# Molecular multifunctionality preservation upon surface deposition for a chiral Single-Molecule Magnet. 

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## 1. Equipment and methods

Electrospray Mass Spectra (ESI-MS) were collected on a Bruker Solarix XR 7T ESI/MALDI-FTICR high resolution mass spectrometer using external mass calibration with NaTFA cluster ions.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to perform metal elemental analysis on nitric acid digested samples using a Bruker Aurora Elite instrument. The instrument was tuned prior to measurement and external calibration was performed using calibration points spanning the range of concentrations encountered in the samples. Nitric acid used was TraceSelect grade, reference material was provided by Inorganic Ventures.

Elemental analyses were performed by the microanalytical service of the Department of Chemistry, University of Copenhagen.

Fourier-Transform Infrared (FTIR) spectra of solid samples of $\mathbf{1}$ were recorded with an Agilent Technologies Cary 630 FTIR instrument.

NMR spectroscopy. ${ }^{1} \mathrm{H}$-NMR spectra were recorded on 500 MHz Bruker Avance III HD instrument equipped with 5 mm observe cryoprobe optimized for ${ }^{13} \mathrm{C} .{ }^{1} \mathrm{H}$ resonances were referenced to residual solvent signals $\left(\mathrm{CDCl}_{3}: \delta=7.26,{ }^{1} \mathrm{H}\right)$

X-ray crystallographic studies employed single crystals of 1 that were coated with mineral oil, placed on nylon loops, and mounted in the nitrogen cold stream of the diffractometer. The singlecrystal X-ray diffraction studies were performed at $122(2) \mathrm{K}$ on a Bruker D8 VENTURE diffractometer equipped with a Mo $K \alpha$ high-brilliance $\mathrm{I} \mu \mathrm{S}$ radiation source ( $\lambda=0.71073 \AA$ ), a multilayer X-ray mirror and a PHOTON 100 CMOS detector, and an Oxford Cryosystems low temperature device. The instrument was controlled with the APEX2 software package using SAINT. ${ }^{1}$ Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the program SADABS. ${ }^{2}$ The structures were solved in Olex2 using the olex2.solve program (Charge Flipping) ${ }^{3}$ and refined using the olex2.refine ${ }^{4}$ program or SHELXL. ${ }^{5}$ All non-hydrogen atoms were refined anisotropically; in disordered fragments, the least occupant parts were refined isotropically, when necessary. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters $\left(\mathrm{U}_{\mathrm{iso}}=1.2 \mathrm{U}_{\mathrm{eq}}\right.$ of the parent atom, except for methyl hydrogens which were constrained to $1.5 \mathrm{U}_{\mathrm{eq}}$ of the parent atom). The 1,2-dithiolan-3-yl rings from lipoic acid in $\mathbf{1}$ are strongly disordered and were, therefore, modeled using appropriate choices of the EADP, ISOR, and DFIX restraints from SHELXL. ${ }^{5}$

Powder X-ray diffraction data were collected at room temperature on a Bruker D8 ADVANCE powder diffractometer operating in a $2 \theta-\theta$ configuration using $\mathrm{Cu} \mathrm{K} \alpha$ radiation $(\lambda=1.5418 \AA$ ). An ensemble of freshly isolated crystals were affixed to a poly(methylmethacrylate) sample holder using a little grease. This method was chosen due to the crystals' loss of crystallinity upon grinding. Diffraction data were collected between $3^{\circ}$ and $70^{\circ}$ in $2 \theta$ in steps of $0.02^{\circ}$ with a total exposure time of 7 hours. The poly(methylmethacrylate) sample holder gives rise to a slight curvature in the lowangle background. The simulated powder patterns were calculated from the relevant .cif files using Mercury 3.7. ${ }^{6}$

Magnetic measurements were performed on a Quantum-Design MPMS-XL SQUID magnetometer equipped with a 5 T direct-current (d.c.) magnet. The magnetization, $M$, was measured in $B_{\text {d.c. }}=$ 1000 G from 2 to 270 K on polycrystalline samples covered with hexadecane in polycarbonate capsules. The susceptibility, $\chi$, was calculated as $\chi=M / B$ and corrected for diamagnetic contributions from the sample (by means of Pascal constants), hexadecane, and capsule. A.c. magnetization data (in-phase, $\chi^{\prime}$, and out-of-phase, $\chi^{\prime \prime}$, magnetic susceptibility components) were obtained with frequencies $0.1-1500 \mathrm{~Hz}$ with an a.c. field amplitude of 3.5 Oe without application of static field.

Optical measurements. Uv-vis absorption spectra were collected in $\mathrm{CHCl}_{3}$ solutions using a Cary 5 spectrophotometer. Circular Dichroism (CD) spectra were recorded on a Jasco J-710 spectropolarimeter. The CD spectra of $\mathbf{1 \Lambda \Lambda} @ t-A u(111)$ and $\mathbf{1 \Delta \Delta} @ t-A u(111)$ were collected as an accumulation of 50 spectra that were averaged and corrected for the background with the CD spectrum of $\boldsymbol{t} \mathbf{- A u ( 1 1 1 ) , ~ a l s o ~ c o l l e c t e d ~ a s ~ a n ~ a c c u m u l a t i o n ~ o f ~} 50$ spectra that were averaged.

Transmission electron microscopy (TEM) was performed using a Tecnai T20 G2 (Philips FEI, Oregon, USA) microscope equipped with a thermionic electron gun operated at 200 kV .

Atomic Force Microscopy (AFM) images were recorded using an Asylum Research Cypher AFM running in AC mode with a scan rate of 2 Hz . The AFM tips were standard tapping mode tips from Olympus (AC240 silicon probes) with a spring constant of $2 \mathrm{nN} / \mathrm{nm}$ and a resonance frequency around 70 kHz .

X-ray Photoelectron Spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra ${ }^{\text {DLD }}$ instrument operated with a monochromatic $\mathrm{Al}_{\mathrm{K} \alpha}$ X-ray source ( $h v=1486.6 \mathrm{eV}$ ) at a power of 150 W . Survey scans were acquired in the $0-1350 \mathrm{eV}$ range at pass energy of 160 eV and step size of 0.5 eV . High-resolution scans of $\mathrm{Au} 4 \mathrm{f}, \mathrm{C} 1 \mathrm{~s}, \mathrm{~S} 2 \mathrm{p}, \mathrm{Mn} 2 \mathrm{p}$ and Cl 2 p regions were acquired at pass energy of 10 eV and step size of 0.1 eV . The pressure in the main chamber during the
analysis was in the $10^{-9}$ torr range. The high resolution spectra were fitted using GaussianLorentzian line shapes and a Shirley background. The spectra of 1 and HDA@AuNPs are shown with energy scale correction, obtained by assigning the C 1 s line to 285 eV binding energy (BE), while for the other samples the correction was made with the $\mathrm{Au} 4 \mathrm{f}_{7 / 2}$ line assigned to 84 eV BE. The systematic error is estimated to be of the order of $5-10 \%$. The measurements were done using a spot size $=0.21 \mathrm{~mm}^{2}$.

## X-ray Absorption Near Edge Structure (XANES) and X-ray Magneto-Circular Dichroism

 (XMCD) experiments at the Mn K-edge were carried out at the ID12 beamline of the European Synchrotron Radiation Facility (Grenoble, France), dedicated to polarization dependent X-ray spectroscopy in the $2-15 \mathrm{keV}$ energy range. A high flux of circularly polarized photons was provided by an HELIOS-II undulator. X-rays were monochromatized by a Si «111» double crystal monochromator. XMCD spectra were obtained using the total fluorescence yield detection mode in backscattering geometry, under an applied magnetic field. Energy calibration was performed by use of the K-edge absorption spectrum of metallic Ti, in which a pre-edge feature is well defined, the photon energy corresponding to it is taken to be equal to 4965.5 eV . The samples were mounted on the cold finger of a constant-flow helium cryostat inserted in the bore of a superconducting solenoid producing a magnetic field up to 17 T . The temperature of the samples was kept around 2.1 K .
## 2. Synthesis and surface deposition procedures

Solvents and starting materials of reagent grade were purchased from Sigma-Aldrich, Alfa Aesar or VWR, and were used without further purification. Methylsalicylaldoxime $\left(\mathrm{Me}-\mathrm{saOH}_{2}\right)$ was prepared by slight modification of known methods. ${ }^{7-8}$ Transparent Au substrates (Au thickness $100 \AA$ ) with titanium as the adhesion layer between the gold layer and the aluminosilicate glass, $\mathrm{t}-\mathrm{Au}(111)$, were purchased from Aldrich. Epitaxial $\mathrm{Au}(111)$ films (Au thickness 200 nm ) grown on mica substrate, $e$ $\mathrm{Au}(111)$, were purchased from Phasis (Switzerland) and used as received.

Methylsalicylaldoxime (Me-saoH2). 2-Hydroxyacetophenone ( $8.16 \mathrm{~g}, \quad 60 \mathrm{mmol})$ and hydroxylamine hydrochloride $(4.17 \mathrm{~g}, 60 \mathrm{mmol})$ were dissolved in 200 ml of EtOH. Sodium acetate $(4.92 \mathrm{~g}, 60 \mathrm{mmol})$ was added and the mixture was refluxed for 4 hours with stirring. A white solid was filtered off, and the solvent removed on a rotary evaporator to yield an oil. The oil was crystallized from diethyl ether. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.16(\mathrm{~s}, 1 \mathrm{H}), 7.44(\mathrm{dd}, \mathrm{J}=8.0,1.6$ $\mathrm{Hz}, 1 \mathrm{H}), 7.30-7.22(\mathrm{~m}, 1 \mathrm{H}), 6.97(\mathrm{dd}, \mathrm{J}=8.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.91(\mathrm{ddd}, \mathrm{J}=8.0,7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H})$, 2.37 (s, 3H).
$\left[\mathbf{M n}_{9} \mathbf{O}_{\mathbf{4}}(\mathbf{M e}-\mathbf{s a o})_{6}\left(\mathrm{~L}_{\mathbf{3}} \mathbf{( M e O}\right)_{\mathbf{3}}(\mathbf{M e O H})_{3}\right] \mathbf{C l}$ (1). $\mathrm{MnCl}_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O} \quad(591 \mathrm{mg}, 3 \mathrm{mmol})$, methylsalicylaldoxime (Me-saoH $\mathbf{2}_{\mathbf{2}}, 302 \mathrm{mg}, 2 \mathrm{mmol}$ ) and lipoic acid ( $\mathbf{H L}, 413 \mathrm{mg}, 1 \mathrm{mmol}$ ) were dissolved in 100 ml of MeOH and stirred for 15 min before adding 1 mL of triethylamine. The resulting dark solution was stirred for 1 h . Subsequently, the solution was filtered and diffused with $\mathrm{Et}_{2} \mathrm{O}$. Dark crystals suitable for single-crystal X-ray diffraction formed after 1 week in $50 \%$ yield. The solutions remain colored after the crystallization of $\mathbf{1}$, suggesting that other species are formed/present in the solution mixture, with 1 being the least soluble. High Resolution ESI-MS (positive mode, $\mathrm{CHCl}_{3}+$ $\left.\mathrm{CH}_{3} \mathrm{OH}\right)$ for $\mathrm{M}^{+}\left(\mathrm{C}_{75} \mathrm{H}_{90} \mathrm{Mn}_{9} \mathrm{~N}_{6} \mathrm{O}_{25} \mathrm{~S}_{6}{ }^{+}\right): m / z=2160.8659\left(\mathrm{C}_{75} \mathrm{H}_{90} \mathrm{Mn}_{9} \mathrm{~N}_{6} \mathrm{O}_{25} \mathrm{~S}_{6}{ }^{+}\right.$requires 2160.8698). Elemental analysis for $\mathrm{C}_{78} \mathrm{H}_{102} \mathrm{ClMn}_{9} \mathrm{~N}_{6} \mathrm{O}_{28} \mathrm{~S}_{6}$ \% Calculated (Found): C: 40.84 (40.78), H: 4.48 (4.50), N: 3.66 (3.60), S 8.39 (9.07). IR bands ( $\mathrm{cm}^{-1}$ ): 3055.4 (w), 2921.5 (m), 2854.5 (w), 2817.9 (w), 2781.4 (w), 1593.9 (m), 1575.6 (s), 1551.3 (vs), 1526.9 (vs), 1429.5 (vs), 1362.5 (m), 1332.1 (m), 1301.6 (vs), 1240.7 (s), 1228.5 (s), 1155.4 (w), 1131.1 (s), 1070.2 (s) 1051.9 (vs), 1021.5 (vs), 972.8 (vs), 936.2 (w), 869.2 (m), 857.1 (s), 802.2 (m), 771.8 (m), 747.4 (s), 668.3 (vs).

Gold nanoparticles (HDA@AuNPs). Hexadecylamine (HDA) capped gold nanoparticles (HDA @AuNPs) were chosen as the starting material due to their solubility in chloroform (the same solvent $\mathbf{1}$ is stable in, as shown by the techniques described above) and because an amine-based surface ligand is easily replaced by a sulfur terminated ligand due to the selective affinity of gold to bind with sulfur. Hexadecylamine-capped gold nanoparticles (HDA@AuNPs) were prepared under a $\mathrm{N}_{2}$ atmosphere by reduction of $\mathrm{HAuCl}_{4} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ with borane tert-butylamine in chloroform, in the
presence of hexadecylamine (HDA), by a previously reported procedure. ${ }^{9}$ The average diameter of the synthesized AuNPs was 7.3 nm , as estimated from TEM images (Figure S 8 for statistics). In a three-neck flask, HDA ( 12.5 g ) was dissolved in $\mathrm{CHCl}_{3}(80 \mathrm{~mL})$ at $40^{\circ} \mathrm{C}$ under nitrogen flow and vigorous stirring. When the solution became colorless, a dispersion of $\mathrm{HAuCl}_{4} \cdot 4 \mathrm{H}_{2} \mathrm{O}(0.45 \mathrm{~g})$ in $\mathrm{CHCl}_{3}(5 \mathrm{~mL})$ was rapidly added. The mixture, heated to reflux, assumed a red color and after 10 min turned to orange. A solution of borane tert-butylamine ( 0.15 g ) in $\mathrm{CHCl}_{3}(3 \mathrm{~mL})$ was then quickly added. The obtained purple-red mixture was stirred under a nitrogen atmosphere for 1 h and cooled down to room temperature. Ethanol $(170 \mathrm{~mL})$ was added to give a violet solution that was centrifuged at 5000 rpm for 5 min , discarding the supernatant. The dark-red precipitate was solubilized in a small volume of $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15 \mathrm{~mL})$ and ethanol was added ( 35 mL ) prior to further centrifugation. The washing procedure was repeated an additinal four times to obtain a dark red solution containing HDA@AuNPs $(180 \mathrm{mg})$ in CHCl $_{3}(20 \mathrm{~mL})$.

Deposition on gold nanoparticles (AuNPs). AuNPs display diamagnetism or paramagnetism depending on the type of surface ligand and the degree of coverage ${ }^{10}$. To estimate their contribution to the magnetic behaviour a sample of HL@AuNPs (HL = lipoic acid) was prepared; lipoic acid moieties are used as anchoring units in 1. After taking into account idealized calculations on the steric hindrance of deposited species and on the maximum coverage of gold NPs, ${ }^{9}$ it was calculated that AuNPs with an average size of 7.3 nm are fully covered when $10 \%$ by weight $\mathbf{1}$ (or $30 \%$ by weight HL) is used. To obtain lipoic acid capped AuNPs (HL@AuNPs), a 2.5 -fold excess of HL ( 60 mg ) was added to a solution of HDA@AuNPs $(80 \mathrm{mg})$ in chloroform $(20 \mathrm{~mL})$ and the mixture was stirred for 24 h at room temperature. In this case the NPs formed agglomerates. Purification was performed via precipitation from the solution over several hours; the yellow colored supernatant was discarded, the black precipitate re-dispersed in $\mathrm{CHCl}_{3}$ and the washing cycle repeated 4 times. $\mathbf{1}$ deposited on AuNPs ( $\mathbf{1}$ @AuNPs) was obtained by introducing a 2.5 -fold excess of $\mathbf{1}(25 \mathrm{mg})$ into a solution of $\mathbf{H D A} @ \mathbf{A u N P s}(100 \mathrm{mg})$ in CHCl $_{3}(25 \mathrm{~mL})$. The mixture was stirred for 24 h at room temperature. In this case some of the NPs started to flocculate, while others remained well dispersed in chloroform. The purification procedure was similar to that reported for the HDA@AuNPs, with ethanol replaced by methanol ( 20 mL ). Thus, after first centrifugation at 5000 rpm , the brown supernatant was discarded, the black precipitate was dispersed in chloroform and the washing cycle was repeated 4 times to afford a colorless solution over a dark precipitate. After these washing cycles, agglomerates of $1 @$ AuNPs are difficult to disperse in chloroform, so sonication was necessary to obtain a violet-blue solution.

Preparation of transparent gold slides. Transparent Au substrates (thickness $100 \AA$ ) with titanium as the adhesion layer between the gold layer and the aluminosilicate glass, referred as $\boldsymbol{t} \mathbf{- \mathbf { A u } ( 1 1 1 )}$ to
distinguish from the thicker non-transparent Au films, were cut into pieces of $25 \mathrm{~mm} \times 12 \mathrm{~mm} \times$ 0.7 mm (length $\times$ width $\times$ thickness). The substrates were cleaned by sonicating for 40 min in 20 wt \% ethanolamine in water at $\sim 50^{\circ} \mathrm{C}$, rinsing with MilliQ water, followed by immersion for 20 s in piranha solution $\left(4: 1 \mathrm{H}_{2} \mathrm{SO}_{4}: \mathrm{H}_{2} \mathrm{O}_{2}\right)$. Warning: piranha mixture is dangerous and should be handled with care.

Deposition of $\mathbf{1 \Delta \Delta}$ and $1 \Lambda \Lambda$ on transparent $A u$ slides. Deposition of $\mathbf{1 \Delta \Delta}$ or $\mathbf{1 \Lambda \Lambda}$ on $\boldsymbol{t}-\mathbf{A u}(111)$ was performed by soaking $\boldsymbol{t} \mathbf{-} \mathbf{A u}(\mathbf{1 1 1})$ in a 2 mM solution of $\mathbf{1 \Delta \Delta}$ or $\mathbf{1} \mathbf{\Lambda} \boldsymbol{\Lambda}$ in chloroform for 24 h , followed by extensive washing with fresh chloroform and drying under $\mathrm{N}_{2}$ stream. The 2 mM solutions of $\mathbf{1} \Delta \boldsymbol{\Delta}$ or $\mathbf{1} \mathbf{\Lambda} \mathbf{\Lambda}$ in chloroform were prepared by dissolution of single crystals of $\mathbf{1}$ in 200 $\mu \mathrm{L}$ of chloroform, where the chirality of each particular single crystal was determined by CD spectropolarimetry. The solutions corresponding to a particular enantiomer were combined and concentrated under vacuum at room temperature. The obtained residue was re-dissolved in a small amount of chloroform and the concentration of $\mathbf{1 \Delta \Delta}$ or $\mathbf{1 \Lambda \Lambda}$ was adjusted with additional chloroform to 2 mM spectrophotometrically.

Deposition of 1 on thick flat $\mathbf{A u ( 1 1 1 )}$ films. Monolayers of $\mathbf{1}$ on $\boldsymbol{e}-\mathbf{A u}(111)$ were prepared by soaking the $\mathrm{Au}(111)$ on a mica substrate, in a 2 mM solution of $\mathbf{1}$ in chloroform. After 24 h of immersion the substrate was extensively washed with fresh chloroform and dried under $\mathrm{N}_{2}$ flux.

## 3. Single crystal and powder X-ray diffraction

### 3.1 Single crystal X-ray diffraction

Bond length and charge balance considerations as well as the Jahn-Teller-distorted octahedral coordination geometry showed that all Mn ions in $\mathbf{1}$ are in the +III oxidation state.

Table S1. Crystalographic data for $\mathbf{1 \Delta \Delta}$ and $\mathbf{1 \Lambda \Lambda}$.

| Compound | $1 \Delta \Delta$ | 1 14 |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{78} \mathrm{H}_{102} \mathrm{ClMn}_{9} \mathrm{~N}_{6} \mathrm{O}_{28} \mathrm{~S}_{6}$ | $\mathrm{C}_{78} \mathrm{H}_{102} \mathrm{ClMn}_{9} \mathrm{~N}_{6} \mathrm{O}_{28} \mathrm{~S}_{6}$ |
| Formula weight | 2293.92 | 2293.92 |
| Temperature/K | 120(2) | 120(2) |
| Crystal system | orthorhombic | orthorhombic |
| Space group | $\mathrm{P} 2_{1} 2_{1} 2_{1}$ | $\mathrm{P} 2_{1} 2_{1} 2_{1}$ |
| a/Å | 13.4007(6) | 13.3925(3) |
| b/Å | 25.1409(11) | 25.1226 (8) |
| c/Å | 26.8999(12) | 27.0041(9) |
| $\alpha /{ }^{\circ}$ | 90 | 90 |
| $\beta /{ }^{\circ}$ | 90 | 90 |
| $\gamma^{\prime}$ | 90 | 90 |
| Volume/A ${ }^{3}$ | 9062.7(7) | 9085.6(5) |
| Z | 4 | 4 |
| $\rho_{\text {calc }} \mathrm{g} / \mathrm{cm}^{3}$ | 1.681 | 1.677 |
| $\mu / \mathrm{mm}^{-1}$ | 1.458 | 1.455 |
| F(000) | 4696.0 | 4696 |
| Crystal size/mm ${ }^{3}$ | $0.19 \times 0.135 \times 0.08$ | $0.41 \times 0.116 \times 0.112$ |
| Radiation | $\mathrm{MoK} \alpha(\lambda=0.71073)$ | $\mathrm{MoK} \alpha(\lambda=0.71073)$ |
| $2 \Theta$ range for data collection/ ${ }^{\circ}$ | 4.442 to 50.054 | 4.428 to 51.346 |
|  | $-15 \leq \mathrm{h} \leq 15$ | $-15 \leq \mathrm{h} \leq 16$ |
| Index ranges | $-29 \leq \mathrm{k} \leq 29$ | $-30 \leq \mathrm{k} \leq 30$ |
|  | $-31 \leq 1 \leq 32$ | $-32 \leq 1 \leq 32$ |
| Reflections collected | 374822 | 115106 |
| Independent reflections | $\begin{gathered} 15955 \\ {\left[\mathrm{R}_{\mathrm{int}}=0.0996, \mathrm{R}_{\text {sigma }}=0.0270\right]} \end{gathered}$ | $\begin{gathered} 17242 \\ {\left[\mathrm{R}_{\text {int }}=0.0537, \mathrm{R}_{\text {sigma }}=0.0326\right]} \end{gathered}$ |
| Data/restraints/parameters | 15955/13/1129 | 17242/164/1066 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.045 | 1.037 |
| Final R indexes [ $\mathrm{I}>=2 \sigma$ (I)] | $\mathrm{R}_{1}=0.0483, \mathrm{wR}_{2}=0.1202$ | $\mathrm{R}_{1}=0.0591, \mathrm{wR}_{2}=0.1619$ |
| Final R indexes [all data] | $\mathrm{R}_{1}=0.0547, \mathrm{wR}_{2}=0.1249$ | $\mathrm{R}_{1}=0.0661, \mathrm{wR}_{2}=0.1696$ |
| Largest diff. peak/hole / e $\AA^{-3}$ | 2.85/-1.61 | 2.41/-1.54 |
| Flack parameter | 0.000(4) | 0.009(5) |
| ${ }^{\mathrm{a}} I>2 \sigma(I), R_{I}=\Sigma\left\|\left(\left\|F_{\mathrm{o}}\right\|-\mid F_{\mathrm{c}}\right)\right\| \Sigma\left\|F_{\mathrm{o}}\right\| \cdot w R_{2}=\left\{\Sigma\left[w\left(F_{\mathrm{o}}^{2}-F_{\mathrm{c}}^{2}\right)^{2}\right] / \Sigma\left[w\left(F_{\mathrm{o}}{ }^{2}\right)^{2}\right]\right\}^{1 / 2}$. GoF (goodness of fit on $\left.\left.F^{2}\right)=\left\{\Sigma\left[w\left(F_{\mathrm{o}}^{2}-F_{\mathrm{c}}\right)^{2}\right)^{2}\right](\mathrm{n}-\mathrm{p})\right\}^{1 / 2}$, where $n$ is the number of reflections and $p$ is the total number of refined parameters. |  |  |

Table S2. Selected torsion angles in $\mathbf{1 \Delta \Delta}$.

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle ${ }^{\circ}$ |
| :---: | :---: | :---: | :---: | :---: |
| Mn4 | N20 | O10 | Mn9 | -40.12 |
| Mn8 | N18 | O21 | Mn4 | -37.80 |
| Mn9 | N47 | O15 | Mn8 | -39.42 |
| Mn1 | O44 | N11 | Mn2 | -14.22 |
| Mn3 | O13 | N43 | Mn5 | -3.33 |
| Mn6 | N33 | O19 | Mn7 | -11.71 |

Table S3. Selected torsion angles in $\mathbf{1 \Lambda \Lambda}$.

| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Angle $^{\circ}$ |
| :--- | :--- | :--- | :--- | :--- |
| Mn6 | O19 | N35 | Mn9 | 40.02 |
| Mn3 | N31 | O5 | Mn9 | 38.23 |
| Mn3 | O18 | N14 | Mn6 | 38.60 |
|  |  |  |  |  |
| Mn1 | O37 | N27 | Mn2 | 13.45 |
| Mn5 | O8 | N48 | Mn8 | 14.77 |
| Mn4 | N47 | O13 | Mn7 | 8.86 |

Table S4. Selected bond lengths and distances in $\mathbf{1 \Delta \Delta}$.

| Atom | Atom | Length/ $\AA$ | Atom | Atom | Length/̊ | Atom | Atom | Length/i̊ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Mn1 | O4 | $1.973(5)$ | Mn4 | O21 | $1.941(5)$ | Mn8 | O4 | $2.335(5)$ |
| Mn1 | O6 | $2.103(6)$ | Mn4 | O22 | $2.201(6)$ | Mn8 | O7 | $1.881(5)$ |
| Mn1 | O8 | $1.903(5)$ | Mn4 | O30 | $1.889(5)$ | Mn8 | O15 | $1.920(5)$ |
| Mn1 | O15 | $2.489(5)$ | Mn5 | O4 | $1.943(5)$ | Mn8 | O16 | $1.883(5)$ |
| Mn1 | O44 | $1.932(5)$ | Mn5 | O14 | $2.124(6)$ | Mn8 | O17 | $2.186(6)$ |
| Mn1 | O46 | $1.921(5)$ | Mn5 | O16 | $2.364(6)$ | Mn8 | N18 | $1.979(6)$ |
| Mn2 | O8 | $1.945(5)$ | Mn5 | O26 | $1.827(6)$ | Mn9 | O7 | $1.894(5)$ |
| Mn2 | O9 | $1.921(5)$ | Mn5 | N43 | $1.978(7)$ | Mn9 | O8 | $2.352(5)$ |
| Mn2 | N11 | $1.969(6)$ | Mn5 | O46 | $1.933(6)$ | Mn9 | O10 | $1.919(5)$ |
| Mn2 | O24 | $2.120(6)$ | Mn6 | O12 | $1.940(5)$ | Mn9 | O25 | $1.878(5)$ |
| Mn2 | O25 | $2.564(5)$ | Mn6 | O27 | $1.923(6)$ | Mn9 | O28 | $2.192(6)$ |
| Mn2 | O37 | $1.837(5)$ | Mn6 | O30 | $2.465(6)$ | Mn9 | N47 | $1.975(6)$ |
| Mn3 | O4 | $1.916(5)$ | Mn6 | N33 | $1.977(7)$ | Mn1 | Mn2 | $3.1443(16)$ |
| Mn3 | O12 | $1.988(5)$ | Mn6 | O41 | $1.835(6)$ | Mn1 | Mn5 | $2.9569(16)$ |
| Mn3 | O13 | $1.923(6)$ | Mn6 | O62 | $2.117(6)$ | Mn2 | Mn7 | $2.9308(16)$ |
| Mn3 | O21 | $2.564(5)$ | Mn7 | O8 | $1.967(5)$ | Mn3 | Mn5 | $3.1530(16)$ |
| Mn3 | O27 | $1.944(5)$ | Mn7 | O9 | $1.930(5)$ | Mn3 | Mn6 | $2.9497(16)$ |
| Mn3 | O29 | $2.105(6)$ | Mn7 | O10 | $2.522(5)$ | Mn4 | Mn8 | $3.2201(15)$ |
| Mn4 | O7 | $1.891(5)$ | Mn7 | O12 | $1.892(5)$ | Mn4 | Mn9 | $3.2622(15)$ |
| Mn4 | O12 | $2.343(5)$ | Mn7 | O19 | $1.909(5)$ | Mn6 | Mn7 | $3.1452(16)$ |
| Mn4 | N20 | $1.980(7)$ | Mn7 | O40 | $2.105(6)$ | Mn8 | Mn9 | $3.2212(16)$ |

Table S5. Selected bond lengths and distances in $\mathbf{1 \Lambda \Lambda}$.

| Atom | Atom | Length/ $\mathbf{A}$ | Atom | Atom | Length/ $\mathbf{A}$ | Atom | Atom | Length/ $\mathbf{A}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Mn1 | O2 | $2.001(6)$ | Mn4 | O36 | $1.845(7)$ | Mn8 | O4 | $1.942(6)$ |
| Mn1 | O10 | $2.112(7)$ | Mn4 | N47 | $2.007(9)$ | Mn8 | O15 | $1.928(7)$ |
| Mn1 | O12 | $1.929(6)$ | Mn4 | O0AA | $2.145(9)$ | Mn8 | O32 | $2.450(6)$ |
| Mn1 | O19 | $2.463(6)$ | Mn5 | O4 | $1.915(6)$ | Mn8 | N48 | $1.981(8)$ |
| Mn1 | O26 | $1.954(7)$ | Mn5 | O5 | $2.511(6)$ | Mn8 | O61 | $1.849(6)$ |
| Mn1 | O37 | $1.940(6)$ | Mn5 | O6 | $1.943(6)$ | Mn8 | O2AA | $2.154(8)$ |
| Mn2 | O6 | $1.926(6)$ | Mn5 | O8 | $1.909(6)$ | Mn9 | O3 | $1.896(5)$ |
| Mn2 | O7 | $2.541(6)$ | Mn5 | O12 | $1.970(6)$ | Mn9 | O5 | $1.931(6)$ |
| Mn2 | O12 | $1.941(6)$ | Mn5 | O1AA | $2.108(7)$ | Mn9 | O7 | $1.896(6)$ |
| Mn2 | O21 | $1.839(6)$ | Mn6 | O2 | $2.340(6)$ | Mn9 | O12 | $2.332(6)$ |
| Mn2 | O23 | $2.137(7)$ | Mn6 | O3 | $1.888(5)$ | Mn9 | O22 | $2.195(6)$ |
| Mn2 | N27 | $1.988(7)$ | Mn6 | N14 | $1.978(7)$ | Mn9 | N35 | $1.980(7)$ |
| Mn3 | O3 | $1.886(5)$ | Mn6 | O16 | $1.889(6)$ | Mn1 | Mn2 | $3.1616(18)$ |
| Mn3 | O4 | $2.334(6)$ | Mn6 | O17 | $2.186(6)$ | Mn1 | Mn4 | $2.9783(19)$ |
| Mn3 | O18 | $1.941(6)$ | Mn6 | O19 | $1.920(6)$ | Mn2 | Mn5 | $2.9350(17)$ |
| Mn3 | O28 | $2.208(6)$ | Mn7 | O2 | $1.912(6)$ | Mn3 | Mn6 | $3.2225(17)$ |
| Mn3 | N31 | $1.989(7)$ | Mn7 | O4 | $1.984(6)$ | Mn3 | Mn9 | $3.2603(16)$ |
| Mn3 | O32 | $1.887(6)$ | Mn7 | O13 | $1.934(7)$ | Mn4 | Mn7 | $3.1702(19)$ |
| Mn4 | O2 | $1.946(6)$ | Mn7 | O15 | $1.952(6)$ | Mn5 | Mn8 | $3.1632(17)$ |
| Mn4 | O16 | $2.382(7)$ | Mn7 | O18 | $2.534(6)$ | Mn6 | Mn9 | $3.2276(17)$ |
| Mn4 | O26 | $1.937(7)$ | Mn7 | O1 | $2.101(7)$ | Mn7 | Mn8 | $2.9533(19)$ |

Table S6. Selected bond angles in $\mathbf{1 \Delta \Delta}$.

| Atom | Ato | Ato | Angle $/^{\circ}$ | Ato | Ato | Ato | Angle $/^{\circ}$ | Ato | Atom | Ato | Angle $/^{\circ}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| O4 | Mn1 | O15 | 79.86(19) | N20 | Mn4 | O22 | 93.4(2) | O7 | Mn8 | O16 | 173.2(2) |
| O44 | Mn1 | O15 | 82.8(2) | O21 | Mn4 | O22 | 91.8(2) | N18 | Mn8 | O17 | 91.5(2) |
| O46 | Mn1 | O15 | 82.6(2) | O30 | Mn4 | O22 | 91.0(2) | O15 | Mn8 | O17 | 94.4(2) |
| O6 | Mn1 | O15 | 172.1(2) | O7 | Mn4 | O22 | 93.9(2) | O16 | Mn8 | 017 | 95.5(2) |
| O8 | Mn1 | O15 | 89.86(19) | O30 | Mn4 | O7 | 173.4(2) | O7 | Mn8 | O17 | 90.5(2) |
| O44 | Mn1 | O4 | 161.0(2) | O26 | Mn5 | N43 | 90.9(3) | N18 | Mn8 | O4 | 89.0(2) |
| O46 | Mn1 | O4 | 80.0(2) | O4 | Mn5 | N43 | 93.6(2) | O15 | Mn8 | O4 | 85.0(2) |
| O8 | Mn1 | O4 | 94.8(2) | O46 | Mn5 | N43 | 174.0(3) | 016 | Mn8 | O4 | 80.8(2) |
| O46 | Mn1 | O44 | 90.1(2) | N43 | Mn5 | O14 | 86.3(3) | 017 | Mn8 | O4 | 176.2(2 |
| O8 | Mn1 | O44 | 92.9(2) | O26 | Mn5 | O14 | 96.3(3) | O7 | Mn8 | O4 | 93.3(2) |
| O8 | Mn1 | O46 | 171.5(2) | O4 | Mn5 | O14 | 93.0(2) | O10 | Mn9 | N47 | 171.2(2 |
| O4 | Mn1 | O6 | 105.7(2) | O46 | Mn5 | O14 | 92.6(2) | O25 | Mn9 | N47 | 87.1(2) |
| O44 | Mn1 | O6 | 90.8(2) | N43 | Mn5 | 016 | 87.9(2) | O7 | Mn9 | N47 | 89.4(2) |
| O46 | Mn1 | O6 | 92.7(2) | O14 | Mn5 | 016 | 169.7(2) | O25 | Mn9 | O 10 | 92.1(2) |
| O8 | Mn1 | O6 | 95.2(2) | O26 | Mn5 | 016 | 92.3(3) | O7 | Mn9 | O 10 | 90.7(2) |
| O37 | Mn2 | N11 | 91.2(2) | O4 | Mn5 | 016 | 78.8(2) | N47 | Mn9 | O28 | 93.7(2) |
| O8 | Mn2 | N11 | 92.3(2) | O46 | Mn5 | 016 | 92.2(2) | O10 | Mn9 | O28 | 95.1(2) |
| O9 | Mn2 | N11 | 173.5(2) | O26 | Mn5 | O4 | 169.9(3) | O25 | Mn9 | O28 | 92.8(2) |
| N11 | Mn2 | O24 | 88.8(2) | O46 | Mn5 | O4 | 80.5(2) | O7 | Mn9 | O28 | 91.6(2) |
| O37 | Mn2 | O24 | 94.8(2) | O26 | Mn5 | O46 | 95.1(3) | O25 | Mn9 | O7 | 174.6(2 |
| O8 | Mn2 | O24 | 95.3(2) | O12 | Mn6 | N33 | 92.4(2) | N47 | Mn9 | O8 | 87.2(2) |
| O9 | Mn2 | O24 | 93.6(2) | O27 | Mn6 | N33 | 173.8(2) | O 10 | Mn9 | O8 | 84.0(2) |
| N11 | Mn2 | O25 | 83.3(2) | O41 | Mn6 | N33 | 90.2(3) | O25 | Mn9 | O8 | 83.9(2) |
| O24 | Mn2 | O25 | 168.63(19 | O27 | Mn6 | O12 | 81.6(2) | O28 | Mn9 | O8 | 176.5(2) |
| O37 | Mn2 | O25 | 93.5(2) | O41 | Mn6 | O 12 | 171.0(3) | O7 | Mn9 | O8 | 91.8(2) |
| O8 | Mn2 | O25 | 77.01(19) | O41 | Mn6 | O27 | 95.5(2) | Mn6 | O12 | Mn3 | 97.3(2) |
| O9 | Mn2 | O25 | 93.54(19) | N33 | Mn6 | O30 | 86.2(2) | Mn7 | O12 | Mn3 | 132.4(3 |
| O37 | Mn2 | O8 | 169.4(2) | O12 | Mn6 | O30 | 78.0(2) | Mn3 | O12 | Mn4 | 98.5(2) |
| O9 | Mn2 | O8 | 81.5(2) | O27 | Mn6 | O30 | 91.1(2) | Mn6 | O12 | Mn4 | 101.2(2 |
| O37 | Mn2 | O9 | 94.6(2) | O41 | Mn6 | O30 | 93.6(2) | Mn7 | O12 | Mn4 | 112.5(2 |
| O13 | Mn3 | O12 | 158.8(2) | O62 | Mn6 | O30 | 168.9(2) | Mn7 | O12 | Mn6 | 110.3(2 |
| O27 | Mn3 | O12 | 79.8(2) | N33 | Mn6 | O62 | 88.9(3) | Mn8 | O15 | Mn1 | 95.0(2) |
| O4 | Mn3 | O12 | 93.8(2) | O12 | Mn6 | O62 | 92.4(2) | Mn8 | O16 | Mn5 | 100.5(2) |
| O4 | Mn3 | O13 | 93.2(2) | O27 | Mn6 | O62 | 92.8(3) | Mn4 | O21 | Mn3 | 92.7(2) |
| O12 | Mn3 | O21 | 80.21(19) | O41 | Mn6 | O62 | 96.3(3) | Mn9 | O25 | Mn2 | 96.7(2) |
| O13 | Mn3 | O21 | 79.7(2) | O12 | Mn7 | O10 | 90.8(2) | Mn6 | O27 | Mn3 | 99.4(2) |
| O27 | Mn3 | O21 | 82.3(2) | O19 | Mn7 | O10 | 83.2(2) | Mn4 | O30 | Mn6 | 98.5(2) |
| O29 | Mn3 | O21 | 171.5(2) | O40 | Mn7 | 010 | 173.7(2) | Mn3 | O4 | Mn1 | 133.1(3 |
| O4 | Mn3 | O21 | 90.18(19) | O8 | Mn7 | O10 | 78.61(19 | Mn5 | O4 | Mn1 | 98.1(2) |
| O13 | Mn3 | O27 | 90.6(2) | O9 | Mn7 | O10 | 83.67(19 | Mn3 | O4 | Mn5 | 109.5(3 |
| O4 | Mn3 | O27 | 170.8(2) | O12 | Mn7 | O19 | 93.7(2) | Mn1 | O4 | Mn8 | 98.5(2) |
| O12 | Mn3 | O29 | 105.9(2) | O12 | Mn7 | O40 | 93.9(2) | Mn3 | O4 | Mn8 | 112.6(2 |
| O13 | Mn3 | O29 | 93.4(3) | O19 | Mn7 | O40 | 92.3(2) | Mn5 | O4 | Mn8 | 99.7(2) |
| O27 | Mn3 | O29 | 92.9(2) | O8 | Mn7 | O40 | 105.0(2) | Mn1 | O46 | Mn5 | 100.2(2 |
| O4 | Mn3 | O29 | 95.2(2) | O9 | Mn7 | O40 | 91.8(2) | Mn8 | 07 | Mn4 | 117.2(3 |
| O21 | Mn4 | N20 | 174.8(3) | O12 | Mn7 | O8 | 95.8(2) | Mn4 | O7 | Mn9 | 119.1(3 |
| O30 | Mn4 | N20 | 87.4(2) | O19 | Mn7 | O8 | 159.6(2) | Mn8 | 07 | Mn9 | 117.2(3 |
| O7 | Mn4 | N20 | 87.8(2) | O9 | Mn7 | O8 | 80.7(2) | Mn1 | O8 | Mn2 | 109.6(2 |
| N20 | Mn4 | O12 | 87.7(2) | O12 | Mn7 | O9 | 173.9(2) | Mn1 | O8 | Mn7 | 131.2(3 |
| O21 | Mn4 | O 12 | 87.1(2) | O19 | Mn7 | O9 | 88.1(2) | Mn2 | O8 | Mn7 | 97.0(2) |
| O22 | Mn4 | O 12 | 173.0(2) | O15 | Mn8 | N18 | 173.9(2) | Mn1 | O8 | Mn9 | 112.7(2 |
| O30 | Mn4 | O 12 | 82.1(2) | O16 | Mn8 | N18 | 87.3(2) | Mn2 | O8 | Mn9 | 102.1(2 |
| O7 | Mn4 | O 12 | 93.1(2) | O7 | Mn8 | N18 | 89.3(2) | Mn7 | O8 | Mn9 | 100.0(2 |
| O30 | Mn4 | O21 | 91.9(2) | O16 | Mn8 | O15 | 90.7(2) | Mn2 | O9 | Mn7 | 99.1(2) |
| O7 | Mn4 | O21 | 92.4(2) | O7 | Mn8 | O15 | 92.0(2) |  |  |  |  |

Table S7. Selected bond angles in $\mathbf{1 \Lambda \Lambda}$.

| Atom | Ato | Atom | Angle $/^{\circ}$ | Atom | Ato | Atom | Angle $/{ }^{\circ}$ | Atom | Ato | Atom | Angle $/^{\circ}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| O12 | Mn1 | O10 | 95.4(3) | O26 | Mn4 | O16 | 91.5(3) | O15 | Mn8 | O2A | 91.8(3) |
| O2 | Mn1 | O10 | 104.7(2) | O36 | Mn4 | O16 | 92.6(3) | O4 | Mn8 | O2A | 91.7(3) |
| O26 | Mn1 | O10 | 92.5(3) | O26 | Mn4 | O2 | 81.4(3) | O61 | Mn8 | O2A | 95.9(3) |
| O37 | Mn1 | O10 | 90.8(3) | O36 | Mn4 | O2 | 171.0(3) | N48 | Mn8 | O32 | 87.9(3) |
| O10 | Mn1 | O19 | 172.3(2) | O36 | Mn4 | O26 | 94.8(3) | O15 | Mn8 | O32 | 90.7(2) |
| O12 | Mn1 | O19 | 89.9(2) | O4 | Mn5 | O12 | 95.8(2) | O2A | Mn8 | O32 | 169.0(2 |
| O2 | Mn1 | O19 | 80.4(2) | O6 | Mn5 | O12 | 80.6(2) | O4 | Mn8 | O32 | 78.1(2) |
| O26 | Mn1 | O19 | 82.8(2) | O8 | Mn5 | O12 | 161.8(3) | O61 | Mn8 | O32 | 94.5(3) |
| O37 | Mn1 | O19 | 83.3(2) | O12 | Mn5 | O1A | 103.3(3) | O15 | Mn8 | O4 | 81.6(2) |
| O12 | Mn1 | O2 | 94.6(2) | O4 | Mn5 | O1A | 94.0(3) | O61 | Mn8 | O4 | 171.9(3 |
| O26 | Mn1 | O2 | 79.6(3) | O6 | Mn5 | O1A | 91.5(3) | O3 | Mn9 | N35 | 89.5(3) |
| O37 | Mn1 | O2 | 162.2(3) | O8 | Mn5 | O1A | 91.4(3) | O5 | Mn9 | N35 | 172.1(3 |
| O12 | Mn1 | O26 | 171.3(3) | O8 | Mn5 | O4 | 93.8(3) | O7 | Mn9 | N35 | 87.0(3) |
| O37 | Mn1 | O26 | 91.3(3) | O12 | Mn5 | O5 | 79.3(2) | N35 | Mn9 | O12 | 87.3(2) |
| O12 | Mn1 | O37 | 92.4(2) | O1A | Mn5 | O5 | 174.2(3) | O22 | Mn9 | O12 | 176.1(2) |
| O12 | Mn2 | N27 | 92.7(3) | O4 | Mn5 | O5 | 90.8(2) | O3 | Mn9 | O12 | 92.3(2) |
| O21 | Mn2 | N27 | 91.0(3) | O6 | Mn5 | O5 | 83.8(2) | O5 | Mn9 | O12 | 84.8(2) |
| O6 | Mn2 | N27 | 174.1(3) | O8 | Mn5 | O5 | 85.1(2) | O7 | Mn9 | O12 | 83.6(2) |
| O21 | Mn2 | O12 | 169.6(3) | O4 | Mn5 | O6 | 174.0(2) | N35 | Mn9 | O22 | 92.9(3) |
| O6 | Mn2 | O12 | 81.8(2) | O8 | Mn5 | O6 | 88.4(3) | O3 | Mn9 | O22 | 91.6(2) |
| N27 | Mn2 | O23 | 87.3(3) | O16 | Mn6 | N14 | 87.4(3) | O5 | Mn9 | O22 | 94.9(2) |
| O12 | Mn2 | O23 | 95.0(2) | O19 | Mn6 | N14 | 173.7(3) | O7 | Mn9 | O22 | 92.5(2) |
| O21 | Mn2 | O23 | 94.9(3) | O3 | Mn6 | N14 | 89.2(3) | O3 | Mn9 | O5 | 90.7(2) |
| O6 | Mn2 | O23 | 95.0(3) | O3 | Mn6 | O16 | 174.1(3) | O7 | Mn9 | O5 | 92.2(2) |
| O21 | Mn2 | O6 | 94.2(3) | N14 | Mn6 | O17 | 92.1(3) | O3 | Mn9 | O7 | 174.8(2 |
| N27 | Mn2 | 07 | 84.1(3) | O16 | Mn6 | O17 | 94.7(3) | Mn1 | O 12 | Mn2 | 109.6(3 |
| O12 | Mn2 | 07 | 77.3(2) | O19 | Mn6 | 017 | 94.0(3) | Mn1 | O 12 | Mn5 | 131.6(3 |
| O21 | Mn2 | 07 | 93.5(2) | O3 | Mn6 | 017 | 90.3(2) | Mn2 | O 12 | Mn5 | 97.3(3) |
| O23 | Mn2 | 07 | 168.1(2) | O16 | Mn6 | O19 | 90.7(3) | Mn1 | O12 | Mn9 | 112.4(3 |
| O6 | Mn2 | 07 | 92.9(2) | O3 | Mn6 | O19 | 92.1(2) | Mn2 | O12 | Mn9 | 102.4(2 |
| O18 | Mn3 | N31 | 174.2(3) | N14 | Mn6 | O 2 | 88.5(3) | Mn5 | 012 | Mn9 | 99.5(2) |
| O3 | Mn3 | N31 | 88.5(3) | O16 | Mn6 | O2 | 81.6(2) | Mn8 | O15 | Mn7 | 99.1(3) |
| O32 | Mn3 | N31 | 86.9(3) | O17 | Mn6 | O2 | 176.2(2) | Mn6 | 016 | Mn4 | 99.6(3) |
| O3 | Mn3 | O18 | 92.2(2) | O19 | Mn6 | O2 | 85.3(2) | Mn3 | O18 | Mn7 | 93.1(2) |
| O32 | Mn3 | O18 | 92.0(3) | O3 | Mn6 | O2 | 93.4(2) | Mn6 | O19 | Mn1 | 95.5(2) |
| N31 | Mn3 | O28 | 93.1(3) | O13 | Mn7 | O1 | 93.9(3) | Mn4 | O2 | Mn1 | 98.0(3) |
| O18 | Mn3 | O28 | 92.6(3) | O15 | Mn7 | O1 | 92.2(3) | Mn7 | O2 | Mn1 | 133.9(3 |
| O3 | Mn3 | O28 | 93.7(2) | O2 | Mn7 | O1 | 95.0(3) | Mn7 | O2 | Mn4 | 110.5(3 |
| O32 | Mn3 | O28 | 91.1(2) | O4 | Mn7 | O1 | 103.0(3) | Mn1 | O2 | Mn6 | 97.2(2) |
| O3 | Mn3 | O32 | 173.5(3) | O2 | Mn7 | O13 | 93.5(3) | Mn4 | O2 | Mn6 | 99.3(3) |
| N31 | Mn3 | O4 | 87.5(2) | O13 | Mn7 | O15 | 90.3(3) | Mn7 | O2 | Mn6 | 112.2(3 |
| O18 | Mn3 | O4 | 86.7(2) | O2 | Mn7 | O15 | 171.6(3) | Mn3 | O3 | Mn6 | 117.3(3 |
| O28 | Mn3 | O4 | 173.3(2) | O1 | Mn7 | O18 | 173.3(2) | Mn3 | O3 | Mn9 | 119.1(3 |
| O3 | Mn3 | O4 | 93.0(2) | O13 | Mn7 | O18 | 81.8(3) | Mn6 | O3 | Mn9 | 117.1(3 |
| O32 | Mn3 | O4 | 82.2(2) | O15 | Mn7 | O18 | 82.8(2) | Mn3 | O32 | Mn8 | 98.6(2) |
| O2 | Mn4 | N47 | 93.3(3) | O2 | Mn7 | O18 | 90.4(2) | Mn5 | O4 | Mn3 | 112.1(2 |
| O26 | Mn4 | N47 | 174.6(3) | O4 | Mn7 | O18 | 80.5(2) | Mn7 | O4 | Mn3 | 98.3(2) |
| O36 | Mn4 | N47 | 90.5(4) | O13 | Mn7 | O4 | 160.7(3) | Mn8 | O4 | Mn3 | 101.0(2 |
| N47 | Mn4 | O0A | 87.8(4) | O15 | Mn7 | O4 | 79.9(2) | Mn5 | O4 | Mn7 | 132.9(3 |
| O2 | Mn4 | O0A | 92.0(3) | O2 | Mn7 | O4 | 94.2(2) | Mn8 | O4 | Mn7 | 97.6(2) |
| O26 | Mn4 | O0A | 91.4(3) | O15 | Mn8 | N48 | 174.0(3) | Mn5 | O4 | Mn8 | 110.2(3 |
| O36 | Mn4 | O0A | 96.2(4) | O4 | Mn8 | N48 | 92.5(3) | Mn9 | O5 | Mn5 | 94.7(2) |
| N47 | Mn4 | O16 | 88.4(3) | O61 | Mn8 | N48 | 90.5(3) | Mn2 | O6 | Mn5 | 98.7(3) |
| O0A | Mn4 | 016 | 170.4(3) | O61 | Mn8 | O15 | 95.4(3) | Mn9 | O7 | Mn2 | 96.5(2) |
| O 2 | Mn4 | O16 | 79.4(2) | N48 | Mn8 | O2A | 88.5(3) |  |  |  |  |



Figure S1. a) ORTEP representation of the molecular structure of $\mathbf{1} \Delta \Delta$. Ellipsoids are at $50 \%$ probability. Hydrogen atoms omitted for clarity; b) Metal core of $\mathbf{1} \Lambda \Lambda$ with emphasis given to the $\mathrm{Mn}-\mathrm{O}$ bonds (yellow) that define the Jahn-Teller elongation of each of the constitutive Mn (III) centres. The directions of all Jahn-Teller distortions are nearly co-parallel, defining the magnetic anisotropy direction of the individual $\mathrm{Mn}(\mathrm{III})$ centres and of $1 \Lambda \Lambda$. Color scheme: Mn - magenta, N - blue, O - red, C - gray, S - yellow, Cl - green


Figure S2. Packing arrangement of molecules of $\mathbf{1}$ in the unit cell. Color code as Figure S1. S: yellow; Cl : green. H atoms omitted for clarity.


Figure S3. Packing arrangement illustrating H-bonds between adjacent molecules of $\mathbf{1}$ along the crystallographic $a$ axis. H atoms from the aromatic ring of Me-sao ${ }^{2-}$ of one molecule form H -bonds with the oximate O atom from the $\mathrm{Me}-\mathrm{sao}^{2-}$ ligand and with one of the O atoms of the capping carboxylate of the neighboring molecule.


Figure S4. Packing arrangement illustrating H-bonds between adjacent molecules of $\mathbf{1}$ along the crystallographic $b$ axis. H atoms from the aromatic ring of $\mathrm{Me}^{-\mathrm{sao}^{2-}}$ of one molecule form H -bonds with the oximate O atom from the $\mathrm{Me}-\mathrm{sao}^{2-}$ ligand and with one of the O atoms of the capping carboxylate of the neighboring molecule.

### 3.2 Powder X-ray diffraction



Figure S5. Powder diffraction profile of bulk 1 (red) compared to the simulated pattern using the single crystal crystal structure (black). No significant differences were observed between experimental and predicted difractograms, except in the intensity of some peaks, due to orientation effects.

## 4. Solution characterizations

4.1 FTIR spectroscopy


Figure S6. FTIR spectra of polycrystalline 1, $\mathbf{1}$ after dissolution in $\mathrm{CHCl}_{3}$ followed by drying, Me$\mathrm{saoH}_{2}$ and of lipoic acid (HL).

### 4.2 Mass spectrometry



Figure S7. ESI-MS spectrum of 1 recorded in positive mode in $\mathrm{CHCl}_{3}: \mathrm{MeOH}(1: 2)$ mixture. The detected species are: $\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\mathrm{sao})_{6}(\mathrm{~L})_{3}(\mathrm{MeO})_{3}\right]^{+} \quad(\mathrm{m} / \mathrm{z}=2160.8659)$, $\quad\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\right.$ $\mathrm{sao})_{6}(\mathrm{MeO})_{3}\left(\mathrm{~L}_{2}\left(\mathrm{HCO}_{2}\right)\right]^{+} \quad(\mathrm{m} / \mathrm{z}=2000.8184), \quad\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\mathrm{sao})_{6}(\mathrm{MeO})_{3}(\mathrm{~L})\left(\mathrm{HCO}_{2}\right)_{2}\right]^{+} \quad(\mathrm{m} / \mathrm{z}=$ 1840.7865), $\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\mathrm{sao})_{6}(\mathrm{MeO})_{3}\left(\mathrm{HCO}_{2}\right)_{3}\right]^{+} \quad(\mathrm{m} / \mathrm{z}=1680.7492), \quad\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\right.$ sao $\left.)_{6}(\mathrm{MeO})_{3}(\mathrm{~L})_{2}\right]^{2+}(m / z=977.9160),\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\mathrm{sao})_{6}(\mathrm{MeO})_{3}(\mathrm{~L})\left(\mathrm{HCO}_{2}\right)\right]^{2+}(\mathrm{m} / \mathrm{z}=897.8966)$, $\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\mathrm{sao})_{6}(\mathrm{MeO})_{3}\left(\mathrm{HCO}_{2}\right)_{2}\right]^{2+}(\mathrm{m} / \mathrm{z}=817.8771)$. Inset: Experimental and simulated isotope pattern corresponding to the $\left[\mathrm{Mn}_{9} \mathrm{O}_{4}(\mathrm{Me}-\mathrm{sao})_{6}(\mathrm{~L})_{3}(\mathrm{MeO})_{3}\right]^{+}$.

## 5. Characterisation of 1 on AuNP and Au(111).

### 5.1 Transmission Electron Microscopy (TEM).



Figure S8. a) TEM image of the HDA@AuNPs; b) Size distribution of the synthesized HDA@AuNPs obtained from the TEM image on the left with ImageJ software and fitted with a Gaussian function (blue line). The diameter was measured for 2878 NPs.


Figure S9. TEM image of purified $\mathbf{1}$ @ AuNPs. a) Free, evenly distributed features; b) agglomerated features. Both a) and b) were observed on the same grid.
5.3 X-ray Photoelectron Spectroscopy (XPS).

b)


Figure S10. Full-range XPS spectra of a) $\mathbf{1}, \mathbf{A u}(111)$ on mica surface and $\mathbf{1} @ \mathbf{A u}(111)$; b) $\mathbf{1}$, HDA@AuNPs and 1@AuNPs.


Figure S11. High-resolution XPS spectra and deconvolutions into components specific to reduced or oxidized species of the $\mathrm{S} 2 p$ region in 1, blank $\mathrm{Au}(111)$ surface, $\mathbf{1} @ \mathbf{A u}(\mathbf{1 1 1})$, HDA@AuNPs, and 1 @AuNPs.


Figure S12. High-resolution XPS spectra of $\mathrm{Au} 4 f$, C1s, N1s, and O1s core levels for 1, blank $\mathrm{Au}(111)$ surface, $\mathbf{1} @ \mathbf{A u}(\mathbf{1 1 1})$, HDA@AuNPs, and $\mathbf{1} @ A u N P s$. The $\mathrm{C} 1 s, \mathrm{Cl} 2 p, \mathrm{~N} 1 s$ and $\mathrm{O} 1 s$ photopeaks display no significant changes for $1,1 @ A u N P s$ and $1 @ \mathbf{A u}(111)$. The very weak component ( 288.5 eV ) of the C1s region, specific to highly oxidized carbon atom in the carboxylic group, could be detected in $1 @ \mathbf{A u}(111)$ as in 1.

Table S8. XPS-derived chemical composition of the top 10 nm of each sample surface (atomic \%).

| Sample | C | O | S | Mn | Cl | N | Au | Si |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Au Blank | $\begin{aligned} & 17.9 \\ & (1.1) \end{aligned}$ | $\begin{gathered} 0.9 \\ (0.5) \end{gathered}$ | N. D. | N. D. | N. D. | N. D. | $\begin{aligned} & 81.2 \\ & (0.1) \end{aligned}$ | N. D. |
| 1 | $\begin{aligned} & 63.5 \\ & (1.4) \end{aligned}$ | $\begin{aligned} & 15.5 \\ & (2.2) \end{aligned}$ | $\begin{gathered} 5.7 \\ (0.1) \end{gathered}$ | $\begin{gathered} 9.8 \\ (1.2) \end{gathered}$ | $\begin{gathered} 1.1 \\ (0.3) \end{gathered}$ | $\begin{gathered} 4.4 \\ (0.7) \end{gathered}$ | N. D. | N. D. |
| 1@Au(111) | $\begin{aligned} & 43.3 \\ & (0.8) \end{aligned}$ | $\begin{aligned} & 11.7 \\ & (0.1) \end{aligned}$ | $\begin{gathered} 1.7 \\ (0.1) \end{gathered}$ | $\begin{gathered} 4.2 \\ (0.2) \end{gathered}$ | $\begin{gathered} 1.2 \\ (0.1) \end{gathered}$ | $\begin{gathered} 1.4 \\ (0.1) \end{gathered}$ | $\begin{aligned} & 36.5 \\ & (1.4) \end{aligned}$ | N. D. |
| HDA@AuNPs | $\begin{aligned} & 88.4 \\ & (1.4) \end{aligned}$ | $\begin{gathered} 3.9 \\ (0.1) \end{gathered}$ | N. D. | N. D. | $\begin{gathered} 1.4 \\ (0.8) \end{gathered}$ | $\begin{gathered} 2.1 \\ (0.8) \end{gathered}$ | $\begin{gathered} 1.7 \\ (0.9) \end{gathered}$ | $\begin{gathered} 2.5 \\ (1.0) \end{gathered}$ |
| $1 @$ AuNPs | $\begin{aligned} & 66.1 \\ & (1.2) \end{aligned}$ | $\begin{gathered} 3.6 \\ (0.6) \end{gathered}$ | $\begin{gathered} 1.4 \\ (0.1) \end{gathered}$ | $\begin{gathered} 2.7 \\ (0.2) \end{gathered}$ | $\begin{gathered} 7.0 \\ (0.3) \end{gathered}$ | $\begin{gathered} 2.7 \\ (0.3) \end{gathered}$ | $\begin{aligned} & 16.5 \\ & (0.8) \end{aligned}$ | N. D. |
| HL@AuNPs | $\begin{aligned} & 42.8 \\ & (0.2) \end{aligned}$ | $\begin{gathered} 9.5 \\ (0.3) \end{gathered}$ | $\begin{gathered} 6.9 \\ (0.1) \end{gathered}$ | N. D. | N. D. | $\begin{gathered} 0.4 \\ (0.1) \end{gathered}$ | $\begin{aligned} & 40.4 \\ & (0.5) \end{aligned}$ | N. D. |
| 1-Theoretical | 60.9 | 21.9 | 4.7 | 7.0 | 0.8 | 4.7 | N. D. | N. D. |

Uncertainties from average values are shown in round brackets. N.D. refers to not detected

Table S9. Elemental ratios derived from the atom \% presented in Table S8.

| Sample | $\mathrm{S} / \mathrm{N}$ | $\mathrm{S} / \mathrm{Cl}$ | $\mathrm{Mn} / \mathrm{S}$ | $\mathrm{Mn} / \mathrm{N}$ | $\mathrm{C} / \mathrm{O}$ | $\mathrm{S} / \mathrm{Au}$ | S Bound <br> thiol/Au |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 1.29 | 5.27 | 1.70 | 2.20 | 4.11 | N. D. | N. D. |
| $\mathbf{1 @ A u ( 1 1 1 )}$ | 1.22 | 1.40 | 2.50 | 3.04 | 3.72 | 0.046 | 0.027 |
| $\mathbf{1 @ A u N P s}$ | 0.53 | 0.20 | 1.87 | 0.98 | 18.4 | 0.087 | 0.049 |
| HL@AuNPs | N. D. | N. D. | N. D. | N. D. | 4 | 0.171 | 0.081 |
| 1-Theoretical | 1.00 | 6.00 | 1.50 | 1.50 | 2.79 | N. D. | N. D. |

N.D. refers to not detected

Table S10. $\mathrm{S} 2 p_{3 / 2}$ peaks and atom \% derived from deconvolution of $\mathrm{S} 2 p$ high resolution spectra.

| Sample | BE (eV) | At \% |
| ---: | :---: | :---: |
|  | 161.9 | 20.8 |
|  | 163.5 | 79.2 |
| 1@Au(111) | 161.8 | 60.3 |
|  | 163.3 | 39.7 |
| 1@AuNPs | 161.9 | 56.2 |
|  | 163.3 | 43.8 |
| HL@AuNPs | 161.9 | 47.3 |
|  | 163.2 | 52.7 |

Table S11. Modified Auger parameter ( $\alpha^{\prime}=\mathrm{BE}$ of the $\mathrm{Mn} 2 \mathrm{p}_{3 / 2}$ peak +KE of the $\mathrm{Mn}_{\mathrm{L}} \mathrm{M}_{23} \mathrm{~V}$ Auger peak).

|  | Mn 2p (BE, eV) | $\mathrm{Mn}_{3} \mathrm{M}_{23} \mathrm{~V}$ <br> $\mathrm{eV})$ | Modified Auger <br> Parameter $(\mathrm{eV})$ |
| :---: | :---: | :---: | :---: |
| 1 | 641.9 | 582.7 | 1224.5 |
|  | $(0.2)$ | $(0.2)$ | $(0.4)$ |
| $\mathbf{1 @ A u ( 1 1 1 )}$ | 641.7 | 582.6 | 1224.3 |
|  | $(0.2)$ | $(0.1)$ | $(0.3)$ |
| 1@AuNPs | 642.0 | 582.5 | 1224.5 |
|  | $(0.1)$ | $(0.3)$ | $(0.4)$ |

Uncertainties from average values are shown in round brackets. N.D. refers to not detected

### 5.4 X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD).



Figure S13. XAS and XMCD spectra of 1 at the Mn K-edge. Due to the quenched orbital momentum of $\mathrm{Mn}(\mathrm{III})$ the XMCD at the Mn K-edge is very weak and noisy.

### 5.5 Atomic Force Microscopy (AFM).



Figure S14. Topographic AFM image of $\mathbf{1}$ @ $\boldsymbol{e}-\mathbf{A u}(\mathbf{1 1 1 )}$


Figure S15. Tapping-mode AFM phase image of $\mathbf{1} @ \boldsymbol{e}-\mathbf{A u}(\mathbf{1 1 1})$, showing the location of the $\mathrm{Mn}_{9}$ cores (black dots) in the monolayer. The positions overlap with the height image with some clusters embedded deeper in the monolayer.


Figure S16. Topographic cross section made at the red line shown in Figure S14a, across several protrusions observed on the surface.


Figure S17. Schematic representation of the molecules of $\mathbf{1}$ either "lying flat" or "standing up" on the $e-\mathrm{Au}(111)$ surface.

### 5.6 FTIR of $1 @ t$-AuNPs



Figure S18. FTIR spectra of $\mathbf{1}$ and $\mathbf{1} @ \boldsymbol{t}$ - $\mathbf{A u}(111)$ in absorbance mode.

### 5.7 Circular Dichroism (CD) spectroscopy

The CD spectra of $\mathbf{1 \Delta \Delta}$ and of $\mathbf{1} \Lambda \Lambda$ in chloroform shown in Figure 3 of the main text are obtained by substraction of the background trace (cuvette + chloroform) shown below from the respective raw $C D$ spectra of $\mathbf{1} \Delta \Delta$ and of $\mathbf{1} \Lambda \Lambda$ in chloroform, also shown below. The sharp background feature below 300 nm is a cuvette artefact of the cuvette used to record the CD spectra of $\mathbf{1 \Delta \Delta}$ and of $\mathbf{1} \Lambda \Lambda$ in chloroform.

The corrected spectra of $\mathbf{1} \Delta \Delta @ \boldsymbol{t} \mathbf{- A u ( 1 1 1 )}$ and of $\mathbf{1} \Lambda \Lambda @ \boldsymbol{t}-\mathbf{A u}(\mathbf{1 1 1 )}$ shown below have been corrected for baseline by averaging them and subsequently subtracting the resulting baseline from each of the individual spectra.


Figure S19. Raw CD spectra of $\mathbf{1} \Delta \Delta, \mathbf{1} \Lambda \Lambda$ and of $R(-)$-lipoic acid in chloroform, background for the measurements of $\mathbf{1} \Delta \Delta$ and of $\mathbf{1} \Lambda \Lambda$, and corrected CD spectra of $\mathbf{1} \Delta \Delta @ \boldsymbol{t}-\mathbf{A u}(\mathbf{1 1 1}), \mathbf{1} \Lambda \Lambda @ t$ Au(111).

## 6. Magnetic properties

1@AuNPs, HDA@AuNPs and HL@AuNPs were investigated with SQUID magnetometry. AuNPs are known to display paramagnetism depending on the type of surface ligand and the degree of coverage. ${ }^{10}$ The magnetization observed at low temperatures for $\mathbf{1}$ @AuNPs was several orders of magnitude higher than for HDA@AuNPs or HL@AuNPs (Figure S28-S29). The replacement of HDA by HL on AuNPs revealed a small increase in the weak paramagnetism (Figure S28-S29). ICP-MS showed that the amount of $\mathbf{1}$ in $\mathbf{1} @$ AuNPs was $9.6 \%$. At 2 K and 5 T applied magnetic field, the magnetic moment of $\mathbf{1}$ is 20.98 emu.g $^{-1}$ while for $\mathbf{1} @$ AuNPs the measured value is 2.06 emu.g ${ }^{-1}$ which corresponds to a mass percentage of $9.8 \%$ of $\mathbf{1}$ in $\mathbf{1} @$ AuNPs. Both values from ICPMS and SQUID magnetometry are in a good agreement with the previously calculated value of 10 \% by weight 1 necessary to fully cover AuNPs with an average size of 7.3 nm . The estimated proportion of 1 in $1 @$ AuNPs allowed comparison of the magnetic properties of the surface deposited species with the bulk by rescaling for a $9.8 \%$ content of $\mathbf{1}$ and transforming the mass to molar quantities.

### 6.1 Experimental



Figure S20. Reduced magnetization plots of a) $\mathbf{1}$ in solid state; b) $19.6 \mathrm{mM} \mathrm{CHCl}_{3}$ solution of $\mathbf{1}$; and c) $1 @$ AuNPs, in the temperature and field ranges 2 to 10 K and 0.5 to 5 T , with $\mu_{\mathrm{B}}$ the Bohr magneton and $k$ the Boltzman constant. The reduced axis reflects the ratio between Zeeman and thermal energy.


Figure S21. Temperature dependence of $\chi^{\prime}$ below 8 K in a polycrystalline sample of $\mathbf{1}$ at $10^{0}, 10^{1}$, $10^{2}$ and $10^{3} \mathrm{~Hz}$ in a 3.5 Oe a.c. field and in a zero d.c. field. Solid lines are guides for the eye.


Figure S22. Frequency dependence of a) $\chi^{\prime}$ and b) $\chi^{\prime \prime}$ in polycrystalline 1, at different temperatures in a 3.5 Oe a.c. field and in zero d.c. field. Solid lines are guides for the eye.


Figure S23. Temperature dependence of a) $\chi^{\prime}$ and b) $\chi^{\prime \prime}$, in a 19.6 mM frozen solution of $\mathbf{1}$ in $\mathrm{CHCl}_{3}$, at different frequencies in a 3.5 Oe a.c. field and in zero d.c. field. Solid lines are guides for the eye.


Figure S24. Frequency dependence of a) $\chi^{\prime}$ and b) $\chi^{\prime \prime}$, for a 19.6 mM frozen solution of $\mathbf{1}$ in $\mathrm{CHCl}_{3}$, at different temperatures in a 3.5 Oe a.c. field and in zero d.c. field. Solid lines are fits for a single relaxation process to a generalized Debye equation, obtained using CC-fit ${ }^{11}$.


Figure S25. Frequency dependence of a) $\chi^{\prime}$ and b) $\chi^{\prime \prime}$, for a 6.8 mM frozen solution of $\mathbf{1}$ in $\mathrm{CHCl}_{3}$, at different frequencies in a 3.5 Oe a.c. field and in zero d.c. field. Solid lines are guides for the eye.


Figure S26. D.c. magnetic hysteresis loops of frozen solutions of $\mathbf{1}$ in $\mathrm{CHCl}_{3}$ at two different concentrations showing different coercive fields at 1.8 K and with a magnetic field sweep rate of $0.33 \mathrm{~T} \mathrm{~min}^{-1}$.


Figure S 27. Temperature dependence of a) $\chi^{\prime}$ and b) $\chi^{\prime \prime}$, in 1 @AuNPs, at different frequencies in a 3.5 Oe a.c. field and in zero d.c. field. Solid lines are guides for the eye.


Figure S28. Temperature dependence of the a) magnetization at 1000 Oe and b) $\chi_{g} T$ product in HDA@AuNPs, HL@AuNPs and 1@AuNPs.


Figure S29. D.c. magnetization hysteresis loops: a) $\mathbf{1}$ @AuNPs at 1.8 and 2.4 K , measured with an MPMS-XL SQUID magnetometer; b) HDA@AuNPs and HL@AuNPs at 1.8 K , measured with an MPMS-XL SQUID magnetometer; c,d) 1@AuNPs at various temperatures (c) and field sweep rates (d) measured with a $\mu$ SQUID magnetometer. ${ }^{12}$ In the weakly paramagnetic HDA@AuNPs and HL@AuNPs no opening of the hysteresis loops was observed under these conditions.


Figure S30. Temperature dependence of a) $\chi^{\prime}$ and b) $\chi^{\prime \prime}$, in HL@AuNPs, at different frequences in a 3.5 Oe a.c. field and in zero d.c. field. Solid lines are guides for the eye.

### 6.2 Modelling

For simplicity we refer specifically to complex 1. However, the discussion is also relevant for $1 @$ AuNPs. $1 @$ AuNPs is hereafter only referred to when relevant.
Modelling of the magnetic properties of $\mathbf{1}$ and of $\mathbf{1} @ A u N P s$, was performed within the framework of the phenomenological spin-Hamiltonian formalism.
Given that $\mathbf{1}$ is an enneanuclear Mn (III)-based SMM and since Mn (III) is a magnetically anisotropic metal center, the simplest general form of spin-Hamiltonian $(\widehat{H})$ appropriate for the phenomenological description of the magnetic properties of $\mathbf{1}$ should contain terms expressing a) the isotropic magnetic exchange interaction between the constitutive Mn (III) centers and the isotropic response of the system to an external magnetic field according to the Zeeman interaction ( $\widehat{H}_{\text {iso }}$ ), and b) the magnetic anisotropy, at zero external magnetic field, of the constitutive $\mathrm{Mn}(\mathrm{III})$ centers ( $\widehat{H}_{\text {aniso }}$ ). Thus:

$$
\begin{equation*}
\widehat{H}=\widehat{H}_{\text {iso }}+\widehat{H}_{\text {aniso }} \tag{1}
\end{equation*}
$$

where

$$
\begin{equation*}
\widehat{H}_{i s o}=-2 \sum_{i, j>i}^{n} \hat{S}_{i} J_{i j} \hat{S}_{j}+\mu_{B} \sum_{i=1}^{n} \vec{B} g_{i} \hat{S}_{i} \tag{2}
\end{equation*}
$$

with $\hat{S}$ a spin operator, $J$ the scalar pairwise isotropic magnetic exchange interaction between constitutive $\mathrm{Mn}($ III $)$ centers, $\mu_{B}$ the Bohr magneton, $\vec{B}$ the external static magnetic field, $g$ the isotropic $g$-factor of Mn (III) set to $g=2$ for simplicity, and the indices $i$ and $j$ running through the $n$ $=9$ constitutive Mn (III) centres;

$$
\begin{equation*}
\widehat{H}_{\text {aniso }}=\sum_{i=1}^{9} D_{M n(I I I)}\left[\hat{S}_{z, i}^{2}-S_{i}\left(S_{i}+1\right) / 3\right] \tag{3}
\end{equation*}
$$

with $D_{M n(I I I)}$ the second-order single-ion uniaxial anisotropy parameter of $\operatorname{Mn}(I I I), \hat{S}_{z, i}$ the Cartesian component of spin operator $\hat{S}$ of the $i^{\text {th }} \mathrm{Mn}$ (III) centre along the z-direction of the local coordinate frame, and $S=2$ the total spin value of Mn (III).
The dimension, $N$, of the square matrix corresponding to the matrix representation of $\widehat{H}$ for $\mathbf{1}$ is:

$$
\begin{equation*}
N=\prod_{i}^{n}\left(2 S_{i}+1\right) \tag{4}
\end{equation*}
$$

resulting in $\mathrm{N}=5^{9}=1953125$ for $\mathbf{1}$. The magnitude of $N$ precludes numerical diagonalization of the full spin-Hamiltonian matrix by conventional approaches ${ }^{13}$ because of unrealistic computer memory and processor time requirements. Thus, to model the magnetic properties of $\mathbf{1}$, a series of simplifying assumptions have to be performed.
The first such assumption is that at temperatures higher than the magnitude of the anisotropy terms entering spin-Hamiltonian (1), these later ones can be considered negligible with respect to the effect of the isotropic magnetic exchange on the magnetic properties of polycrystalline $\mathbf{1}$. Thus,

$$
\begin{equation*}
\widehat{H}=\widehat{H}_{i s o}=-2 \sum_{i, j>i}^{n} \hat{S}_{i} J_{i j} \hat{S}_{j}+\mu_{B} \sum_{i=1}^{n} \vec{B} g_{i} \hat{S}_{i} \tag{5}
\end{equation*}
$$

Within the Irreducible Tensor Operator (ITO) formalism ${ }^{14}$, the isotropic exchange parameter, $J_{i j}$, is associated to a tensor operator $\hat{O}_{q}^{K}$ of order $\mathrm{K}=0$ and thus, necessarily of projection $\mathrm{q}=0(-\mathrm{K} \leq \mathrm{q} \leq$ K , with K and q integers), since it is associated to the scalar product, $\hat{S}_{i} \cdot \hat{S}_{j}$, of the Cartesian spin-
operators. The matrix elements of a tensor operator $\widehat{O}_{q}^{K}$ within the coupled total spin, $S$, basis $\left|s, S, M_{S}\right\rangle$ is given by:

$$
\left\langle s, S, M_{S}\right| \hat{O}(k, K, q)\left|s^{\prime}, S^{\prime}, M_{S}^{\prime}\right\rangle=(-1)^{S-M_{S}}\left(\begin{array}{ccc}
S & K & S^{\prime}  \tag{6}\\
-M_{S} & q & M_{S}^{\prime}
\end{array}\right)\left\langle s, S\|k, K\| s^{\prime}, S^{\prime}\right\rangle
$$

where $s, s^{\prime}$ and $k$ are all necessary additional quantum numbers to fully define the problem, $M_{S}$ is the projection of $S$ along the quantization axis, the first term of the right hand side is a phase, the second one is a $3-j$ symbol and the third is a reduced matrix element, independent of $M_{S}$. For the 3-j symbol to be non-zero a) the triangle relation has to hold for $S, K$ and $S^{\prime}$, from where $S=S^{\prime}$, since $K$ $=0$; and b) $M_{S}^{\prime}-M_{S}=q$, has to hold. Thus, the isotropic exchange interaction has non-zero matrix elements only between basis-function of the same total spin $S$. Furthermore, since for the isotropic exchange associated tensor operator $\widehat{O}_{q}^{K}, q=0$, the matrix element of equation (6) is independent of $M_{S}$, to a phase factor of $\pm 1$ which is irrelevant for the computation of eigenvalues. Thus, only one of the $2 S+1$ projections of each total $S$ multiplet is necessary to be included into this block-diagonal form of $\widehat{H}_{\text {iso }}$, since the information contained in the $2 S$ others is redundant. Finally, since $\hat{S}^{2}$ commutes with $\hat{S}_{z}, \hat{S}^{2}$ and $\hat{S}_{z}$ have a simultaneous eigenbasis specified by their respective eigenvalues $S$ and $M_{S}$. This allows to transform the matrix representation of $\widehat{H}_{\text {iso }}$ for $\mathbf{1}$ into blockdiagonal form, where each block corresponds to basis-functions of the same total spin $S$ and projection $M_{S}$. Use of this methodology allows to transform the matrix representation of $\widehat{H}_{\text {iso }}$ for $\mathbf{1}$, into block-diagonal form made up from nineteen blocks each corresponding to a total spin value $S$, ranging from 0 to 18 , the dimensions of which are given below in Table S8.

Table S8. Total spin, $S$, and associated dimension, $\mathrm{N}_{S}$, of the corresponding block in the blockdiagonal form of the matrix representation of $\widehat{\boldsymbol{H}}_{\text {iso }}$ for $\mathbf{1}$.

| $\boldsymbol{S}$ | $\mathbf{N}_{\boldsymbol{S}}$ |
| :---: | :---: |
| 18 | 1 |
| 17 | 8 |
| 16 | 36 |
| 15 | 120 |
| 14 | 330 |
| 13 | 783 |
| 12 | 1644 |
| 11 | 3108 |
| 10 | 5355 |
| 9 | 8470 |
| 8 | 12356 |
| 7 | 16668 |
| 6 | 20796 |
| 5 | 23925 |
| 4 | 25200 |
| 3 | 23940 |
| 2 | 19845 |
| 1 | 13140 |
| 0 | 4600 |
| sum | $\mathbf{1 8 0 3 2 5}$ |



Figure S31. Mn(III) centers and bridging ligand moieties in 1. Mn: purple; N: blue; O: red; C: gray.
The dimensions of the block-diagonal form of the matrix representation of $\widehat{H}_{\text {iso }}$ for $\mathbf{1}$ (Table S8) are compatible with standard numerical diagonalization approaches ${ }^{13}$. The number of independent isotropic magnetic exchange parameters that can, in principle, be included in $\widehat{H}_{\text {iso }}$ is determined by the number of different super-exchange paths between the $\mathrm{Mn}(\mathrm{III})$ centers in $\mathbf{1}$. These superexchange paths are defined by the various bridging ligands. Additional exchange interactions originating from magnetic dipole interactions are neglected because they are usually much smaller in magnitude than the exchange interactions via bridging ligands, as they depend inversely to the cube of the intermetallic distance. In the basal $\left[\mathrm{Mn}^{\text {III }}{ }_{6}\right]$ subunit of $\mathbf{1}$, the almost co-planar Mn (III) ions (Mn1 to Mn6, Figure S31) are alternately connected from the exterior a) by three $-\mathrm{N}-\mathrm{O}-$ oximates and by three bidentate carboxylates (Mn1-Mn2, Mn3-Mn4, Mn5-Mn6); and b) by three methoxides (Mn2-Mn3, Mn4-Mn5, Mn1-Mn6). From the inside the metal-ions of the [ $\mathrm{Mn}^{\mathrm{III}}{ }_{6}$ ] subunit are linked, in groups of three (Mn1-Mn2-Mn3, Mn3-Mn4-Mn5 and Mn1-Mn5-Mn6) in three fused triangles via three $\mu_{4}-\mathrm{O}^{2-}$ bridges that also bridge the $\mathrm{Mn} 1-\mathrm{Mn} 2-\mathrm{Mn} 3, \mathrm{Mn} 3-\mathrm{Mn} 4-\mathrm{Mn} 5$ and Mn1-Mn5-Mn6 triangles to the Mn (III) centres (Mn8, Mn9, Mn7, respectively) of the upper $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{3}\right]$ subunit (Figure S31). These bridging paths define three types of magnetic exchange interactions within the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ subunit: a) $J_{12}=J_{34}=J_{56}=J_{1 \mathrm{a}}$; b) $J_{23}=J_{45}=J_{16}=J_{1 \mathrm{~b}}$; and c) $J_{13}=$ $J_{35}=J_{15}=J_{1 \mathrm{c}}$ (Figure S32a).
In the upper $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ subunit, the three Mn (III) ions are linked by a central $\mu_{3}-\mathrm{O}^{2-}$, while the edges of the $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{3}\right]$ triangle consist of three bridging $-\mathrm{N}-\mathrm{O}-$ oximates of Me-sao ${ }^{2-}$ (Figure S31). Thus, a unique isotropic magnetic exchange parameter ( $J_{78}=J_{89}=J_{79}=J_{2}$, Figure S32.) is sufficient to describe the magnetic exchange interactions within the upper $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ subunit.
As previously mentioned, the upper $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ and the lower $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ subunits are linked by three $\mu_{4}-$ $\mathrm{O}^{2-}$ bridges. They are also bridged by: a) three phenoxide $\mathrm{O}-\mathrm{atoms}$ of $\mathrm{Me}^{-\mathrm{Sao}^{2-}}$ from the upper [ $\mathrm{Mn}^{\mathrm{III}}{ }_{3}$ ] subunit ( Mn 2 to $\mathrm{Mn} 8, \mathrm{Mn} 4$ to $\mathrm{Mn} 9, \mathrm{Mn6}$ to Mn 7 ); b) three oximato O-atoms from the three bridging aldoximes from the upper $\left[\mathrm{Mn}^{\mathrm{III}}\right]$ subunit ( Mn 1 to $\mathrm{Mn} 7, \mathrm{Mn} 3$ to $\mathrm{Mn} 8, \mathrm{Mn} 5$ to Mn 9 ) and


Figure S32. Isotropic magnetic exchange parameters within 1. a) The various exchange paths within the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ subunit and between the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ and $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ subunits are considered inequivalent; b) Reduction of the free parameters of the spin-Hamiltonian model of a) by considering the various exchange paths within the $\left[\mathrm{Mn}^{\mathrm{III}}\right]$ subunit and between the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ and [ $\mathrm{Mn}^{\mathrm{III}}{ }_{3}$ ] to be equivalent.
c) three $-\mathrm{N}-\mathrm{O}-$ oximate bridges ( Mn 1 to Mn 8 , Mn 3 to Mn 9 , Mn 5 to Mn 7 ). These super-exchange bridging paths between the upper $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ and the lower $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right.$ ] subunits define three further isotropic magnetic exchange interactions: a) $J_{18}=J_{39}=J_{57}=J_{3 \mathrm{a}}$; b) $J_{28}=J_{49}=J_{67}=J_{36}$; and c) $J_{17}$ $=J_{38}=J_{59}=J_{3 \mathrm{c}}$ (Figure S32a). Thus in 1, 7 different types of magnetic exchange interaction parameters can be considered in the idealized case where effective trigonal symmetry is assumed for the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{9}\right]$ unit, the effective trigonal axis being normal to the plane of both the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ and $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ subunits.
However, even the above simplified description of the magnetic exchange paths in $\mathbf{1}$ will unavoidably lead to over-parametrisation of the spin-Hamiltonian model $\widehat{H}_{\text {iso }}$ since it is not possible to extract seven independent exchange parameters from the experimental temperature dependence of the $\chi^{T}$ product of $\mathbf{1}$, even though in this case the $\chi T$ versus T curve presents several distinct features. Thus, further simplification of the employed model is necessary. To this end we assume that a unique exchange parameter describes the magnetic exchange within the $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{6}\right]$ subunit and that also a unique parameter describes the magnetic exchange between the $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ and $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ subunits. Thus, $J_{1}, J_{2}$ and $J_{3}$ are the isotropic exchange parameters within $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right],\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$ and between $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{6}\right]$ and $\left[\mathrm{Mn}^{\mathrm{III}}{ }_{3}\right]$, respectively (Figure S32b). Again, this spin-Hamiltonian model is characterized by trigonal symmetry but the number of independent parameters is now reduced to three.
Inclusion in $\widehat{H}_{\text {iso }}$ of: a) the exchange terms, depicted as intermetallic connections in Figure S32b, as fit parameters; and b) of isotropic g-factors for all $\mathrm{Mn}(\mathrm{III})$ centers, as mentioned above, as fixed parameters, allowed the temperature dependence of the $\chi T$ product of $\mathbf{1}$ to be numerically fitted, by use of the Levenberg-Marquardt algorithm ${ }^{15}$, to the isotropic spin-Hamiltonian $\widehat{H}_{\text {iso }}$. This resulted in the best fit parameters $J_{1}=-7.6 \mathrm{~cm}^{-1}, J_{2}=1.8 \mathrm{~cm}^{-1}$ and $J_{3}=-1.6 \mathrm{~cm}^{-1}$. Under these conditions, the ground spin state of $\mathbf{1}$, at zero external magnetic field, is a doubly degenerate $S=5$, with numerous excited states lying in close proximity (Figure S33a). Employing the same methodology to model the temperature dependence of the $\chi T$ product of $\mathbf{1} @$ AuNPs results in the best fit parameters: $J_{1}=-$ $4.5 \mathrm{~cm}^{-1}, J_{2}=2.7 \mathrm{~cm}^{-1}$ and $J_{3}=-2.8 \mathrm{~cm}^{-1}$ (Figure S32b). At zero external magnetic field the ground spin state of $\mathbf{1} @$ AuNPs is a singly degenerate $S=6$, again with numerous excites states lying in close proximity.


Figure S33. Zero-field eigenvalues of $\widehat{H}_{\text {iso }}$ versus total spin $S$. a) For $\mathbf{1}$ with best fit parameters: $J_{1}$ $=-7.6 \mathrm{~cm}^{-1}, J_{2}=1.8 \mathrm{~cm}^{-1}$ and $J_{3}=-1.6 \mathrm{~cm}^{-1}$; b) For $\mathbf{1} @$ AuNPs with best fit parameters: $J_{1}=-4.5$ $\mathrm{cm}^{-1}, J_{2}=2.7 \mathrm{~cm}^{-1}$ and $J_{3}=-2.8 \mathrm{~cm}^{-1}$. In parenthesis is given the degeneracy of each level. No eigenstates are located within the energy range of the axis break between 3.5 and $4.0 \mathrm{~cm}^{-1}$.

However, description of the low temperature magnetic properties of $\mathbf{1}$ in terms of the magnetic properties of the total spin ground state $S$ is meaningless. This is because the exchange-induced energy separation of the ground spin state from the excited ones (Figure S33) is much smaller than the zero external magnetic field splitting of the $m_{s}$ components of the $S$ multiplets of $\mathbf{1}$, induced by projection of the magnetic anisotropy of the $\mathrm{Mn}(\mathrm{III})$ ions on the $S$ multiplets of $\mathbf{1}$. Thus, the correct description of the low temperature magnetic properties of $\mathbf{1}$ requires inclusion of anisotropy terms in the spin-Hamiltonian model of $\mathbf{1}$. Thus the anisotropic spin-Hamiltonian (1) has to be numerically diagonalized to this purpose. However, as previously described, this is practically impossible for the full spin-Hamiltoniam matrix representation of $\widehat{H}$ since the dimension of the associated square matrix is of the order of $210^{6}$. To circumvent these technical limitations we adapted to the spin-Hamiltonian formalism an iterative approach that exploits the sparse nature of the Hamiltonian matrix ${ }^{16-17}$, known as the Davidson algorithm ${ }^{18-19}$. The Davidson algorithm is an iterative subspace diagonalization approach that allows the exact computation of a number of lowlying eigenstates of the full spin-Hamiltonian, $\widehat{H}$, of the system starting from a set of, in principle arbitrarily chosen, guess vectors, each of dimension $N$, within realistic computation times and memory storage requirements. This approach, allows for any spin-Hamiltonian term to be included in the spin-Hamiltonian of the system and for all terms to be treated simultaneously and not in a sequential perturbation way. Thus, the methodology used allows for the simultaneous inclusion of single-ion and exchange anisotropy terms, as well as of any other relevant terms, in the spinHamiltonian without requiring that the total spin $S$ is a good quantum number. The converged lowlying eigenvectors, each of dimension $N$, may directly be used to compute quantities such as spin expectation values or transition moments. Alternatively, they may be used in a unitary transformation of the full Hamiltonian to generate an effective operator accurate in the subspace defined by the converged eigenvectors.
To model to low temperature magnetic properties of $\mathbf{1}$, we employed the above described iterative subspace approach. As a starting point, we used the best-fit magnetic exchange parameters $J_{1}=-7.6$ $\mathrm{cm}^{-1}, J_{2}=1.8 \mathrm{~cm}^{-1}$ and $J_{3}=-1.6 \mathrm{~cm}^{-1}$, determined by fitting the temperature dependence of the $\chi T$ product of $\mathbf{1}$ to $\widehat{H}_{\text {iso }}$, and a guess value $D_{\mathrm{Mn}(I I I)}=-3 \mathrm{~cm}^{-1}$, for the second order uniaxial anisotropy of the Mn (III) centres in $\mathbf{1}$. We used a single single-ion anisotropy parameter since all the Jahn-Teller distortion axes of the Mn (III) centres in $\mathbf{1}$ are nearly co-parallel (Figure S1). With these parameters, we generate the matrix representation of $\widehat{H}$ in the direct product basis. This results in a Hermitian matrix of dimension $\mathrm{N}=1953125$ that we numerically diagonalise by use of our implementation of the Davidson algorithm, to determine the thirty-two lowest-lying eigenstates, at zero applied magnetic field. These thirty-two lowest-lying eigenstates are subsequently used as the basis for the generation of the matrix representation of $\widehat{H}$, by a unitary transformation, in this effective subspace, resulting to an effective Hamiltonian represented by a Hermitian matrix of dimension $\mathrm{N}_{\text {sub }}=32$. This effective subspace was then used to numerically fit $\widehat{H}$, keeping the exchange parameters constant and only using $D_{\mathrm{Mn}(\mathrm{II})}$ as fit parameter, to the field dependence of the magnetisation of $\mathbf{1}$. The magnetisation of $\mathbf{1}$ was fitted by use of the Levenberg-Marquardt algorithm ${ }^{15}$, at 2 K and in the field range 0 to 5 Tesla, (Figure S34). This resulted in the best fit parameter $D_{\mathrm{Mn}(\mathrm{III})}=-3.4 \mathrm{~cm}^{-1}$, for 1.


Figure S34. Reduced magnetization of $\mathbf{1}$ at 2 K and in the field range 0.5 to 5 T . The solid red line corresponds to the best fit curve with $J_{1}=-7.6 \mathrm{~cm}^{-1}, J_{2}=1.8 \mathrm{~cm}^{-1}$ and $J_{3}=-1.6 \mathrm{~cm}^{-1}, D_{\mathrm{Mn}(\text { III })}=-3.4$ $\mathrm{cm}^{-1}$.

Under these conditions, the lowest lying eigenstates of $\widehat{H}$ for $\mathbf{1}$, is a doubly degenerate pair of levels (Figure S35) originating from the doubly degenerate $S=5$ of the isotropic model of $\widehat{H}_{\text {iso }}$ (Figure S33) and corresponding to the $m_{s}= \pm 5$ projections. However, the first excited state corresponds to another $m_{s}= \pm 5$ doublet (Figure S35) of an excited $S=5$ spin state, demonstrating the inapplicability of the total spin state concept for the description of the low temperature magnetic properties of $\mathbf{1}$. The expectation value of the $\hat{S}^{2}$ operator, $\left\langle\hat{S}^{2}\right\rangle$, the associated total spin $S$ and the energy of the corresponding eigenvector of the 32 lowest eigenvectors of $\mathbf{1}$ (Figure S35) are given in Table S9. Notice that $S$ is no more an integer number, as a consequence of $S$-mixing effects induced by the uniaxial anisotropy of $\mathrm{Mn}(\mathrm{III})$.


Figure S35. Eigenstates of the anisotropic spin-Hamiltonian (1), determined by exact numerical diagonalization by use of the Davidson algorithm. In parenthesis is given the degeneracy of each level. The value of a given $S$ corresponds to the ordinate of the center of the corresponding line.

Table S9. Expectation value of the $\hat{S}^{2}$ operator, $\left\langle\hat{S}^{2}\right\rangle$, the associated total spin $S$ and the energy of the corresponding eigenvector of the 32 lowest eigenvectors of $\mathbf{1}$.

| index | $\left\langle\hat{S}^{2}\right\rangle$ | $S$ | $\mathrm{E} / \mathrm{cm}^{-1}$ |
| :---: | :---: | :---: | :---: |
| 1 | 31.84 | 5.16 | -416.73 |
| 2 | 31.84 | 5.16 | -416.73 |
| 3 | 31.84 | 5.16 | -416.73 |
| 4 | 31.84 | 5.16 | -416.73 |
| 5 | 31.37 | 5.12 | -416.54 |
| 6 | 31.37 | 5.12 | -416.54 |
| 7 | 23.10 | 4.33 | -415.12 |
| 8 | 23.10 | 4.33 | -415.12 |
| 9 | 23.10 | 4.33 | -415.12 |
| 10 | 23.10 | 4.33 | -415.12 |
| 11 | 42.25 | 6.02 | -414.37 |
| 12 | 42.25 | 6.02 | -414.37 |
| 13 | 56.38 | 7.03 | -414.37 |
| 14 | 56.38 | 7.03 | -414.37 |
| 15 | 56.38 | 7.03 | -414.16 |
| 16 | 56.38 | 7.03 | -414.16 |
| 17 | 43.66 | 6.13 | -413.29 |
| 18 | 43.66 | 6.13 | -413.29 |
| 19 | 43.66 | 6.13 | -413.29 |
| 20 | 43.66 | 6.13 | -413.29 |
| 21 | 23.06 | 4.33 | -412.36 |
| 22 | 23.06 | 4.33 | -412.36 |
| 23 | 33.60 | 5.32 | -410.70 |
| 24 | 33.60 | 5.32 | -410.70 |
| 25 | 33.60 | 5.32 | -410.70 |
| 26 | 33.60 | 5.32 | -410.70 |
| 27 | 22.37 | 4.26 | -409.31 |
| 28 | 22.37 | 4.26 | -409.31 |
| 29 | 22.37 | 4.26 | -409.31 |
| 30 | 22.37 | 4.26 | -409.31 |
| 31 | 45.19 | 6.24 | -407.86 |
| 32 | 45.19 | 6.24 | -407.86 |
|  |  |  |  |
| 2 |  |  |  |

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