).

Table S2. Selected bond lengths (in Å) and bond angles (in degrees) of the experimental structure of the anion in $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$.

Atom–Atom	Length [Å] (exp.)
Pd1–Pd1'	2.69687(19)
Pd1–P1	2.3954(4)
Pd1–P2	2.3778(4)
Pd1–P3'	2.3873(4)
Pd1–P4'	2.4006(4)
P1–P4	2.1961(5)
P1–P7	2.2199(5)
P2–P3	2.2123(5)
P2–P7	2.2054(5)
P3–P5	2.2038(5)
P4–P5	2.2100(5)
P5–P6	2.1430(5)
P6–P7	2.1432(5)

Atom–Atom–Atom	Angle [°]
P1–Pd1–P4'	168.002(12)
P2–Pd1–Pd'1	82.247(10)
P2–Pd1–P1	74.227(12)
P2–Pd1–P3'	168.293(13)
P2–Pd1–P4'	103.829(13)
P3'–Pd1–Pd1'	86.059(10)
P3'–Pd1–P4'	74.460(12)
P4'–Pd1–Pd1'	84.972(10)
P4–P1–Pd1	97.320(16)
P4–P1–P7	103.259(19)
P7–P1–Pd1	97.962(16)
P3–P2–Pd1	98.410(16)
P7–P2–Pd1	98.893(17)
P7–P2–P3	103.144(19)
P2–P3–Pd1'	93.277(15)
P5–P3–Pd1'	99.326(16)
P5–P3–P2	102.905(19)
P1–P4–P5	103.109(18)
P5–P4–Pd1'	98.745(16)
P3–P5–P4	82.039(17)
P6–P5–P3	107.78(2)
P6–P5–P4	108.40(2)
P5–P6–P7	96.853(19)
P2–P7–P1	81.210(17)
P6–P7–P1	107.84(2)
P6–P7–P2	108.08(2)

Symmetry transformations used to generate equivalent atoms:
': -X, 2-Y, 2-Z;

3 Energy Dispersive Spectrometer (EDS)

EDS analysis of single crystal of compound $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$ was carried out using a Oxford X-Max 80 instrument (UK). The spectra are shown in Figure S3. Several measurements produced unreasonably large values for the % Na. Removal of Na from the calculations afforded excellent agreement with the expected atomic ratio of close to $Pd_{2.00}P_{14.00}$. We believe that accumulation of Na at the crystal surface upon exposure to air is responsible for the anomalous results. This is observed commonly for very these very air-sensitive compounds.

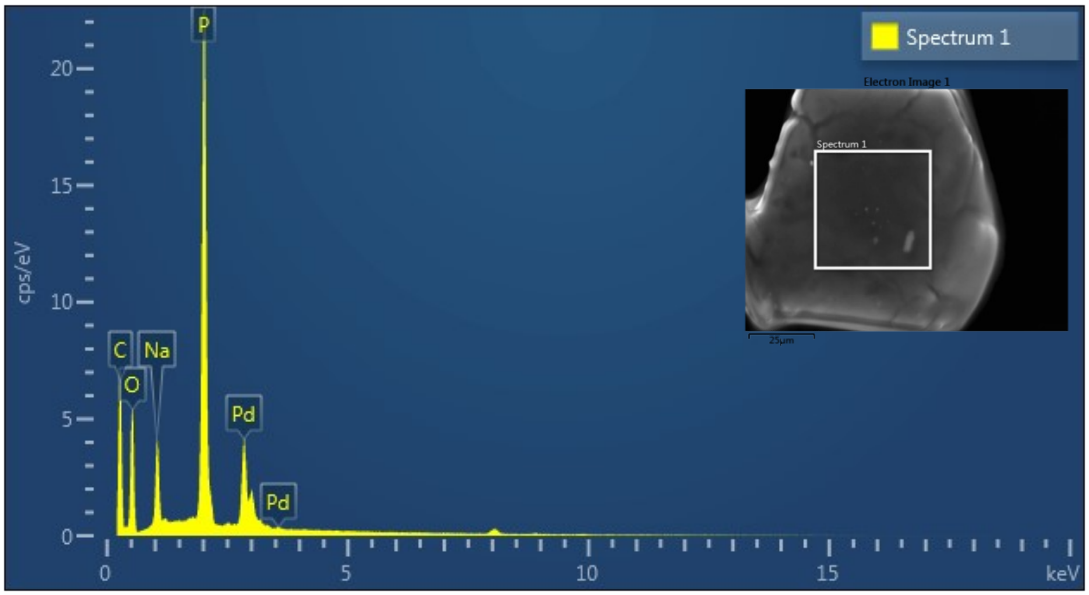

Figure S3. **EDS analysis of $[Na(crypt\text{-}222)]_4[Pd_2P_{14}]$.**

4 References for the Supporting Information

[1] 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

[2] Santandrea, R. P.; Mensing, C.; von Schnering, H. G. *Thermo chim. Acta* **1986**, *98*, 301.

[3] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3–8.

[4] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3–8.

[5] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Cryst.* **2016**, *B72*, 171–179.

[6] D. Kratzert, *FinalCif*, *V154*, https://dkratzert.de/finalcif.html.