Electronic Supplementary Information

Expanding manganese(IV) aqueous chemistry: unusually stable water-soluble hexahydrazide clathrochelate complexes

Sergii I. Shylin, [a,b] James L. Pogrebetsky,[a] Alina O. Husak,[a,c] Dmytro Bykov,[d] Andriy Mokhir,[e] Frank Hampel,[e] Sergiu Shova,[f] Andrew Ozarowski,[g] Elzbieta Gumienna-Kontecka,[h] and Igor O. Fritsky, [a,c*]

[a] *Department of Chemistry, Taras Shevchenko National University of Kyiv, 64, Volodymyrska Str., 01601 Kiev, Ukraine*
[b] *Department of Chemistry – Ångström Laboratory, Uppsala University, PO Box 523, 75120 Uppsala, Sweden*
[c] *PBMR Labs Ukraine, Murmanska 1, 02094 Kiev, Ukraine*
[d] *National Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*
[e] *Department of Chemistry and Pharmacy, Friedrich-Alexander-University Erlangen-Nürnberg, Nikolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany*
[f] *"Poni Petru" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania*
[g] *National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA*
[h] *Faculty of Chemistry, University of Wrocław, F. Joliot-Curie Str. 14, 50-383 Wrocław, Poland*

Table of Contents

Methods

Materials. All the reagents and solvents used in this work were purchased from commercial sources and were used as received without further purification. Oxalodihydrazide **(oxh)** (99.99% Enamine Ltd.) was used without further purification.

Synthesis of $(Ph_4As)_2[Mn(L\text{-}6H)]\cdot 13.5H_2O$ (1). $MnCl_2\cdot 4H_2O$ (0.0198 g, 0.1 mmol) was dissolved in 10 ml of water and aqueous ammonia (28%, 0.2 ml, 1.96 mmol) was added to the solution obtained. The precipitate formed was than filtered and washed with water (15 ml) after which it was transferred to the warm (~50ºC) solution of **oxh** (0.0354 g, 3 mmol) in 20 ml of water upon stirring. Then excess quantities of aqueous ammonia (28%, 0.52 ml, 5 mmol) and paraform (0.018 g, 6 mmol) were added immediately. The resulting mixture was stained a dark green colour within few minutes. Then the reaction mixture was stirred for 1 hour at 90ºC and tetraphenylarsonium bromide (0.084 g, 0.18 mmol, dissolved in 5 ml of water) was added. The product was extracted by chloroform (2 x 10 ml), and the extract was then dried on a rotary evaporator. The residue was dissolved in a small amount (5 ml) of water and set aside for crystallization at the ambient conditions. Single crystals suitable for X-ray analysis were obtained in 48 h. Yield 0.062 g (42%). Elemental analysis for $C_{60}N_{12}H_{79}O_{19.5}MnAs_2$ (1485.13), calculated, %: C 48.52; H 5.36; N 11.32. Found, %: C 48.72; H 5.32; N 11.15. ESI-HRMS (*m/z*, negative mode): $[M+H^+]^-$ calcd for $C_{12}H_{13}N_{12}O_6Mn$ 476.0456. Found: 476.0473 (38%). $[M+Ph_4As^+]^-$ calcd for $C_{36}H_{32}N_{12}O_6MnAs$: 858.1159 (Fig. S15). Found: 858.1035 (100%). ESI-HRMS (*m/z*, positive mode): $[Ph_4As]^+$ calcd for $C_{24}H_{20}As$ 383.0776. Found: 38.0756 (100%). UV-vis (H_2O): λ_{max} (ε, mol^{-1} dm^3 cm^{-1}): 291 nm (16050), 321 nm (17240), 400 nm (shoulder, 4255), 507 nm (3378), 658 nm (4277). Infrared absorption bands (Fig. S16): 3416 cm^{-1}(s) O–H stretch, 3084 cm^{-1}(w) C–H stretch, 3057 cm^{-1}(w) C–H stretch, 1641 cm^{-1}(vs) C=O Amide I, 1614 cm^{-1}(w), 1577 cm^{-1}(m), 1484 cm^{-1}(m), 1440 cm^{-1}(m).

Synthesis of $[Na_2(H_2O)_3Mn^{IV}(L\text{-}6H)]_n\cdot 4nH_2O$ (2). $MnCl_2\cdot 4H_2O$ (0.0198 g, 0.1 mmol) was dissolved in 10 ml of water and added to the warm (~50ºC) solution of **oxh** (0.0354 g, 3 mmol) in 20 ml of water upon stirring. Paraform (0.018 g, 6 mmol) was added to tetrabutylammonium hydroxide (40% aqueous solution, 3.26 ml, 5 mmol), and after a few minutes the resulting solution was poured to the solution of **oxh** and manganese(II) chloride upon stirring. The resulting mixture was stained a dark green color within few minutes. After 30 minutes the solution was filtered and the filtrate was dried on a rotary evaporator. The residue was dissolved in acetone (5 ml) and solution of $NaClO_4\cdot 2H_2O$ (0.0317 g, 0.2 mmol) in 10 ml of acetone was added. The resulting precipitate was filtered, then dissolved in a small amount (5 ml) of water and set aside for crystallization at the ambient conditions. Single crystals suitable for X-ray analysis were obtained in 48 h. Yield 0.041 g (63%). Elemental analysis for $C_{12}H_{26}MnN_{12}Na_2O_{13}$ (647.37): calculated, %: C, 22.27; H, 4.05; N, 25.97. Found, %: C, 22.03; H, 4.18; N, 25.79. UV-vis (H_2O): λ_{max} (ε, mol^{-1} dm^3 cm^{-1}): 291 nm (14370), 321 nm (15160), 400 nm (shoulder, 3740), 507 nm (2960), 658 nm (3720). Infrared absorption bands (Fig. S16): 3429 cm^{-1}(s) O–H stretch, 2948 cm^{-1}(w) C–H stretch, 2863 cm^{-1}(w) C–H stretch, 1646 cm^{-1} (vs) C=O Amide I.

Single crystal X-ray Crystallographic analyses. Measurements for **1** were carried out on an Oxford-Diffraction XCALIBUR E CCD diffractometer at 160(2) K with horizontally mounted graphite crystal as a monochromator and Mo-K_α radiation (λ = 0.71073 Å) using the *ω*-scan technique.

Intensity data for **2** was obtained at 173(2) K on an Agilent SuperNova diffractometer with Atlas detector and Cu-K_α radiation (λ = 1.54184 Å). Data was collected and processed using CrysAlisPro package of Oxford Diffraction.[1] An empirical absorption correction (multi-scan) was applied to all data *(CrysAlis PRO*).[1]
The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction *(CrysAlis PRO*).[1] The structures were solved by direct methods using Olex2 software[2] with the SHELXT structure solution program[3] and refined by full-matrix least-squares on all F_o^2 using *SHELXL2018*/1 anisotropically for all non-hydrogen atoms. The C-H hydrogen atoms were placed in fixed, idealized positions (d_{C-H} = 0.96 Å) and refined as those riding to the corresponding non-hydrogen atoms. The O-H hydrogen atoms were located from the difference Fourier map and verified by corresponding H-bonds parameters.

Elemental analysis. Elemental analysis was conducted by the Microanalytical Service of the University of Kyiv using a Vario Micro Cube (Elementar) elemental analyzer.

Mass-spectrometry measurements. High resolution electrospray mass spectra (ESI-HRMS) were collected on a Finnigan TSQ 700 mass spectrometer. Complexes were dissolved in water or in water-methanol (1:9) mixture to obtain solutions with concentrations of 10^{-4}-10^{-6} M.

Infrared vibrational spectroscopic measurements. IR spectra were recorded on a Perkin-Elmer 180 spectrometer in the range of 400-4000 cm^{-1}. Solid samples of the compounds were homogenized with excess amounts of KBr and a pressed pellet was measured at room temperature.

Electronic absorption (UV-VIS) spectroscopic measurements. Electronic absorption spectra were recorded on a Varian Cary 50 spectrophotometer in the range from 200 nm to 800 nm in the indicated solvent at room temperature.

Magnetochemical study. Temperature-dependent magnetic susceptibility measurements were carried out with a Quantum-Design MPMS-XL-5 SQUID magnetometer equipped with a 5 T magnet in a temperature range of 1.85 – 300K. The powdered samples were contained in a gel bucket and fixed in a nonmagnetic sample holder. Diamagnetic corrections of the constituent atoms for **1** were obtained with the use of Pascal's constants and found to be -857.0×10^{-6} cm^3 mol^{-1}. Experimental susceptibilities were also corrected for the magnetization of the sample holder (0.0001 cm^3 mol^{-1}).

EPR spectroscopy. High-field, high-frequency EPR spectra at temperatures ranging from ca. 3 K to 290 K were recorded on a home-built spectrometer at the EMR facility of the NHMFL.[4] The instrument is equipped with a superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T. Microwave frequencies over the range of 52-416 GHz were generated by a phase-locked Virginia Diodes source, producing a base frequency of 8-20 GHz, which was multiplied by a cascade of frequency multipliers. The instrument is a transmission-type device and uses no resonance cavity.

Electrochemical Measurements. All electrochemical measurements (cyclic voltammetry) were performed under a dry nitrogen atmosphere at 25±1°C using 10^{-3} M solutions either in water or acetonitrile with 1 M supporting electrolyte. The potential was scanned with different sweep rates ranging from 10 to 1000 mV s^{-1} and a conventional three electrode cell with a Metrohm 6.1204.120

Platinum Unpolished Rotating Disk Electrode as a working electrode, a Metrohm 6.0343.000 platinum auxiliary electrode and a Metrohm 6.0728.020 Ag/AgCl reference electrode on a Metrohm 757 VA Computrace instrument. All the reported half-wave potentials in acetonitrile were referenced against the ferrocenium/ferrocene (Fc/Fc^{+}) redox couple as internal standard (10 mM ferrocene solution).

DFT calculations. DFT calculations were conducted using ORCA package.[5] Starting geometries were derived from crystallographic studies and optimized using BP86 functional and def2-TZVP basis set.[6] The model consists of 43 atoms and 1047 basis functions. Enlarged DFT numerical integration grid was used in these calculations together with tight convergence threshold for the self-consistent-field procedure (Grid 6 and TightSCF in ORCA notation). The resolution of the identity approximation was invoked as well as Grimmes semi-empirical dispersion correction.[7] The optimized structures were verified by calculating molecular Hessian.[8] The single point calculations on the optimized structures were using B3LYP functional.[9] The solvent effects were included with CPCM.[10] Electronic g-tensor calculations were done at the same level of theory using procedure outlined by Neese.[11] Orbitals, densities and structures were visualized with the Chimera program.[12]

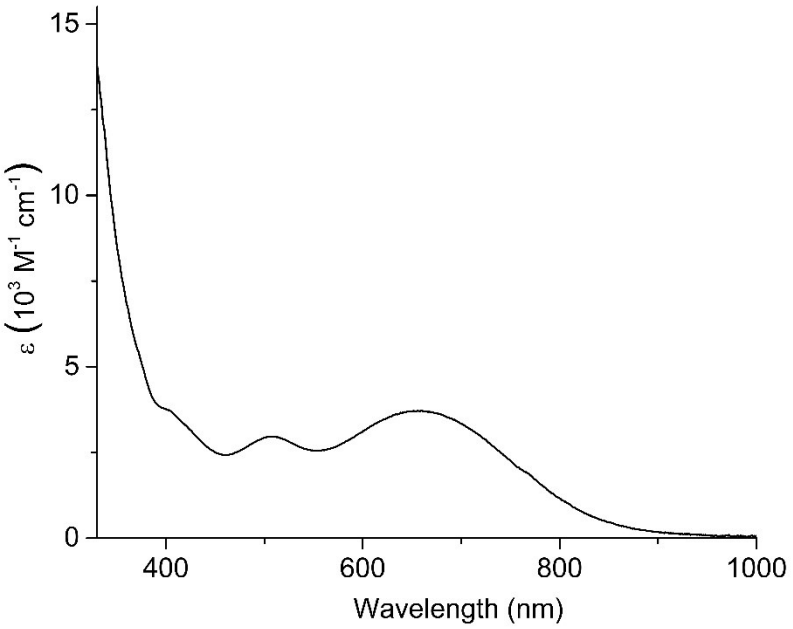

Figure S1. Electronic absorption spectrum of **1** (aqueous solution, 10^{-4} M).

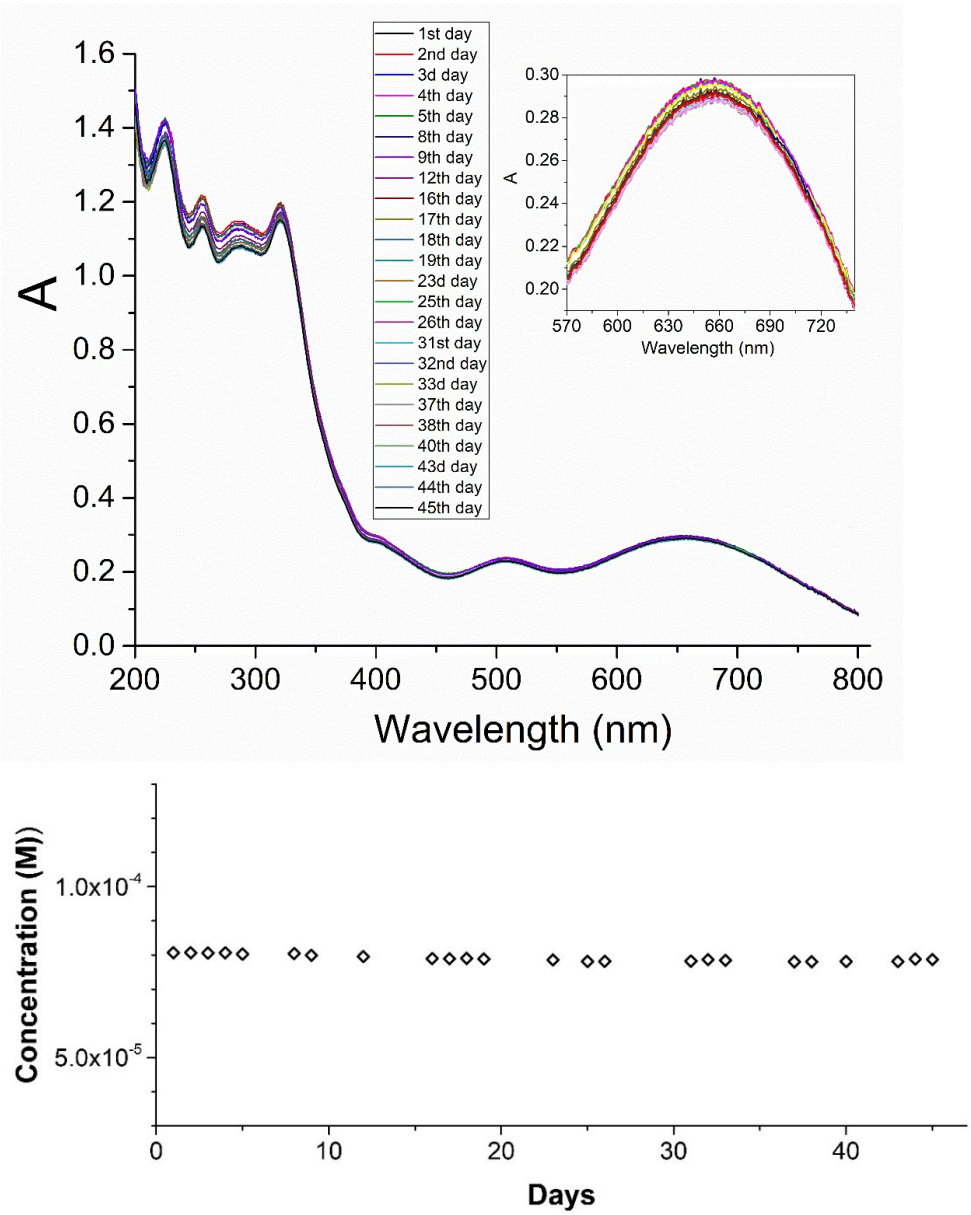

Figure S2: Top: changes in electronic absorption spectra of aqueous solution of **1** ($0.8 \cdot 10^{-4}$ M) with time. Experiment took place for 45 days at 20 °C. Inset: spectral changes around absorption maximum at 658 nm. (b) Bottom: changes in concentration of **1** in aqueous solution with time. The concentration of the initial solutions after 45 days has dropped by ca. 3.5%.

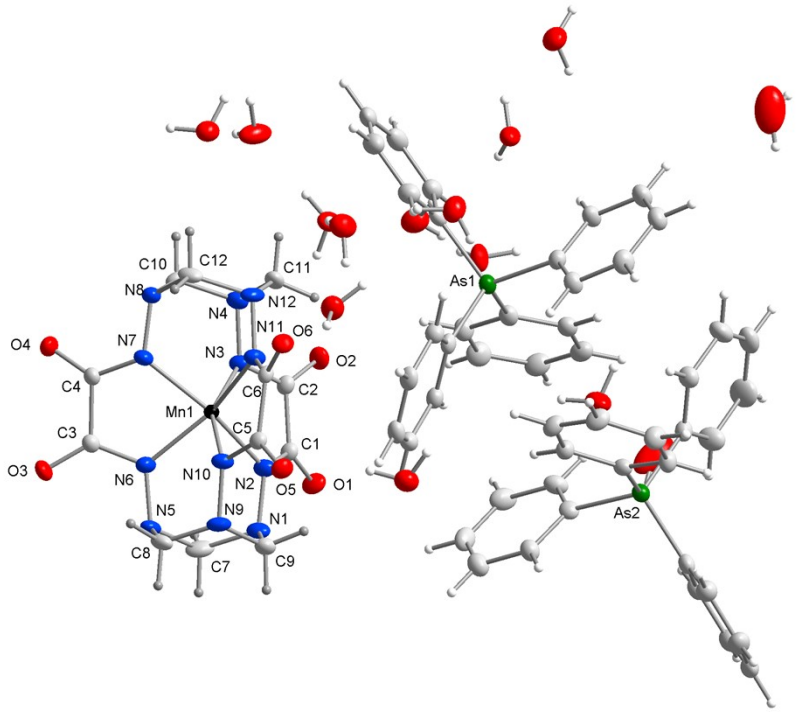

Figure S3. View of the asymmetric part of $(Ph_4As)_2[Mn(L\text{-}6H)]\cdot 13.5H_2O$ **(1)** showing the atom numbering scheme.

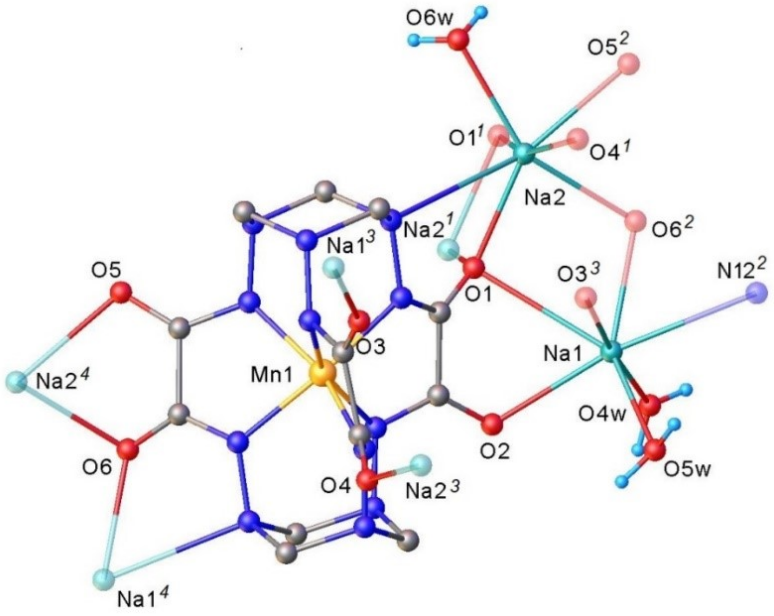

Figure S4. View of the asymmetric part of $[Na_2(H_2O)_3Mn^{IV}(L\text{-}6H)]_n \cdot 4nH_2O$ **(2)** showing the atom numbering scheme.

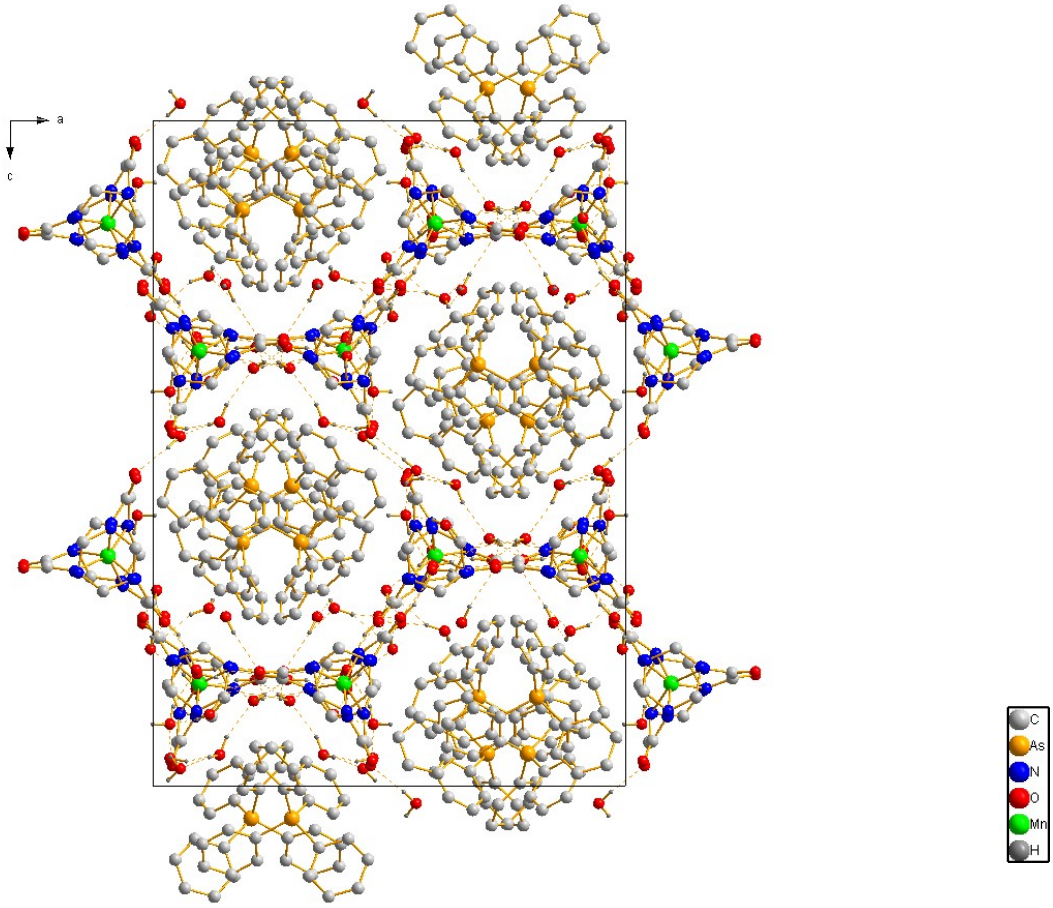

Figure S5. Packing diagram for $(Ph_4As)_2[Mn(\mathbf{L}\text{-}6H)]\cdot 13.5H_2O$ (**1**) (viewed parallel to the *ac* plane). Hydrogen bonds are indicated as dashed lines. C-H hydrogen atoms omitted for clarity. The complex anions united by H-bonds with the help of solvate water molecules form hollow honeycomb-like channels disposed along *b* direction of the crystal. These empty channels are filled with columns formed by Ph_4As^+ cations associated between each other due to stacking and van der Waals interactions.

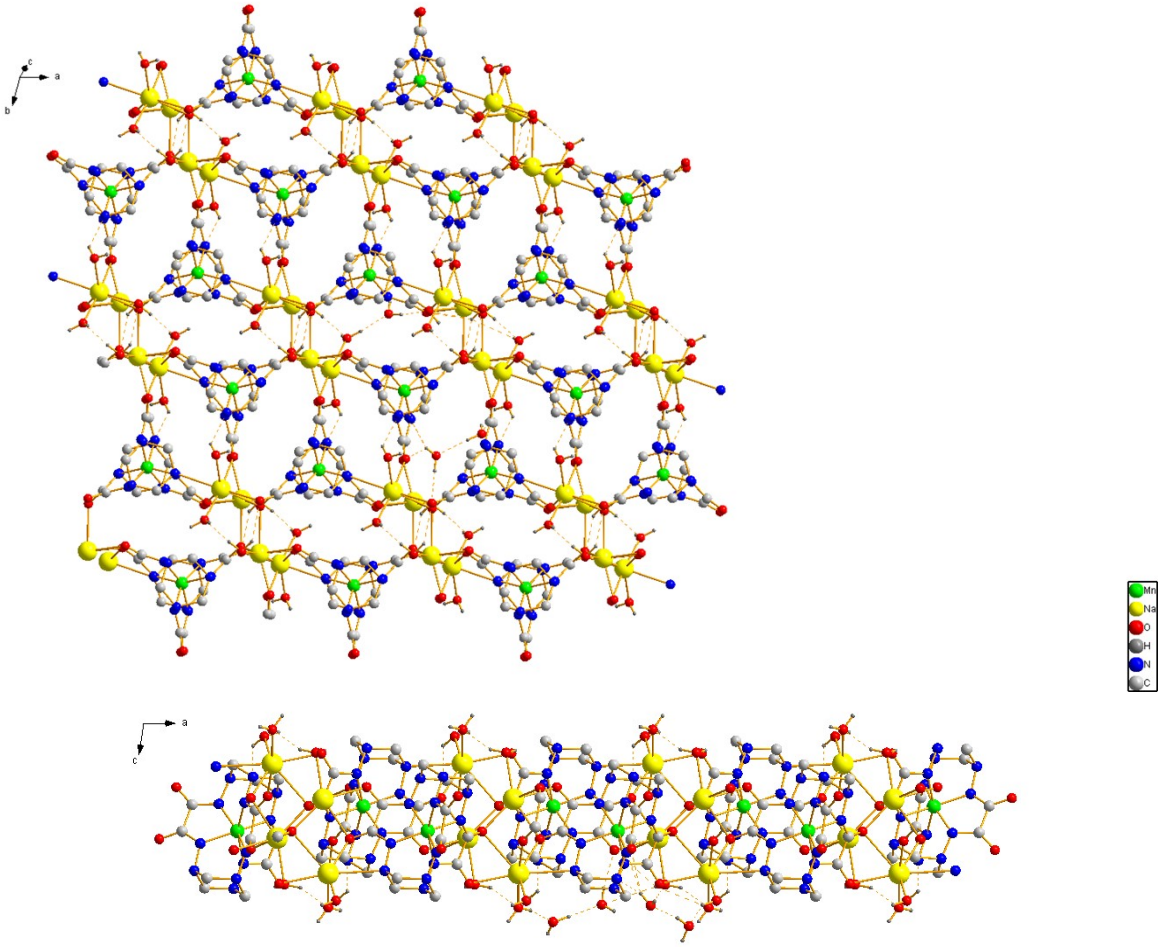

Figure S6. Packing diagrams of $[Na_2(H_2O)_3Mn^{IV}(L\text{-}6H)]_n \cdot 4nH_2O$ **(2)** demonstrating association of sodium cations with cage anions and organization of them into layers of two-dimensional coordination network. Top: a view perpendicular to the "crown" of the cage anions. Bottom: a view parallel to the *ac* plane.

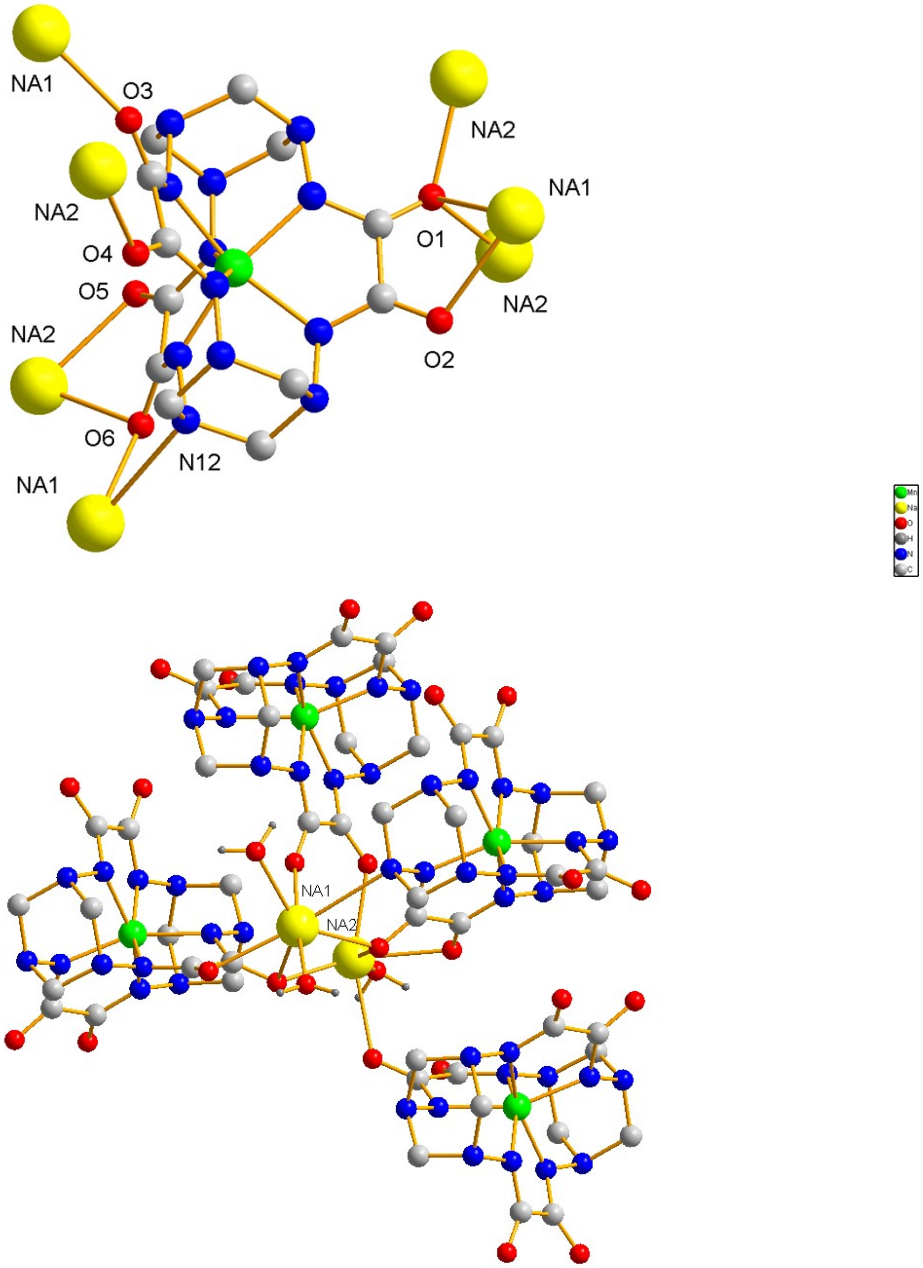

Figure S7. Coordination of sodium cations in $[Na_2(H_2O)_3Mn^{IV}(L\text{-}6H)]_n \cdot 4nH_2O$ **(2)**). Top: association of seven (two basic and five translational) sodium cations around the complex anion. Bottom: a diagram demonstrating the completed coordination spheres of sodium cations Na1 and Na2 and their association with four neighboring clathrochelate anions in the crystal packing.

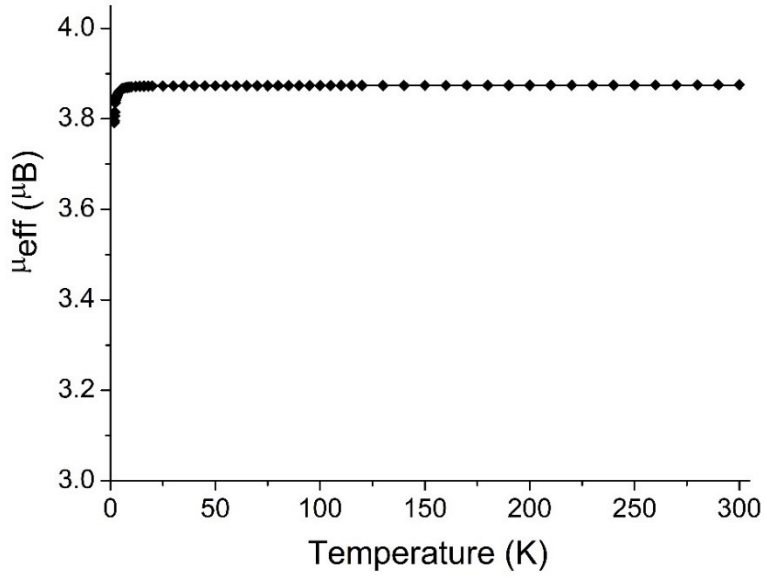

Figure S8. Temperature dependence of magnetic moment for the crystalline sample of **1**. The experimental curve (diamonds) can be fitted (solid line) with taking into account Zeeman splitting resulting in $g = 2.000$, and the observed drop of magnetic moment below 5 K is due to magnetization saturation at 0.5 T. Attempts to introduce D and E parameters into model did not give any improvement of the fit and did not result in obtaining of stable meaningful values of these parameters. Thus, introduction into the model D and E/D parameters obtained from high-field EPR (0.28 cm^{-1} and 0.1, respectively) resulted in close final values (0.165 cm^{-1} and 0.106, respectively, with $g = 2.001$).

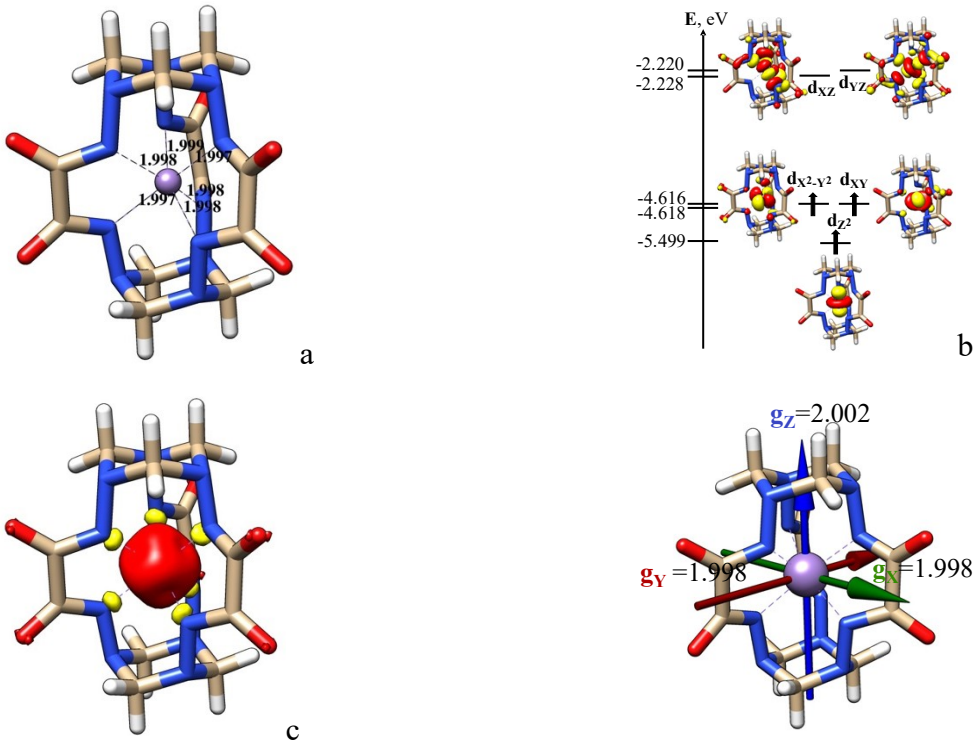

Figure S9. DFT electronic structure calculations of the clathrochelate anion in **1**. (a) Geometrical parameters from BP86/TZVP optimization revealing the quartet ground state of Mn(IV), S = 1.5. The high-spin state is 30.3 kcal/mol lower in energy than the hypothetical low-spin S = 0.5 Mn(IV) state. (b) The frontier molecular orbitals diagram showing 3 SOMO (singly occupied molecular orbital) metal-based orbitals and two unoccupied LUMO orbitals. The lowest lying molecular orbital is of d_{z^2} symmetry and two others almost degenerate SOMO orbitals are $d_{x^2-y^2}$ and d_{xy}. All SOMO orbitals are essentially nonbonding in their character and almost entirely metal-based. The LUMOs are strongly antibonding molecular orbitals. (c) Spin density. (d) Electronic g-tensor orientation. Atom coordinates for the optimized structure of **1** are given in Table S8.

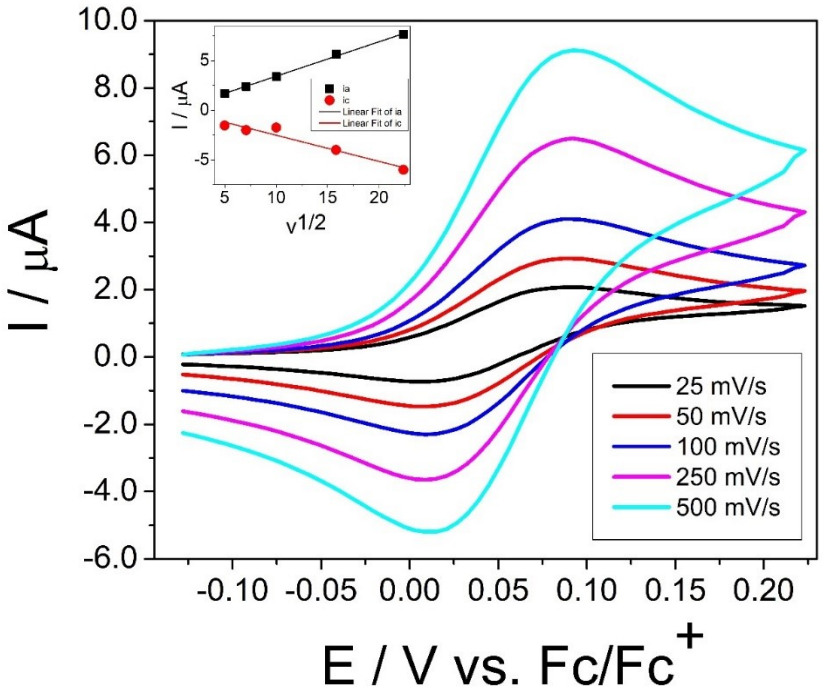

Figure S10. Cyclic voltammograms of **1** (1 mM) as a function of scan rate, recorded in acetonitrile solution showing the Mn^{5+}/Mn^{4+} redox couple. Scan rates (in mV s^{-1}): black – 25; red – 50; blue – 100; magenta – 250; cyan – 500. Inset: a plot of $i_{p,\,c}$ (red) and $i_{p,\,a}$ (black) as a function of the square root of the scan rate $v^{1/2}$, showing the linear relationship.

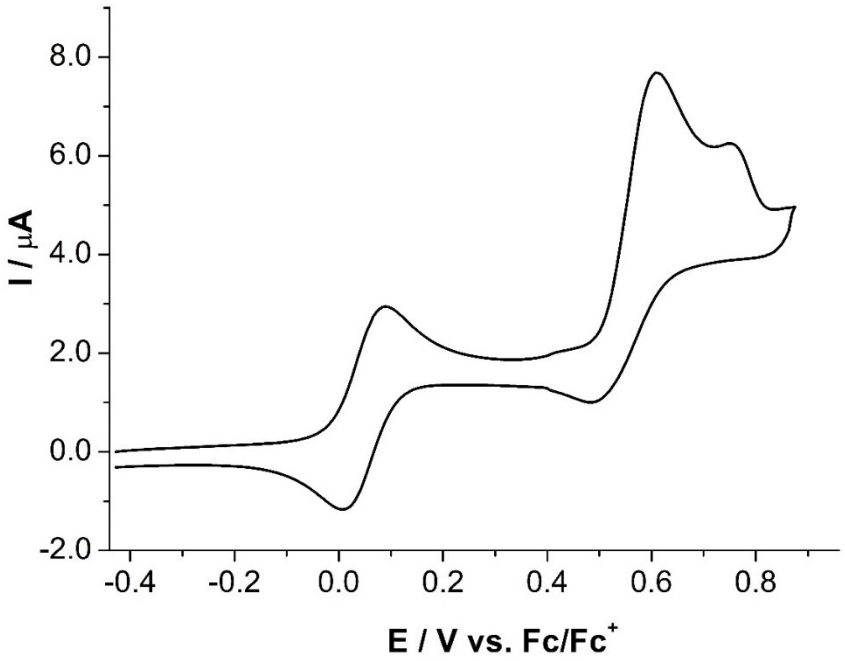

Figure S11. Cyclic voltammogram of **1** in acetonitrile solution (1 mM) at 50 mV s^{-1} scan rate.

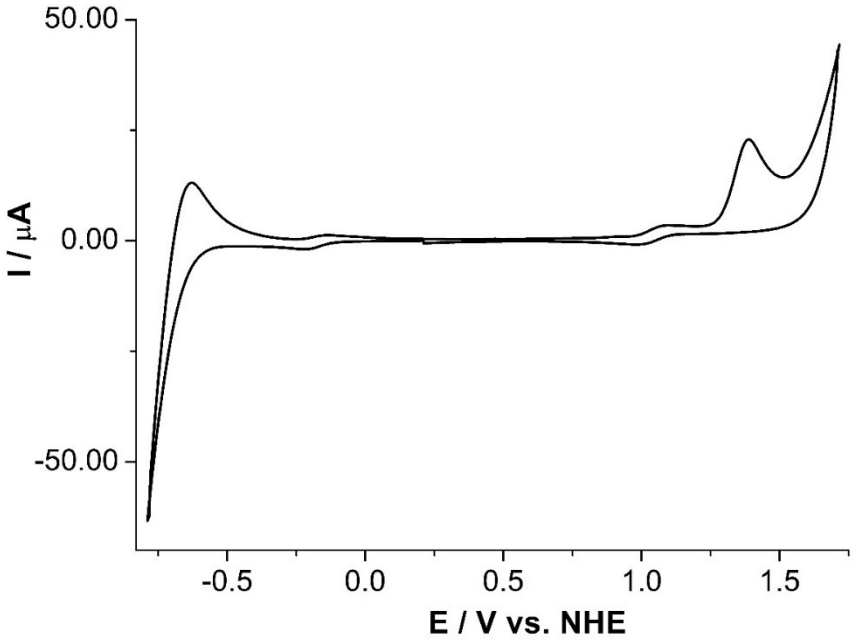

Figure S12. Cyclic voltammogram of **1** in aqueous solution (1 mM) at a scan rate of 10 mV s^{-1}.

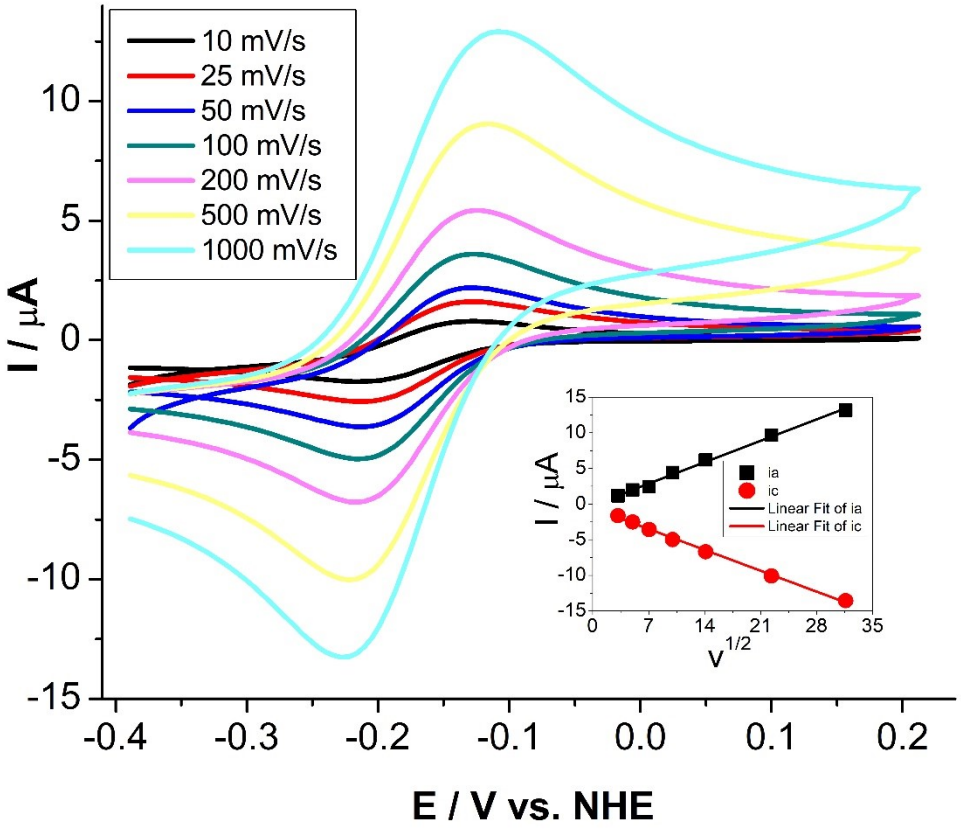

Figure S13. Cyclic voltammograms of **1** (1 mM) as a function of scan rate, recorded with $NaClO_4$ (1 M) as supporting electrolyte in aqueous solution, showing the Mn^{4+}/Mn^{3+} redox couple. Scan rates (in mV s^{-1}): black – 10; red – 25; blue – 50; dark cyan – 100; magenta – 250; yellow – 500; cyan – 1000. Inset: a plot of $i_{p,\,c}$ (red) and $i_{p,\,a}$ (black) as a function of the square root of the scan rate $v^{1/2}$, showing the linear relationship.

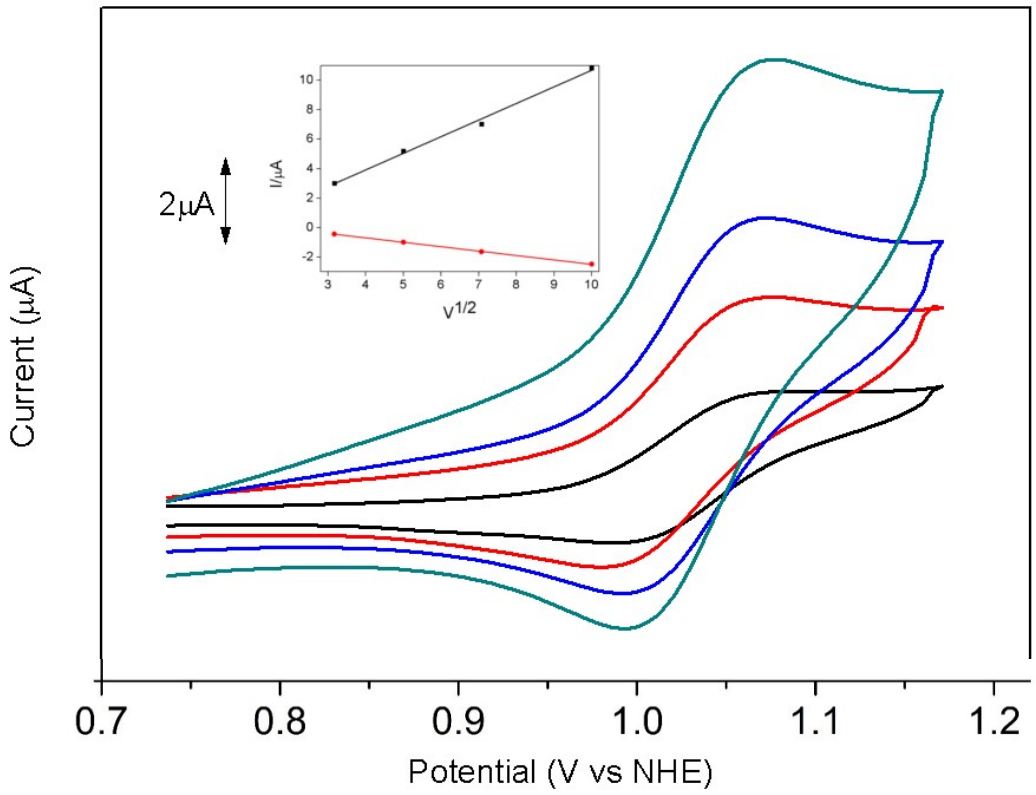

Figure S14. Cyclic voltammograms of **1** (1 mM) as a function of scan rate, recorded with $NaClO_4$ (1 M) as supporting electrolyte in aqueous solution showing the Mn^{5+}/Mn^{4+} redox couple. Scan rates (in mV s^{-1}): black – 10; red – 25; blue – 50; dark cyan – 100. Inset: a plot of $i_{p,c}$ (red) and $i_{p,a}$ (black) as a function of the square root of the scan rate $v^{1/2}$, showing the linear relationship.

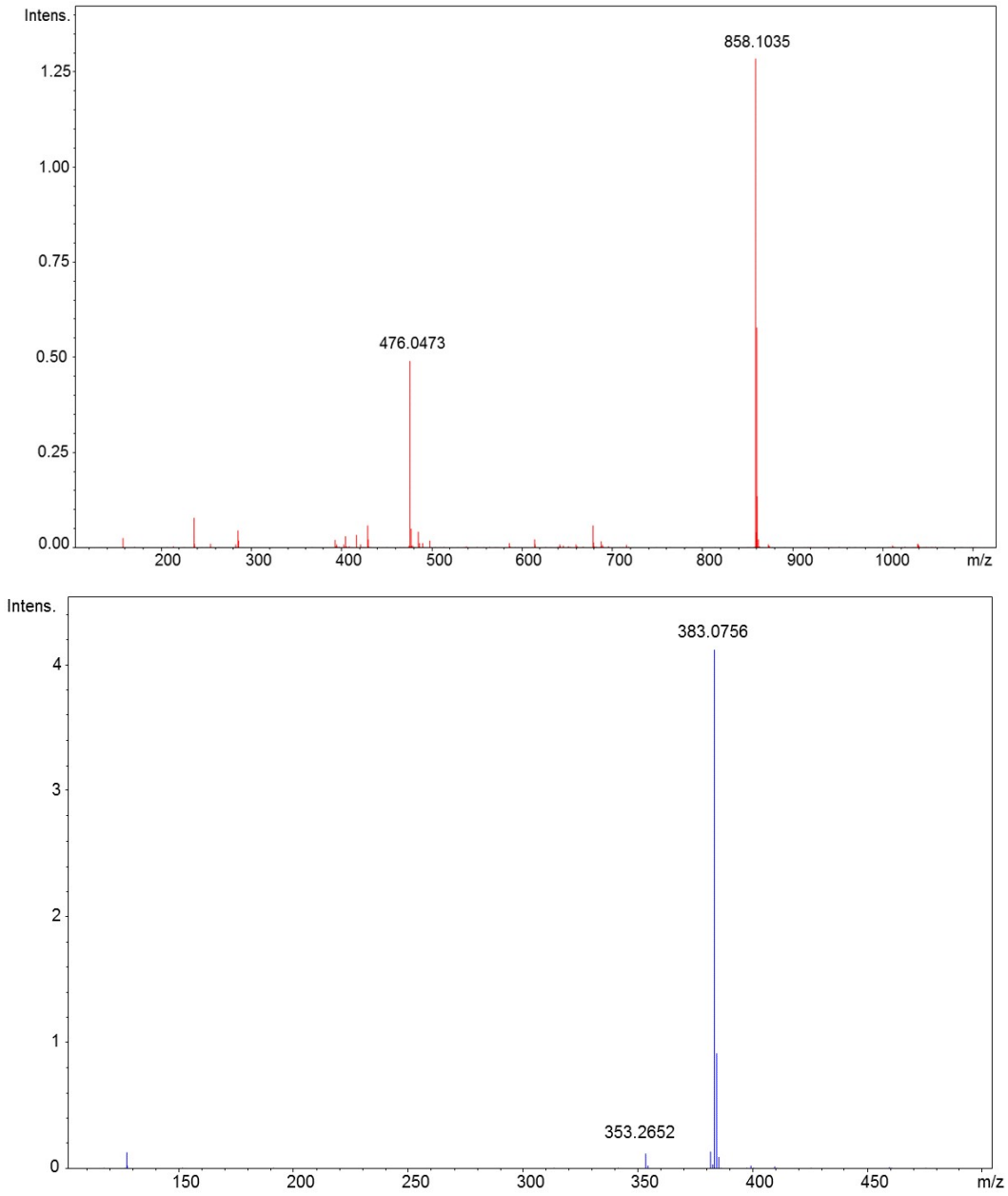

Figure S15. ESI-MS spectra of **1** in water-methanol (1:9) mixture recorded in negative (top) and positive (bottom) modes. Features at *m/z* of 476.0473 and 858.1035 (negative mode) correspond to $\{[Mn^{IV}C_{12}N_{12}O_6H_{12}]^{2-} + H^+\}^-$ and $\{[Mn^{IV}C_{12}N_{12}O_6H_{12}]^{2-} + (C_6H_5)_4As^+\}^-$, respectively. A feature at *m/z* of 383.0756 (positive mode) corresponds to $(C_6H_5)_4As^+$.

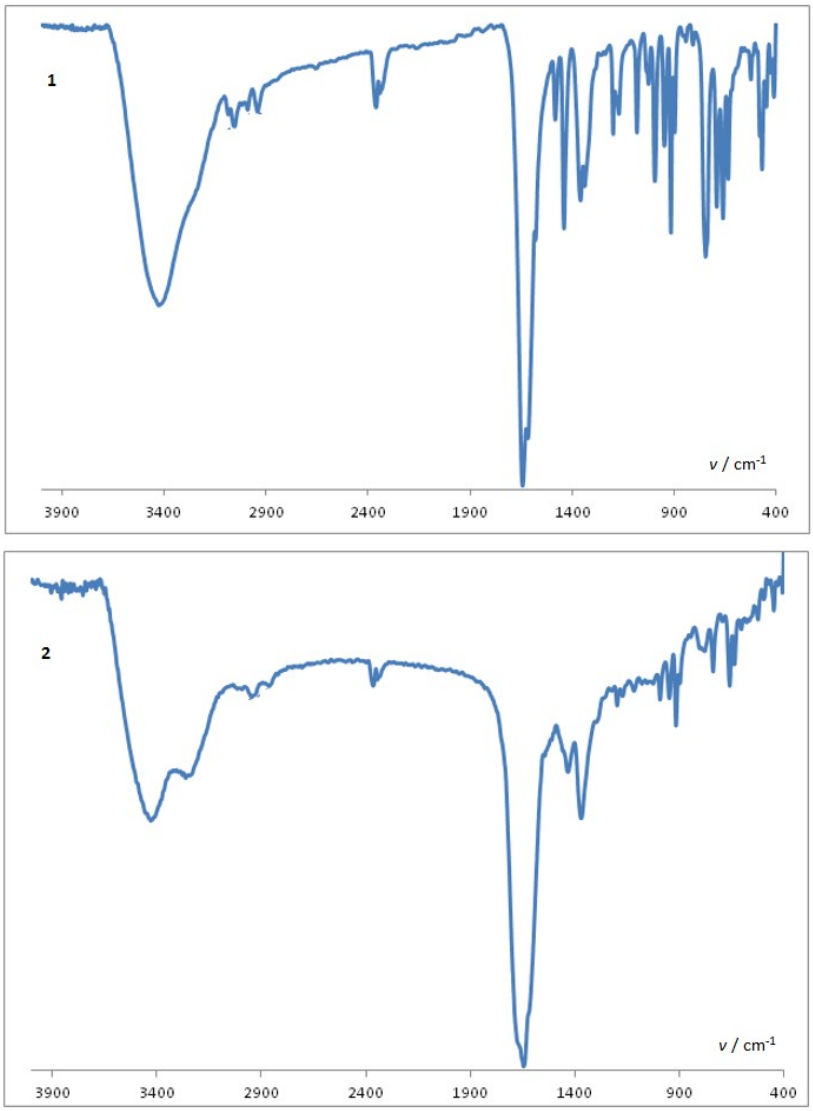

Figure S16. FTIR spectra of **1** (top) and **2** (bottom) recorded in KBr.

Table S1. Crystal data and structure refinement parameters for the X-ray structures of **1** and **2**.

Compound	$(Ph_4As)_2[Mn^{IV}(\mathbf{L}\text{-}6H)]\cdot 13.5H_2O$ (**1**)	[Na2(H2O)3MnIV(L-6H)]n·4nH2O (**2**)
Molecular formula	$C_{60}H_{79}As_2MnN_{12}O_{19.50}$	$C_{12}H_{26}MnN_{12}Na_2O_{13}$
Formula wt. (g mol^{-1})	1485.13	647.37
Temperature (K)	173(2)	160(2)
Radiation (λ, Å)	1.54184	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	*P-1*
a (Å)	21.0876 (3)	9.9513(7)
b (Å)	21.1132 (2)	11.2457(8)
c (Å)	29.7036 (3)	11.7458(9)
α (°)	90.00	106.127(7)
β (°)	90.00	93.290(6)
γ (°)	90.00	106.007(6)
Volume ($Å^3$)	13224.8 (3)	1200.93(16)
Z	8	2
ρ_{calcd} (mg m^{-3})	1.492	1.790
μ (mm^{-1})	3.43	0.68
Crystal size (mm^3)	0.14 × 0.13 × 0.12	0.40× 0.15 × 0.10
Theta range (°)	3.0 to 61.6	1.8 to 25.0
Reflections collected	32460	8613
Independent reflections	9514 [R_{int} = 0.041]	4238 [R_{int} = 0.029]
Completeness	0.927	1.000
Goodness-of-fit on F^2	1.03	1.04
Final *R* indices	$R_1{}^a$ = 0.044	$R_1{}^a$ = 0.036
[$R > 2\sigma$ (I)]	$wR_2{}^b$ = 0.122	$wR_2{}^b$ = 0.0824
R indices (all data)	$R_1{}^a$ = 0.050	$R_1{}^a$ = 0.0449
	$wR_2{}^b$ = 0.1215	$wR_2{}^b$ = 0.087
Largest diff. peak and hole (e $Å^{-3}$)	0.59 and -0.51	0.49 and -0.39

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c]GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

Table S2: Bond lengths (Å) and angles (°) for **1**.

C101—C102	1.393 (4)	C232—C233	1.385 (5)
C101—C106	1.385 (5)	C233—H233	0.9500
C101—As1	1.908 (3)	C233—C234	1.372 (6)
C102—H102	0.9500	C234—H234	0.9500
C102—C103	1.388 (5)	C234—C235	1.372 (6)
C103—H103	0.9500	C235—H235	0.9500
C103—C104	1.388 (5)	C235—C236	1.390 (5)
C104—H104	0.9500	C236—H236	0.9500
C104—C105	1.387 (5)	C1—C2	1.529 (4)
C105—H105	0.9500	C1—N2	1.340 (4)
C105—C106	1.388 (5)	C1—O1	1.233 (4)
C106—H106	0.9500	C2—N3	1.355 (4)
C111—C112	1.400 (5)	C2—O2	1.227 (4)
C111—C116	1.390 (5)	C3—C4	1.523 (4)
C111—As1	1.915 (3)	C3—N6	1.335 (4)
C112—H112	0.9500	C3—O3	1.234 (4)
C112—C113	1.392 (5)	C4—N7	1.345 (4)
C113—H113	0.9500	C4—O4	1.234 (4)
C113—C114	1.375 (6)	C5—C6	1.518 (4)
C114—H114	0.9500	C5—N10	1.328 (4)
C114—C115	1.387 (6)	C5—O5	1.245 (4)
C115—H115	0.9500	C6—N11	1.334 (4)
C115—C116	1.390 (5)	C6—O6	1.237 (4)
C116—H116	0.9500	C7—H7A	0.9900
C121—C122	1.391 (5)	C7—H7B	0.9900
C121—C126	1.389 (5)	C7—N1	1.464 (5)
C121—As1	1.903 (3)	C7—N5	1.469 (5)
C122—H122	0.9500	C8—H8A	0.9900
C122—C123	1.389 (5)	C8—H8B	0.9900
C123—H123	0.9500	C8—N5	1.478 (5)
C123—C124	1.387 (5)	C8—N9	1.445 (5)
C124—H124	0.9500	C9—H9A	0.9900
C124—C125	1.383 (6)	C9—H9B	0.9900
C125—H125	0.9500	C9—N1	1.435 (5)
C125—C126	1.383 (5)	C9—N9	1.470 (4)
C126—H126	0.9500	C10—H10A	0.9900
C131—C132	1.402 (5)	C10—H10B	0.9900
C131—C136	1.400 (5)	C10—N4	1.458 (4)
C131—As1	1.903 (3)	C10—N8	1.469 (5)
C132—H132	0.9500	C11—H11A	0.9900
C132—C133	1.379 (5)	C11—H11B	0.9900

C133—H133	0.9500	C11—N4	1.461 (5)
C133—C134	1.381 (5)	C11—N12	1.462 (5)
C134—H134	0.9500	C12—H12A	0.9900
C134—C135	1.381 (5)	C12—H12B	0.9900
C135—H135	0.9500	C12—N8	1.453 (5)
C135—C136	1.395 (5)	C12—N12	1.481 (5)
C136—H136	0.9500	N1—N2	1.436 (4)
C201—C202	1.374 (5)	N2—Mn1	1.971 (3)
C201—C206	1.402 (5)	N3—N4	1.430 (3)
C201—As2	1.914 (3)	N3—Mn1	1.978 (3)
C202—H202	0.9500	N5—N6	1.431 (4)
C202—C203	1.395 (5)	N6—Mn1	1.974 (3)
C203—H203	0.9500	N7—N8	1.430 (3)
C203—C204	1.382 (7)	N7—Mn1	1.971 (3)
C204—H204	0.9500	N9—N10	1.433 (3)
C204—C205	1.379 (7)	N10—Mn1	1.992 (3)
C205—H205	0.9500	N11—N12	1.434 (4)
C205—C206	1.382 (5)	N11—Mn1	1.970 (3)
C206—H206	0.9500	O312—H31A	0.8497
C212—C213	1.383 (5)	O312—H31B	0.8496
C212—C217	1.401 (4)	O313—H31C	0.8495
C212—As2	1.900 (3)	O313—H31D	0.8498
C213—H213	0.9500	O303—H30A	0.8505
C213—C214	1.392 (5)	O303—H30B	0.8500
C214—H214	0.9500	O309—H30C	0.8502
C214—C215	1.395 (5)	O309—H30D	0.8501
C215—H215	0.9500	O307—H30E	0.8505
C215—C216	1.368 (5)	O307—H30F	0.8509
C216—H216	0.9500	O302—H30G	0.8499
C216—C217	1.384 (5)	O302—H30H	0.8499
C217—H217	0.9500	O310—H31E	0.8487
C221—C222	1.382 (5)	O310—H31F	0.8497
C221—C226	1.402 (4)	O308—H30I	0.8508
C221—As2	1.903 (3)	O308—H30J	0.8507
C222—H222	0.9500	O301—H30K	0.8502
C222—C223	1.391 (6)	O301—H30L	0.8494
C223—H223	0.9500	O306—H30M	0.8503
C223—C224	1.377 (5)	O306—H30N	0.8499
C224—H224	0.9500	O311—H31G	0.8498
C224—C225	1.377 (6)	O311—H31H	0.8502
C225—H225	0.9500	O304—H30O	0.8498
C225—C226	1.381 (5)	O304—H30P	0.8494
C226—H226	0.9500	O314—H31I	0.8500

C231—C232	1.398 (5)	O314—H31J	0.8503
C231—C236	1.392 (5)	O305—H30Q	0.8700
C231—As2	1.901 (3)	O305—H30R	0.8699
C232—H232	0.9500		
C102—C101—As1	117.4 (3)	C232—C233—H233	119.5
C106—C101—C102	120.7 (3)	C234—C233—C232	120.9 (4)
C106—C101—As1	121.9 (2)	C234—C233—H233	119.5
C101—C102—H102	120.2	C233—C234—H234	120.0
C103—C102—C101	119.5 (3)	C235—C234—C233	120.0 (3)
C103—C102—H102	120.2	C235—C234—H234	120.0
C102—C103—H103	120.2	C234—C235—H235	119.8
C104—C103—C102	119.7 (3)	C234—C235—C236	120.4 (4)
C104—C103—H103	120.2	C236—C235—H235	119.8
C103—C104—H104	119.7	C231—C236—H236	120.1
C105—C104—C103	120.6 (3)	C235—C236—C231	119.7 (3)
C105—C104—H104	119.7	C235—C236—H236	120.1
C104—C105—H105	120.1	C212—As2—C201	112.76 (15)
C104—C105—C106	119.9 (3)	C212—As2—C221	108.99 (14)
C106—C105—H105	120.1	C212—As2—C231	106.77 (14)
C101—C106—C105	119.6 (3)	C221—As2—C201	106.48 (14)
C101—C106—H106	120.2	C231—As2—C201	109.92 (13)
C105—C106—H106	120.2	C231—As2—C221	112.01 (15)
C112—C111—As1	118.6 (3)	N2—C1—C2	110.6 (2)
C116—C111—C112	120.7 (3)	O1—C1—C2	121.9 (3)
C116—C111—As1	120.7 (3)	O1—C1—N2	127.4 (3)
C111—C112—H112	120.4	N3—C2—C1	109.7 (2)
C113—C112—C111	119.2 (4)	O2—C2—C1	121.9 (3)
C113—C112—H112	120.4	O2—C2—N3	128.3 (3)
C112—C113—H113	120.0	N6—C3—C4	110.4 (3)
C114—C113—C112	120.1 (4)	O3—C3—C4	121.1 (3)
C114—C113—H113	120.0	O3—C3—N6	128.4 (3)
C113—C114—H114	119.6	N7—C4—C3	110.4 (3)
C113—C114—C115	120.7 (3)	O4—C4—C3	121.7 (3)
C115—C114—H114	119.6	O4—C4—N7	127.9 (3)
C114—C115—H115	119.9	N10—C5—C6	110.9 (3)
C114—C115—C116	120.2 (4)	O5—C5—C6	121.4 (3)
C116—C115—H115	119.9	O5—C5—N10	127.7 (3)
C111—C116—C115	119.1 (4)	N11—C6—C5	110.4 (3)
C111—C116—H116	120.4	O6—C6—C5	121.9 (3)
C115—C116—H116	120.4	O6—C6—N11	127.6 (3)
C122—C121—As1	118.8 (2)	H7A—C7—H7B	107.6
C126—C121—C122	121.0 (3)	N1—C7—H7A	108.7

C126—C121—As1	120.1 (3)	N1—C7—H7B	108.7
C121—C122—H122	120.4	N1—C7—N5	114.3 (3)
C123—C122—C121	119.3 (3)	N5—C7—H7A	108.7
C123—C122—H122	120.4	N5—C7—H7B	108.7
C122—C123—H123	120.2	H8A—C8—H8B	107.5
C124—C123—C122	119.6 (4)	N5—C8—H8A	108.5
C124—C123—H123	120.2	N5—C8—H8B	108.5
C123—C124—H124	119.7	N9—C8—H8A	108.5
C125—C124—C123	120.7 (3)	N9—C8—H8B	108.5
C125—C124—H124	119.7	N9—C8—N5	115.1 (3)
C124—C125—H125	119.9	H9A—C9—H9B	107.5
C124—C125—C126	120.2 (3)	N1—C9—H9A	108.5
C126—C125—H125	119.9	N1—C9—H9B	108.5
C121—C126—H126	120.4	N1—C9—N9	115.2 (3)
C125—C126—C121	119.2 (4)	N9—C9—H9A	108.5
C125—C126—H126	120.4	N9—C9—H9B	108.5
C132—C131—As1	119.7 (3)	H10A—C10—H10B	107.6
C136—C131—C132	120.6 (3)	N4—C10—H10A	108.7
C136—C131—As1	119.6 (2)	N4—C10—H10B	108.7
C131—C132—H132	120.6	N4—C10—N8	114.4 (3)
C133—C132—C131	118.8 (3)	N8—C10—H10A	108.7
C133—C132—H132	120.6	N8—C10—H10B	108.7
C132—C133—H133	119.5	H11A—C11—H11B	107.6
C132—C133—C134	120.9 (3)	N4—C11—H11A	108.6
C134—C133—H133	119.5	N4—C11—H11B	108.6
C133—C134—H134	119.7	N4—C11—N12	114.7 (3)
C135—C134—C133	120.7 (3)	N12—C11—H11A	108.6
C135—C134—H134	119.7	N12—C11—H11B	108.6
C134—C135—H135	120.1	H12A—C12—H12B	107.6
C134—C135—C136	119.8 (3)	N8—C12—H12A	108.6
C136—C135—H135	120.1	N8—C12—H12B	108.6
C131—C136—H136	120.4	N8—C12—N12	114.6 (3)
C135—C136—C131	119.1 (3)	N12—C12—H12A	108.6
C135—C136—H136	120.4	N12—C12—H12B	108.6
C101—As1—C111	107.98 (14)	C9—N1—C7	109.6 (3)
C121—As1—C101	109.23 (14)	C9—N1—N2	110.8 (3)
C121—As1—C111	109.76 (15)	N2—N1—C7	109.4 (3)
C121—As1—C131	109.11 (14)	C1—N2—N1	114.9 (2)
C131—As1—C101	109.90 (14)	C1—N2—Mn1	118.0 (2)
C131—As1—C111	110.83 (13)	N1—N2—Mn1	121.50 (19)
C202—C201—C206	120.8 (3)	C2—N3—N4	114.3 (2)
C202—C201—As2	122.9 (3)	C2—N3—Mn1	116.9 (2)
C206—C201—As2	116.3 (3)	N4—N3—Mn1	120.79 (19)

C201—C202—H202	120.3	C10—N4—C11	109.7 (3)
C201—C202—C203	119.4 (4)	N3—N4—C10	111.2 (2)
C203—C202—H202	120.3	N3—N4—C11	108.9 (3)
C202—C203—H203	120.1	C7—N5—C8	109.4 (3)
C204—C203—C202	119.8 (4)	N6—N5—C7	109.7 (2)
C204—C203—H203	120.1	N6—N5—C8	109.1 (3)
C203—C204—H204	119.6	C3—N6—N5	115.7 (2)
C205—C204—C203	120.8 (4)	C3—N6—Mn1	118.4 (2)
C205—C204—H204	119.6	N5—N6—Mn1	121.6 (2)
C204—C205—H205	120.0	C4—N7—N8	113.7 (3)
C204—C205—C206	120.0 (4)	C4—N7—Mn1	117.1 (2)
C206—C205—H205	120.0	N8—N7—Mn1	121.20 (19)
C201—C206—H206	120.4	C12—N8—C10	109.7 (3)
C205—C206—C201	119.2 (4)	N7—N8—C10	109.1 (2)
C205—C206—H206	120.4	N7—N8—C12	110.6 (3)
C213—C212—C217	120.7 (3)	C8—N9—C9	109.2 (3)
C213—C212—As2	119.7 (2)	N10—N9—C8	110.6 (3)
C217—C212—As2	119.4 (3)	N10—N9—C9	108.9 (2)
C212—C213—H213	120.2	C5—N10—N9	115.0 (3)
C212—C213—C214	119.5 (3)	C5—N10—Mn1	117.2 (2)
C214—C213—H213	120.2	N9—N10—Mn1	121.2 (2)
C213—C214—H214	120.3	C6—N11—N12	115.2 (3)
C213—C214—C215	119.5 (4)	C6—N11—Mn1	118.4 (2)
C215—C214—H214	120.3	N12—N11—Mn1	121.1 (2)
C214—C215—H215	119.7	C11—N12—C12	109.5 (3)
C216—C215—C214	120.7 (3)	N11—N12—C11	110.2 (3)
C216—C215—H215	119.7	N11—N12—C12	108.8 (2)
C215—C216—H216	119.7	N2—Mn1—N3	79.29 (11)
C215—C216—C217	120.6 (3)	N2—Mn1—N6	87.24 (11)
C217—C216—H216	119.7	N2—Mn1—N10	85.84 (11)
C212—C217—H217	120.5	N3—Mn1—N10	153.74 (12)
C216—C217—C212	119.0 (3)	N6—Mn1—N3	113.00 (13)
C216—C217—H217	120.5	N6—Mn1—N10	87.51 (12)
C222—C221—C226	120.0 (3)	N7—Mn1—N2	155.17 (13)
C222—C221—As2	121.7 (2)	N7—Mn1—N3	87.20 (11)
C226—C221—As2	118.3 (3)	N7—Mn1—N6	78.94 (11)
C221—C222—H222	120.3	N7—Mn1—N10	113.75 (12)
C221—C222—C223	119.5 (3)	N11—Mn1—N2	112.00 (12)
C223—C222—H222	120.3	N11—Mn1—N3	87.12 (12)
C222—C223—H223	119.8	N11—Mn1—N6	154.98 (12)
C224—C223—C222	120.3 (4)	N11—Mn1—N7	87.76 (12)
C224—C223—H223	119.8	N11—Mn1—N10	78.51 (11)
C223—C224—H224	119.9	H31A—O312—H31B	109.5

C225—C224—C223	120.3 (4)	H31C—O313—H31D	109.5
C225—C224—H224	119.9	H30A—O303—H30B	109.4
C224—C225—H225	119.8	H30C—O309—H30D	109.4
C224—C225—C226	120.3 (3)	H30E—O307—H30F	109.4
C226—C225—H225	119.8	H30G—O302—H30H	109.5
C221—C226—H226	120.2	H31E—O310—H31F	109.5
C225—C226—C221	119.5 (3)	H30I—O308—H30J	109.4
C225—C226—H226	120.2	H30K—O301—H30L	109.6
C232—C231—As2	121.4 (3)	H30M—O306—H30N	109.5
C236—C231—C232	119.6 (3)	H31G—O311—H31H	109.5
C236—C231—As2	119.0 (3)	H30O—O304—H30P	109.5
C231—C232—H232	120.4	H31I—O314—H31J	109.5
C233—C232—C231	119.3 (4)	H30Q—O305—H30R	109.5
C233—C232—H232	120.4		

Table S3: Bond lengths (Å) and angles (°) for **2**.

Mn1—N6	1.9708 (19)	O7W—H7O	0.8513
Mn1—N5	1.971 (2)	O7W—H7P	0.8505
Mn1—N3	1.977 (2)	N1—C1	1.343 (3)
Mn1—N4	1.978 (2)	N1—N7	1.421 (3)
Mn1—N2	1.9829 (19)	N2—C2	1.333 (3)
Mn1—N1	1.9831 (19)	N2—N8	1.426 (3)
Na1—O3^{i}	2.3327 (19)	N3—C3	1.349 (3)
Na1—O4W	2.354 (2)	N3—N9	1.422 (3)
Na1—O6^{ii}	2.4091 (19)	N4—C4	1.345 (3)
Na1—O5W	2.436 (2)	N4—N10	1.423 (3)
Na1—O2	2.526 (2)	N5—C5	1.348 (3)
Na1—N12^{ii}	2.837 (2)	N5—N11	1.425 (3)
Na1—O1	2.875 (2)	N6—C6	1.338 (3)
Na2—O1	2.2755 (19)	N6—N12	1.434 (3)
Na2—O6W	2.381 (2)	N7—C7	1.460 (3)
Na2—O4^{i}	2.421 (2)	N7—C11	1.484 (3)
Na2—O6^{ii}	2.4348 (19)	N8—C12	1.465 (3)
Na2—O5^{ii}	2.4832 (18)	N8—C8	1.474 (3)
Na2—O1^{iii}	2.609 (2)	N9—C9	1.464 (3)
Na2—C6^{ii}	2.952 (3)	N9—C7	1.493 (3)
Na2—C5^{ii}	3.058 (3)	N10—C8	1.469 (3)
		N10—C10	1.478 (3)
		N11—C11	1.465 (3)
O1—C1	1.240 (3)	N11—C9	1.475 (3)
O2—C2	1.243 (3)	N12—C10	1.468 (3)
O3—C3	1.231 (3)	N12—C12	1.481 (3)
O4—C4	1.235 (3)	C1—C2	1.508 (3)
O5—C5	1.236 (3)	C3—C4	1.522 (3)
O6—C6	1.237 (3)	C5—C6	1.529 (3)
O1W—H1O	0.8513	C7—H7A	0.9700
O1W—H1P	0.8506	C7—H7B	0.9700
O2W—H2O	0.8225	C8—H8A	0.9700
O2W—H2P	0.8521	C8—H8B	0.9700
O3W—H3O	0.8511	C9—H9A	0.9700
O3W—H3P	0.8512	C9—H9B	0.9700
O4W—H4O	0.8513	C10—H10A	0.9700
O4W—H4P	0.8505	C10—H10B	0.9700
O5W—H5O	0.8500	C11—H11A	0.9700
O5W—H5P	0.8499	C11—H11B	0.9700
O6W—H6O	0.8500	C12—H12A	0.9700
O6W—H6P	0.8743	C12—H12B	0.9700

N6—Mn1—N5	80.37 (8)	C5—N5—N11	114.7 (2)
N6—Mn1—N3	109.71 (8)	C5—N5—Mn1	116.93 (16)
N5—Mn1—N3	87.78 (8)	N11—N5—Mn1	121.23 (15)
N6—Mn1—N4	87.41 (8)	C6—N6—N12	114.2 (2)
N5—Mn1—N4	158.42 (8)	C6—N6—Mn1	116.47 (16)
N3—Mn1—N4	79.64 (8)	N12—N6—Mn1	121.76 (15)
N6—Mn1—N2	86.82 (8)	N1—N7—C7	110.40 (18)
N5—Mn1—N2	110.04 (8)	N1—N7—C11	109.28 (18)
N3—Mn1—N2	157.88 (9)	C7—N7—C11	109.71 (18)
N4—Mn1—N2	86.76 (8)	N2—N8—C12	110.03 (19)
N6—Mn1—N1	157.67 (8)	N2—N8—C8	109.42 (18)
N5—Mn1—N1	86.94 (8)	C12—N8—C8	109.74 (18)
N3—Mn1—N1	87.90 (8)	N3—N9—C9	111.09 (19)
N4—Mn1—N1	109.84 (8)	N3—N9—C7	109.37 (17)
N2—Mn1—N1	80.35 (8)	C9—N9—C7	109.77 (19)
O3^{i}—Na1—O4W	174.43 (8)	N4—N10—C8	110.91 (17)
O3^{i}—Na1—O6^{ii}	80.26 (6)	N4—N10—C10	109.49 (18)
O4W—Na1—O6^{ii}	99.01 (7)	C8—N10—C10	109.51 (19)
O3^{i}—Na1—O5W	78.70 (7)	N5—N11—C11	111.33 (18)
O4W—Na1—O5W	98.72 (7)	N5—N11—C9	108.89 (17)
O6^{ii}—Na1—O5W	139.97 (8)	C11—N11—C9	109.26 (19)
O3^{i}—Na1—O2	101.75 (7)	N6—N12—C10	109.94 (18)
O4W—Na1—O2	83.13 (7)	N6—N12—C12	108.86 (17)
O6^{ii}—Na1—O2	127.24 (7)	C10—N12—C12	109.82 (19)
O5W—Na1—O2	90.36 (7)	N6—N12—Na1^{iv}	104.92 (13)
O3^{i}—Na1—N12^{ii}	81.75 (6)	C10—N12—Na1^{iv}	115.41 (13)
O4W—Na1—N12^{ii}	93.02 (7)	C12—N12—Na1^{iv}	107.63 (14)
O6^{ii}—Na1—N12^{ii}	61.78 (6)	O1—C1—N1	128.6 (2)
O5W—Na1—N12^{ii}	81.71 (7)	O1—C1—C2	120.4 (2)
O2—Na1—N12^{ii}	170.58 (7)	N1—C1—C2	110.96 (19)
O3^{i}—Na1—O1	72.84 (6)	O2—C2—N2	128.8 (2)
O4W—Na1—O1	112.11 (7)	O2—C2—C1	119.7 (2)
O6^{ii}—Na1—O1	68.58 (6)	N2—C2—C1	111.5 (2)
O5W—Na1—O1	134.29 (6)	O3—C3—N3	127.2 (2)
O2—Na1—O1	62.25 (6)	O3—C3—C4	121.6 (2)
N12^{ii}—Na1—O1	127.11 (6)	N3—C3—C4	111.2 (2)
O1—Na2—O6W	127.21 (8)	O4—C4—N4	127.7 (2)
O1—Na2—O4^{i}	117.20 (7)	O4—C4—C3	121.8 (2)
O6W—Na2—O4^{i}	86.52 (7)	N4—C4—C3	110.5 (2)
O1—Na2—O6^{ii}	79.11 (6)	O5—C5—N5	128.5 (2)
O6W—Na2—O6^{ii}	151.13 (7)	O5—C5—C6	121.0 (2)
O4^{i}—Na2—O6^{ii}	90.99 (7)	N5—C5—C6	110.5 (2)

O1—Na2—O5^{ii}	145.95 (7)	O5—C5—Na2^{iv}	51.45 (12)
O6W—Na2—O5^{ii}	81.50 (7)	N5—C5—Na2^{iv}	166.21 (16)
O4^{i}—Na2—O5^{ii}	77.92 (6)	C6—C5—Na2^{iv}	71.45 (12)
O6^{ii}—Na2—O5^{ii}	69.88 (6)	O6—C6—N6	128.0 (2)
O1—Na2—O1^{iii}	79.63 (6)	O6—C6—C5	120.2 (2)
O6W—Na2—O1^{iii}	89.13 (7)	N6—C6—C5	111.8 (2)
O4^{i}—Na2—O1^{iii}	161.31 (7)	O6—C6—Na2^{iv}	53.79 (12)
O6^{ii}—Na2—O1^{iii}	84.10 (6)	N6—C6—Na2^{iv}	143.49 (15)
O5^{ii}—Na2—O1^{iii}	83.46 (6)	C5—C6—Na2^{iv}	79.13 (13)
C1—O1—Na2	128.84 (16)	N7—C7—N9	113.91 (19)
C1—O1—Na2^{iii}	125.01 (15)	N7—C7—H7A	108.8
Na2—O1—Na2^{iii}	100.37 (6)	N9—C7—H7A	108.8
C1—O1—Na1	91.83 (15)	N7—C7—H7B	108.8
Na2—O1—Na1	96.01 (6)	N9—C7—H7B	108.8
Na2^{iii}—O1—Na1	107.56 (6)	H7A—C7—H7B	107.7
C2—O2—Na1	110.34 (15)	N10—C8—N8	114.0 (2)
C3—O3—Na1^{i}	154.87 (17)	N10—C8—H8A	108.7
C4—O4—Na2^{i}	131.46 (17)	N8—C8—H8A	108.7
C5—O5—Na2^{iv}	105.64 (15)	N10—C8—H8B	108.7
C6—O6—Na1^{iv}	121.42 (16)	N8—C8—H8B	108.7
C6—O6—Na2^{iv}	102.02 (14)	H8A—C8—H8B	107.6
Na1^{iv}—O6—Na2^{iv}	105.23 (7)	N9—C9—N11	114.36 (19)
H1O—O1W—H1P	109.4	N9—C9—H9A	108.7
H2O—O2W—H2P	107.7	N11—C9—H9A	108.7
H3O—O3W—H3P	109.5	N9—C9—H9B	108.7
Na1—O4W—H4O	125.4	N11—C9—H9B	108.7
Na1—O4W—H4P	122.8	H9A—C9—H9B	107.6
H4O—O4W—H4P	109.5	N12—C10—N10	114.28 (18)
Na1—O5W—H5O	115.6	N12—C10—H10A	108.7
Na1—O5W—H5P	101.4	N10—C10—H10A	108.7
H5O—O5W—H5P	115.7	N12—C10—H10B	108.7
Na2—O6W—H6O	97.4	N10—C10—H10B	108.7
Na2—O6W—H6P	110.6	H10A—C10—H10B	107.6
H6O—O6W—H6P	97.9	N11—C11—N7	114.06 (19)
H7O—O7W—H7P	109.4	N11—C11—H11A	108.7
C1—N1—N7	114.95 (18)	N7—C11—H11A	108.7
C1—N1—Mn1	114.72 (16)	N11—C11—H11B	108.7
N7—N1—Mn1	121.24 (14)	N7—C11—H11B	108.7
C2—N2—N8	115.38 (19)	H11A—C11—H11B	107.6
C2—N2—Mn1	115.33 (16)	N8—C12—N12	114.35 (19)
N8—N2—Mn1	121.76 (13)	N8—C12—H12A	108.7
C3—N3—N9	114.3 (2)	N12—C12—H12A	108.7
C3—N3—Mn1	116.53 (16)	N8—C12—H12B	108.7

N9—N3—Mn1	120.13 (14)	N12—C12—H12B	108.7
C4—N4—N10	114.25 (19)	H12A—C12—H12B	107.6
C4—N4—Mn1	117.54 (16)	N10—N4—Mn1	121.21 (15)
C1—N1—N7—C7	-155.9 (2)	O3—C3—C4—O4	23.3 (4)
Mn1—N1—N7—C7	58.8 (2)	N3—C3—C4—O4	-157.0 (2)
C1—N1—N7—C11	83.4 (2)	O3—C3—C4—N4	-156.2 (2)
Mn1—N1—N7—C11	-61.9 (2)	N3—C3—C4—N4	23.4 (3)
C2—N2—N8—C12	-152.1 (2)	Na2^{iv}—O5—C5—N5	-162.3 (2)
Mn1—N2—N8—C12	59.6 (2)	Na2^{iv}—O5—C5—C6	17.5 (2)
C2—N2—N8—C8	87.2 (2)	N11—N5—C5—O5	12.5 (3)
Mn1—N2—N8—C8	-61.0 (2)	Mn1—N5—C5—O5	163.3 (2)
C3—N3—N9—C9	-154.50 (19)	N11—N5—C5—C6	-167.42 (18)
Mn1—N3—N9—C9	59.5 (2)	Mn1—N5—C5—C6	-16.6 (2)
C3—N3—N9—C7	84.2 (2)	N11—N5—C5—Na2^{iv}	-71.8 (8)
Mn1—N3—N9—C7	-61.8 (2)	Mn1—N5—C5—Na2^{iv}	79.0 (8)
C4—N4—N10—C8	-150.0 (2)	Na1^{iv}—O6—C6—N6	17.4 (3)
Mn1—N4—N10—C8	60.0 (2)	Na2^{iv}—O6—C6—N6	133.8 (2)
C4—N4—N10—C10	89.0 (2)	Na1^{iv}—O6—C6—C5	-162.25 (15)
Mn1—N4—N10—C10	-60.9 (2)	Na2^{iv}—O6—C6—C5	-45.8 (2)
C5—N5—N11—C11	-151.1 (2)	Na1^{iv}—O6—C6—Na2^{iv}	-116.41 (14)
Mn1—N5—N11—C11	59.4 (2)	N12—N6—C6—O6	12.3 (3)
C5—N5—N11—C9	88.3 (2)	Mn1—N6—C6—O6	162.57 (18)
Mn1—N5—N11—C9	-61.1 (2)	N12—N6—C6—C5	-168.05 (17)
C6—N6—N12—C10	-152.40 (19)	Mn1—N6—C6—C5	-17.8 (2)
Mn1—N6—N12—C10	59.0 (2)	N12—N6—C6—Na2^{iv}	90.5 (3)
C6—N6—N12—C12	87.3 (2)	Mn1—N6—C6—Na2^{iv}	-119.3 (2)
Mn1—N6—N12—C12	-61.3 (2)	O5—C5—C6—O6	21.7 (3)
C6—N6—N12—Na1^{iv}	-27.72 (19)	N5—C5—C6—O6	-158.4 (2)
Mn1—N6—N12—Na1^{iv}	-176.27 (10)	Na2^{iv}—C5—C6—O6	36.12 (17)
Na2—O1—C1—N1	24.6 (4)	O5—C5—C6—N6	-158.0 (2)
Na2^{iii}—O1—C1—N1	-123.2 (2)	N5—C5—C6—N6	21.9 (3)
Na1—O1—C1—N1	123.8 (3)	Na2^{iv}—C5—C6—N6	-143.58 (18)
Na2—O1—C1—C2	-154.72 (17)	O5—C5—C6—Na2^{iv}	-14.4 (2)
Na2^{iii}—O1—C1—C2	57.5 (3)	N5—C5—C6—Na2^{iv}	165.51 (17)
Na1—O1—C1—C2	-55.5 (2)	N1—N7—C7—N9	-67.5 (2)
N7—N1—C1—O1	8.5 (4)	C11—N7—C7—N9	53.0 (3)
Mn1—N1—C1—O1	156.0 (2)	N3—N9—C7—N7	69.3 (3)
N7—N1—C1—C2	-172.2 (2)	C9—N9—C7—N7	-52.8 (3)
Mn1—N1—C1—C2	-24.6 (3)	N4—N10—C8—N8	-66.9 (3)
Na1—O2—C2—N2	-152.4 (2)	C10—N10—C8—N8	54.0 (3)
Na1—O2—C2—C1	27.0 (3)	N2—N8—C8—N10	66.8 (2)
N8—N2—C2—O2	7.8 (4)	C12—N8—C8—N10	-54.1 (3)

Mn1—N2—C2—O2	158.2 (2)	N3—N9—C9—N11	-67.8 (2)
N8—N2—C2—C1	-171.64 (19)	C7—N9—C9—N11	53.3 (3)
Mn1—N2—C2—C1	-21.3 (3)	N5—N11—C9—N9	67.5 (2)
O1—C1—C2—O2	29.8 (4)	C11—N11—C9—N9	-54.2 (3)
N1—C1—C2—O2	-149.7 (2)	N6—N12—C10—N10	-67.1 (2)
O1—C1—C2—N2	-150.7 (2)	C12—N12—C10—N10	52.7 (3)
N1—C1—C2—N2	29.9 (3)	Na1^{iv}—N12—C10—N10	174.56 (14)
Na1^{i}—O3—C3—N3	73.8 (5)	N4—N10—C10—N12	68.2 (2)
Na1^{i}—O3—C3—C4	-106.6 (4)	C8—N10—C10—N12	-53.6 (3)
N9—N3—C3—O3	12.0 (3)	N5—N11—C11—N7	-66.0 (3)
Mn1—N3—C3—O3	159.3 (2)	C9—N11—C11—N7	54.3 (3)
N9—N3—C3—C4	-167.60 (17)	N1—N7—C11—N11	66.7 (2)
Mn1—N3—C3—C4	-20.3 (2)	C7—N7—C11—N11	-54.4 (3)
Na2^{i}—O4—C4—N4	144.8 (2)	N2—N8—C12—N12	-67.3 (2)
Na2^{i}—O4—C4—C3	-34.7 (3)	C8—N8—C12—N12	53.1 (3)
N10—N4—C4—O4	12.7 (4)	N6—N12—C12—N8	67.8 (3)
Mn1—N4—C4—O4	163.8 (2)	C10—N12—C12—N8	-52.6 (3)
N10—N4—C4—C3	-167.81 (19)	Na1^{iv}—N12—C12—N8	-179.03 (16)
Mn1—N4—C4—C3	-16.7 (2)		

Symmetry codes: (i) -*x*+2, -*y*+1, -*z*+1; (ii) *x*+1, *y*, *z*; (iii) -*x*+2, -*y*, -*z*+1; (iv) *x*-1, *y*, *z*.

Table S4: Hydrogen bonding details of **1** (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O312-H···O306^{i}	0.85	1.99	2.823(4)	168.2
O312-H···O309	0.85	2.03	2.850(4)	163.3
O313-H···N1^{ii}	0.85	2.58	3.071(4)	118.1
O313-H···O1^{ii}	0.85	2.11	2.940(3)	164.9
O313-H···O312^{iii}	0.85	1.91	2.728(4)	162.1
O303-H···O3^{iii}	0.85	2.01	2.850(3)	170.7
O303-H···O302^{iv}	0.85	1.91	2.718(4)	158
O309-H···N12	0.85	2.41	3.107(4)	139.4
O309-H···O6	0.85	2.27	2.988(3)	142.4
O309-H···O308	0.85	1.87	2.717(4)	176.5
O307-H···O303^{v}	0.85	1.91	2.742(4)	166.8
O307-H···O311^{ii}	0.85	1.91	2.740(3)	165.1
O302-H···O310^{i}	0.85	1.98	2.794(4)	159.7
O302-H···N8^{iii}	0.85	2.54	3.234(4)	140.1
O302-H···O4^{iii}	0.85	2.18	2.940(3)	149.5
O310-H···O309	0.85	1.99	2.798(5)	157.9
O310-H···O304^{i}	0.85	2.02	2.851(4)	167.1
O308-H···O307	0.85	1.86	2.708(4)	170.8
O308-H···N9^{ii}	0.85	2.52	3.174(4)	134.7
O308-H···O5^{ii}	0.85	2.19	2.957(3)	149
O301-H···O303^{vi}	0.85	2.59	3.335(8)	146.2
O301-H···O302	0.85	2.51	3.264(9)	148.1
O301-H···O314^{vii}	0.85	2.32	2.990(9)	135.5
O306-H···O305	0.85	2.04	2.810(4)	150.6
O306-H···O2	0.85	2.04	2.888(3)	172.3
O311-H···O5	0.85	2.16	2.959(4)	155.4
O311-H···O305^{i}	0.85	1.94	2.782(4)	170.7
O304-H···O4^{iii}	0.85	2.02	2.813(3)	154.4
O304-H···O6^{i}	0.85	2.06	2.853(4)	155.5
O314-H···O5^{iii}	0.85	2.23	2.907(4)	136.3
O305-H···O304	0.87	2.01	2.828(4)	156.9

Symmetry codes: (i) -0.5 + *x*, 1.5 – *y*, 1 – *z*; (ii) 0.5 – *x*, *y* + 0.5, *z*; (iii) *x*, 1.5 – *y* , 0.5 + *z*; (iv) 1 – *x*, *y* + 0.5, 1.5 – *z*; (v) 1 – *x*, 2 – *y*, 1 – *z*; (vi) 1 – *x*, *y* – 0.5, 1.5 – *z*; (vii) 0.5 – *x*, *y* – 0.5, *z*.

Supplementary Table S5: Hydrogen bonding details of **2** (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*O*···O3*W*	0.85	1.95	2.790 (2)	171
O1*W*—H1*P*···O2^{v}	0.85	1.89	2.703 (2)	160
O1*W*—H1*P*···N8^{v}	0.85	2.69	3.160 (3)	116
O2*W*—H2*O*···O5^{vi}	0.82	2.03	2.839 (3)	166
O2*W*—H2*O*···N11^{vi}	0.82	2.67	3.140 (3)	118
O2*W*—H2*P*···O1*W*^{v}	0.85	2.00	2.839 (3)	168
O3*W*—H3*O*···O4	0.85	2.37	3.019 (2)	133
O3*W*—H3*O*···N10	0.85	2.08	2.865 (3)	152
O3*W*—H3*P*···O6*W*^{i}	0.85	1.93	2.772 (3)	169
O4*W*—H4*O*···O7*W*^{ii}	0.85	1.82	2.660 (2)	169
O4*W*—H4*P*···O3*W*^{v}	0.85	1.97	2.795 (3)	164
O5*W*—H5*O*···O1*W*	0.85	2.14	2.875 (3)	144
O5*W*—H5*P*···N9^{i}	0.85	2.29	2.967 (3)	137
O6*W*—H6*P*···O4*W*^{iii}	0.87	1.96	2.789 (3)	157
O7*W*—H7*O*···O2*W*	0.85	1.93	2.777 (3)	172
O7*W*—H7*P*···O2*W*^{vii}	0.85	1.95	2.785 (3)	169

Symmetry codes: (i) -*x*+2, -*y*+1, -*z*+1; (ii) *x*+1, *y*, *z*; (iii) -*x*+2, -*y*, -*z*+1; (v) -*x*+2, -*y*+1, -*z*+2; (vi) -*x*+1, -*y*, -*z*+1; (vii) -*x*+1, -*y*, -*z*+2.

Table S6: The main geometrical parameters of the coordination sphere for **1**, **2** and $(Ph_4As)_2$[Fe(**L**-6H)]·13.28H_2O.[13]

	1	**2**	$(Ph_4As)_2$[Fe(**L**-6H)]·13.28H_2O[13]
φ, º	28.0	32.3	28.0
α, º	78.91	80.12	79.23
a, Å	1.976	1.977	1.957
h, Å	2.39	2.39	2.38

φ – a distortion angle (φ=0º for a trigonal prism and φ=60º for a trigonal antiprism)
α – the bite angle
a – the distance between the encapsulated metal ion and the coordinated nitrogen atom
h – the distance between the coordination polyhedron bases

Table S7. Shape analysis of manganese(IV) and sodium geometry in complexes **1** and **2** using SHAPE 2.1 software[14] ($S_Q(P)$ values)*

Complex **1**					
Central ion	Hexagon (D_{6h})	Pentagonal pyramid (C_{5v})	Octahedron (O_h)	Trigonal prism (D_{3h})	Johnson pentagonal pyramid J2 (C_{5v})
Mn(1)	34.733	19.534	5.108	3.926	23.521
Complex **2**					
Central ion	Hexagon (D_{6h})	Pentagonal pyramid (C_{5v})	Octahedron (O_h)	Trigonal prism (D_{3h})	Johnson pentagonal pyramid J2 (C_{5v})
Mn(1)	34.367	20.511	3.863	5.108	24.450
	Hexagonal pyramid (D_{6v})	Pentagonal bipyramid (D_{5h})	Capped octahedron ($C3_v$)	Capped trigonal prism (C_{2v})	Johnson pentagonal bipyramid J13 (D_{5h})
Na(1)	22.097	4.100	4.945	3.571	6.221
	Hexagon (D_{6h})	Pentagonal pyramid (C_{5v})	Octahedron (O_h)	Trigonal prism (D_{3h})	Johnson pentagonal pyramid J2 (C_{5v})
Na(2)	29.120	21.132	3.434	13.327	23.256

* $S_Q(P)$ is a measure of the distortion of the central atom coordination polyhedron from the ideal geometry.[14] $S_Q(P) = 0$ if the polyhedron indicates the ideal geometry, while distortions from the ideal geometry resulted in higher values of $S_Q(P)$.

Table S8. XYZ coordinates of the optimized (BP86/TZVP) structure of **1**.

C	9.385203135	12.581821756	12.860576070
C	9.550991022	14.110927666	12.904584280
C	10.320769828	12.893464300	8.159620397
C	10.199036562	14.427300580	8.155071591
C	5.770664477	12.812281998	9.705768082
C	5.750979021	14.327459485	9.973210237
C	9.711244506	10.466497985	10.725285726
H	9.732862820	9.364980529	10.660877638
H	10.610055023	10.824619862	11.239560308
C	8.416160875	10.608751065	8.708479324
H	8.393294268	11.073050279	7.716236985
H	8.405467022	9.509965109	8.605810592
C	7.312739159	10.470870700	10.836526295
H	6.442720294	10.834605492	11.394552322
H	7.285613079	9.368965635	10.781210787
C	9.883393277	16.542951787	10.292871517
H	10.888778514	16.154293242	10.095886258
H	9.917222320	17.643552188	10.366763090
C	8.001052279	16.451937042	11.780716638
H	7.992084500	17.551008864	11.880438529
H	7.643173448	15.993586058	12.709416021
C	7.651576189	16.613512147	9.410703881
H	6.998273674	16.274557087	8.598945884
H	7.642678800	17.715972867	9.460315615
N	8.537056161	10.838681412	11.543686976
N	8.579231239	12.233010592	11.813541649
N	9.487704469	14.620127934	11.638067793
N	9.406062046	16.037424025	11.577790022
N	9.691990524	10.979841224	9.357685974
N	9.833351837	12.393614924	9.334546454
N	9.109722408	14.807319145	8.887519098
N	9.026759862	16.203728964	9.136162694
N	7.217221323	10.985663783	9.453419264
N	7.054654908	12.396654709	9.490849297
N	6.911057399	14.703631325	10.589969141
N	7.097090595	16.109061844	10.685433317
O	9.927775538	11.828740049	13.680116149
O	9.713858155	14.733622555	13.962337281
O	10.798400942	12.259703582	7.209221069
O	11.000664357	15.158002561	7.557960562
O	4.742116001	12.122953190	9.699525645
O	4.796666862	15.048691028	9.653663781
Mn	8.495581283	13.525593433	10.292075767

References

1. *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET)

2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. OLEX2: A Complete Structure Solution, Refinement and Analysis Program, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

3. G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2015, **71**, 3–8.

4. A. K. Hassan, L. A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer and L. C. Brunel, *J. Magn. Reson.*, 2000, **142**, 300–312.

5. F. Neese, *WIREs Comput. Mol.Sci.*, 2012, **2**, 73-78.

6. A. D. Becke, *J. Chem. Phys.*, 1986, **84**, 4524–4529.

7. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

8. D. Bykov, T. Petrenko, R. Izsák, S. Kossmann, U. Becker, E. Valeev and F. Neese, *Mol. Phys.*, 2015, **113**, 1961–1977.

9. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

10. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.

11. F. Neese, *J. Chem. Phys.*, 2005, **122**, 34107.

12. E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng and T. E. Ferrin, *J. Comput. Chem.*, 2004, **25**, 1605–1612.

13. S. Tomyn, S. I. Shylin, D. Bykov, V. Ksenofontov, E. Gumienna-Kontecka, V. Bon and I. O. Fritsky, *Nat. Commun.*, 2017, **8**, 14099.

14. M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, SHAPE, version 2.1, Universitat de Barcelona, Barcelona, Spain, 2013.