Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of Polyoxometalate Clusters using Carbohydrates as Reducing Agents Leads to Isomer-Selection

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Supplementary Information

Contents

1. Materials

Sodium molybdate dihydrate (≥99.5%), D-(–)-fructose (≥99%), D-(+)-glucose (≥99.5%), sodium dithionite (>99%), and deuterium oxide (99.9 atom % D), and hydrochloric acid (ACS reagent, 37%) were purchased from Sigma Aldrich and used without further purification. Phosphoric acid (85% solution, HPLC grade) was purchased from Honeywell Fluka. Deionised water was prepared in-house and used as the solvent for all experiments. LiChrosolv® Water for chromatography (LC-MS Grade) and Acetonitrile gradient grade for liquid chrom atography LiChrosolv® were used for MS experiments and purchased from Sigma Aldrich.

2. Instrumentation and Methods

Nuclear Magnetic Resonance Spectroscopy

Analysis was performed on a Bruker Ascend Aeon 600 MHz NMR spectrometer equipped with a room temperature BBFO probe head. The ^{31}P-NMR measurements were performed at 300 K in 50:50 D_2O:H_2O for crude reaction mixture aliquots, or in 100% D_2O for purified crystals, with 16 scans taken per experiment. Data was analysed using Bruker TopSpin 3.5 and OriginPro 2016.

Crystallography

A suitable single crystal was selected and mounted onto a rubber loop using Fomblin oil. Single crystal X-ray diffraction data of all samples was recorded on a Bruker Apex II Quasar CCD diffractometer (λ (MoK_α) = 0.71073 Å) at 150 K equipped with a microfocus x-ray source (50kV, 1.0mA). Data collection and reduction were performed using the Apex3 software package and structure solution and refinement were carried out by SHELXT-2018 [1] and SHELXL-2018 [2] using WinGX suite. [3] Corrections for incident and diffracted beam absorption effects were applied using empirical absorption correction. All the Mo atoms, P atoms and the oxygen and nitrogen atoms (except those partially occupied sites) were refined anisotropically. Solvent water molecule sites with partial occupancy were found and included in the structure refinement. The X-ray crystallographic data for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition number CCDC-1903343-1903344. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Inductively coupled plasma optical emission spectrometry (ICP-OES)

Approximately 5 mg of thoroughly dried sample was weighed exactly and dissolved in 1 mL of HPLC grade water followed by dropwise addition of 3 mL of 70% HNO_3 (wt. %, aqueous). The sample was covered with a watch glass and heated to a boil. Once dissolved, the sample was cooled to room

temperature then quantitatively transferred to a clean dry 50.0 mL volumetric flask using HPLC grade water and made up to the mark. A reagent blank was prepared simultaneously under the same conditions. A series of appropriate ICP elemental standards, 1 ppm – 100 ppm, was prepared from commercially available stock solutions. Analysis was performed using an Agilent 5100 SVDV ICP-OES spectrophotometer with peak tracking and Intelliquant enabled.

Thermogravimetric Analysis (TGA)

Analysis was performed on a TA Instruments Q500 Thermogravimetric Analyser under nitrogen flow with a heating rate of 10° C/min from room temperature up to 1000°C.

Ultraviolet-Visible-Near IR Spectroscopy (UV-Vis-NIR)

Samples (8-10 mg) were dissolved in 15 ml deionized water. 500 µL of this solution was diluted to 5.5 mL with deionized water (0.06 mg/mL). The spectra were recorded on a Jasco V-670 spectrophotometer with a scan rate of 100 nm/min from 1200 to 400 nm. For all experiments a background of deionized water was recorded.

Electrospray Ionization Travelling Wave Ion Mobility Separation Mass Spectrometry (ESI-TWIMS-MS)

ESI-TWIMS-MS analyses were performed in the negative polarity mode of a Waters Synapt™ G2 HDMS™ Q-ToF equipped with a standard Waters LockSpray Exact Mass Ionization Source (note that LockSpray was not employed for these measurements) and T-Wave™ Ion Mobility cell. Data was analysed using MassLynx 4.1, DriftScope 2.2 and OriginPro 2016. All data were collected in the negative polarity setting of the mass analyser. Samples were dissolved in a 1:1 mixture of LC-MS grade LiChrosolv® Acetonitrile and Water. Samples were prepared with a concentration of approximately 1 ppm and infused through 127 µm ID PEEK tubing to the ESI source via syringe pump at a rate of 10 µL/min. The emitter tip angle was calibrated for optimal sensitivity of the target analytes. The scan range for initial screening experiments ranged between 300 - 4000 *m/z* with more narrow *m/z* windows (2200 - 3000 *m/z*) and longer scan times (5 s) employed for higher-quality isotope patterns when required. The spectra in this manuscript are the result of several 5 second individual scans combined over a 10-minute infusion. Source and mass analyser parameters in Table S1 were used for all samples.

Table S1. Instrument parameters for ESI-TWIMS-MS analysis.

Parameter	**Setting**
Source Temperature	80 °C
Capillary	2750 V
Sampling Cone (V)	20.0 V
Extraction Cone (V)	4.0 V

Desolvation Temperature (°C)	180 °C
Cone Gas Flow (L/hr)	100 L/hr
Desolvation Gas Flow (L/hr)	1000 L/hr
Mobility Gas	Nitrogen
IMS Wave Velocity (m/s)	1000.0 m/s
IMS Wave Height (V)	40.0 V

Note regarding ESI source settings: Electrospray source settings are extremely important to avoid decomposition of POM clusters. These species are sensitive to high capillary voltage and aggressive desolvation temperatures and these must be kept relatively low to minimize decomposition. Accordingly, in-source fragmentation via collision with the heated bath gas must be kept to a minimum. This is best managed by employing a modest cone voltage rather than adjusting the API gas flow rate which should largely be determined based on the carrier solvent for best results.

CHN Elemental Analysis

An Exeter Analytical CE 440 Elemental Analyser (Exeter Analytical (UK), Ltd; Sir William Lyons Road, Coventry CV4 7EZ, United Kingdom) was used to analyse samples for CHN content. Approximately 2 mg of each sample was weighed exactly using an electrical Ultra microbalance (Mettler Toledo UMX2, Mettler-Toledo Ltd., 64 Boston Road, Beaumont Leys, Leicester, LE4 1AW). Each sample was weighed in duplicates into a tin capsule and sealed before being introduced to the autosampler. The instrument was calibrated by using Acetanilide as a calibrant. All samples were analysed in duplicates. After every two samples, the instrument was recalibrated and checked for accuracy and stability.

Cyclic Voltammetry and Bulk Electrolysis

Electrochemical measurements were performed using a CH Instruments CH 760D potentiostat. Bulk electrolysis was performed in an H-Cell separated by Nafion membrane (Nafion 110). Carbon felt was used as working electrode and Pt wire was used as the counter electrode. The bulk electrolysis potential was set as +0.7V vs. Ag/AgCl (3.25M KCl) until the electrolysis current reached 0.1%. Cyclic voltammetry was performed with a glassy carbon electrode as the working electrode, $Hg/HgSO_4$ (1M H_2SO_4) as reference electrode and carbon felt as a counter electrode.

Cerimetric Redox Titration

Cerimetric redox titration was carried out with 0.015M $Ce(NH_4)_2(NO_3)_6$ in 0.5M H_2SO_4 as the titrant and compound **1** (20 mg) in 20 ml H_2SO_4 (0.5M) as the analyte. The redox electrode potential was measured with a potentiometer Mettler Toledo MP220 and recorded during titration.

3. Synthetic Procedures

Synthesis of γ-{P_2Mo_{18}}: $(NH_4)_4H_8[\gamma\text{-}P_2Mo_{18}O_{62}]\cdot 19(H_2O)$

Sodium molybdate dihydrate (5.00 g, 20.7 mmol) and fructose (500 mg, 0.13 eq.) were added to a 100 mL round bottom flask with (22.5 mL) deionized water and stirred until dissolved. To this solution, 0.75 mL of 85% (wt. %, aqueous) H_3PO_4 (11.0 mmol, 0.53 eq.) was added dropwise followed by addition of 4.0 mL of concentrated HCl. The mixture was refluxed overnight during which the colour of the solution changed to dark blue. After 24 hours, the solution was cooled to room temperature and transferred to a 100 mL Erlenmeyer flask. To the cooled solution, 2.4 g of NH_4Cl was added and stirred for 1 hour. Afterwards, the solution was stored at 5°C for 4-5 hours until dark blue, block-shaped crystals start to form. These crystals were obtained via filtration over a Buchner funnel and washed with the mother liquor and 20 mL of H_2O:i-PrOH (1:15). The crystals were air-dried and placed in a desiccator overnight. Yield: 27% (1.35 g, 0.42 mmol) based on $Na_2MoO_4\cdot 2(H_2O)$. TGA weight loss from compound, $(NH_4)_4H_8[\gamma\text{-}P_2Mo_{18}O_{62}]\cdot 19(H_2O)$, observed 8.9% (calcd. 10.7%). Elemental analysis for $(NH_4)_4H_8[\gamma\text{-}P_2Mo_{18}O_{62}]\cdot 19(H_2O)$ (3203.3 $g\cdot mol^{-1}$): calcd. (%) Mo 53.92, Na 0, P 1.93, N 1.75, H 1.95, found: Mo 53.88, Na 0.08, P 1.66, N 1.70, H 1.84.

Synthesis of α-{P_2Mo_{18}}: $(NH_4)_6[\alpha\text{-}P_2Mo_{18}O_{62}]\cdot 14(H_2O)$

The same conditions as in the general procedure for γ-{P_2Mo_{18}} were used to prepare the alpha isomer of the Molybdenum Dawson, $(NH_4)_6[\alpha\text{-}P_2Mo_{18}O_{62}]\cdot 14(H_2O)$, albeit without reducing agent incorporation. Sodium molybdate dihydrate (5.00 g, 20.7 mmol) was added to a 100 mL round bottom flask with (22.5 mL) deionized water and stirred until dissolved. To this solution, 0.75 mL of 85% (wt. %, aqueous) H_3PO_4 (11.0 mmol, 0.53 eq.) was added dropwise followed by dropwise addition of 4.0 mL of concentrated HCl. After reflux the solution was cooled to room temperature and 5.0 g NH_4Cl was added. The precipitate which formed was filtered and dried via vacuum filtration. Afterwards, the yellow crystalline solid was dissolved in a 25 mL Erlenmeyer flask with 2.0 mL water. Following 15 minutes of stirring, undissolved yellow precipitate was removed by filtration and discarded. The clear filtrate was kept and to this 150 mg of NH_4Cl was added with stirring and this solution was stored at 5°C. Yellow needle-like crystals of high purity formed after 2 days and were collected by filtration and washed thoroughly with 20 mL of H_2O:i-PrOH (1:15). Crystals must be collected within 2 days of crystallization, otherwise a green/yellow precipitate is formed and reduces yield. This type of compound has been previously characterized in the literature. [4–6] Yield: 19% (0.55 g, 0.175 mmol) based on $Na_2MoO_4\cdot 2(H_2O)$. Elemental analysis for $(NH_4)_6[\alpha\text{-}P_2Mo_{18}O_{62}]\cdot 19(H_2O)$ (3134.33 $g\cdot mol^{-1}$): calcd. (%) Mo 54.98, Na 0, P 1.97, N 2.68, H 1.67, found: Mo 54.22, Na 0.23, P 2.08, N 2.78, H 1.34.

4. Supplementary Data

^{31}P-NMR (Nuclear Magnetic Resonance) Spectroscopy

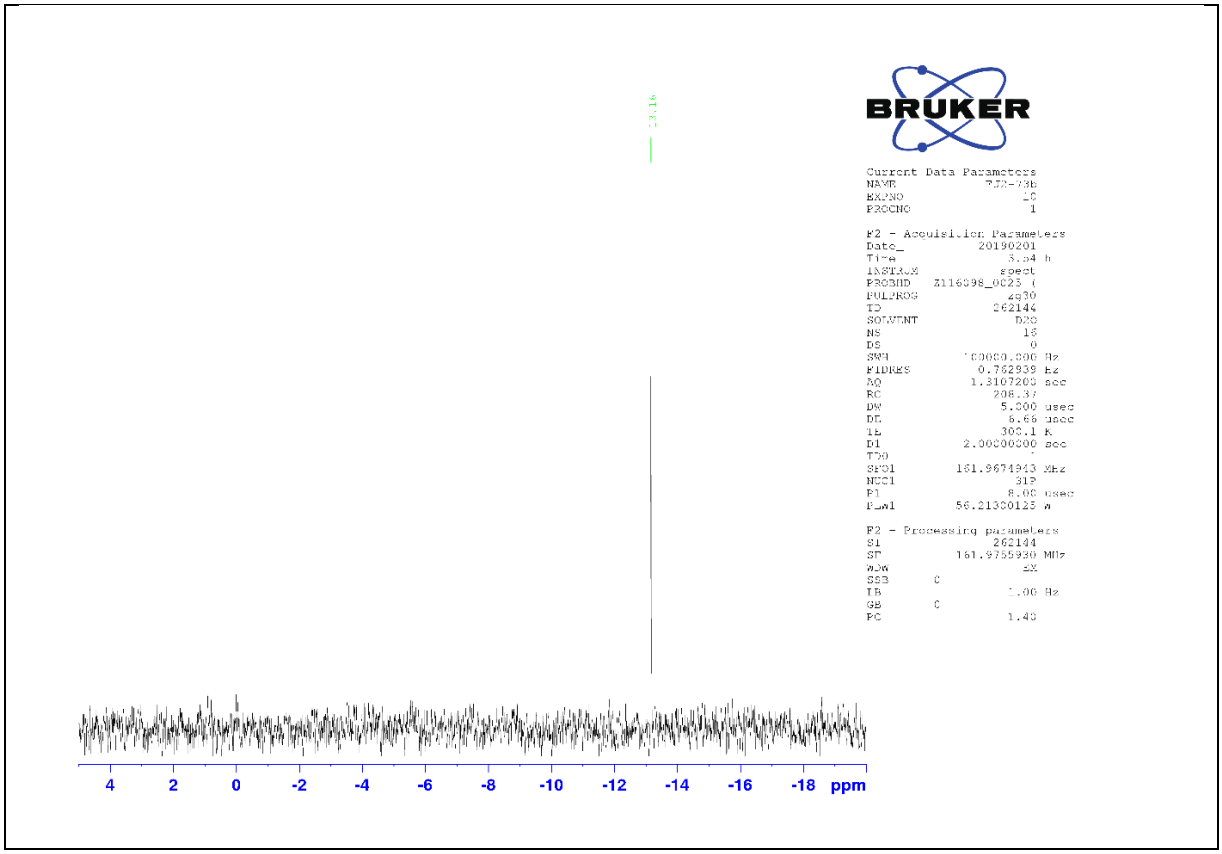

Fig. S1 ^{31}P-NMR in D_2O of isolated crystals of $(NH_4)_4H_8[\gamma\text{-}P_2Mo_{18}O_{62}]\cdot 19(H_2O)$. Crystals were isolated according to synthetic procedure detailed in supporting information synthetic procedures section.

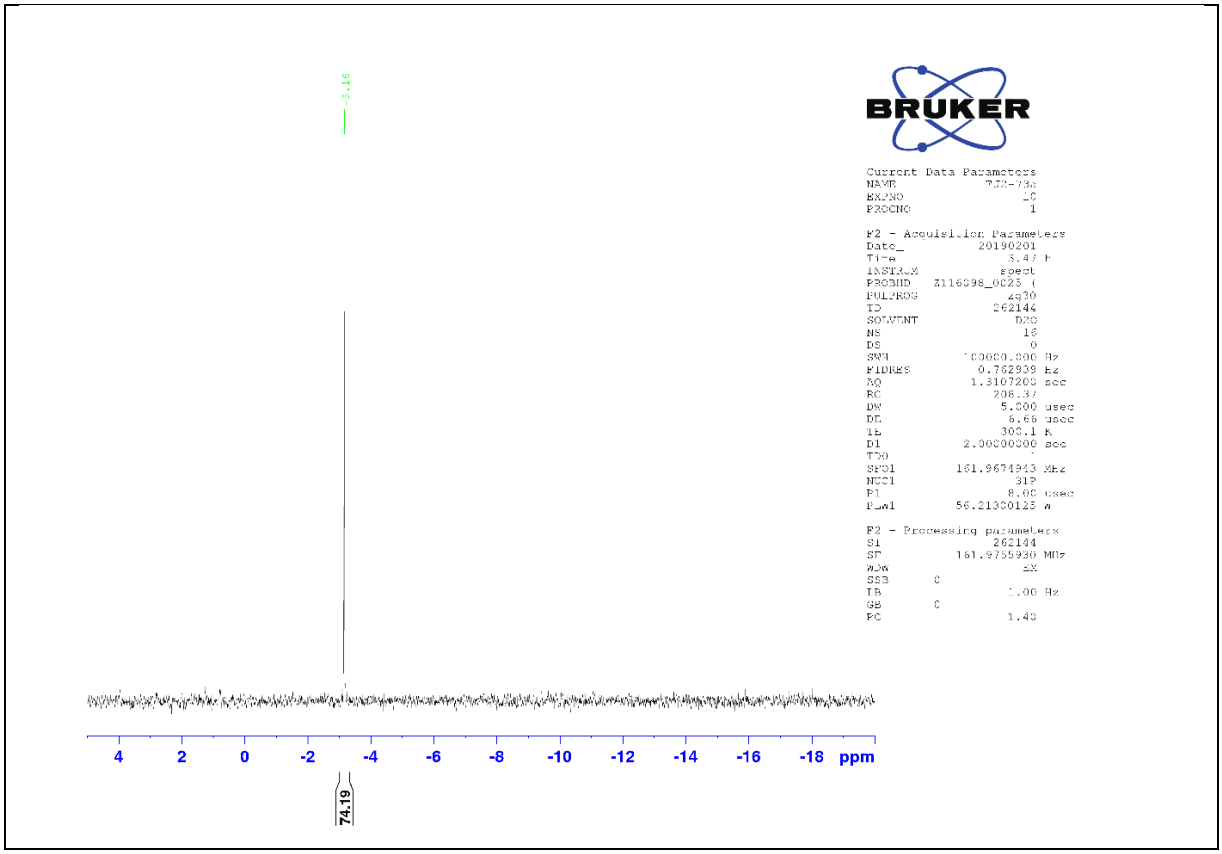

Fig. S2 ^{31}P-NMR in D_2O of isolated crystals of $(NH_4)_6[\alpha\text{-}P_2Mo_{18}O_{62}]\cdot 14(H_2O)$. Crystals were isolated according to synthetic procedure for detailed in supporting information synthetic procedures section.

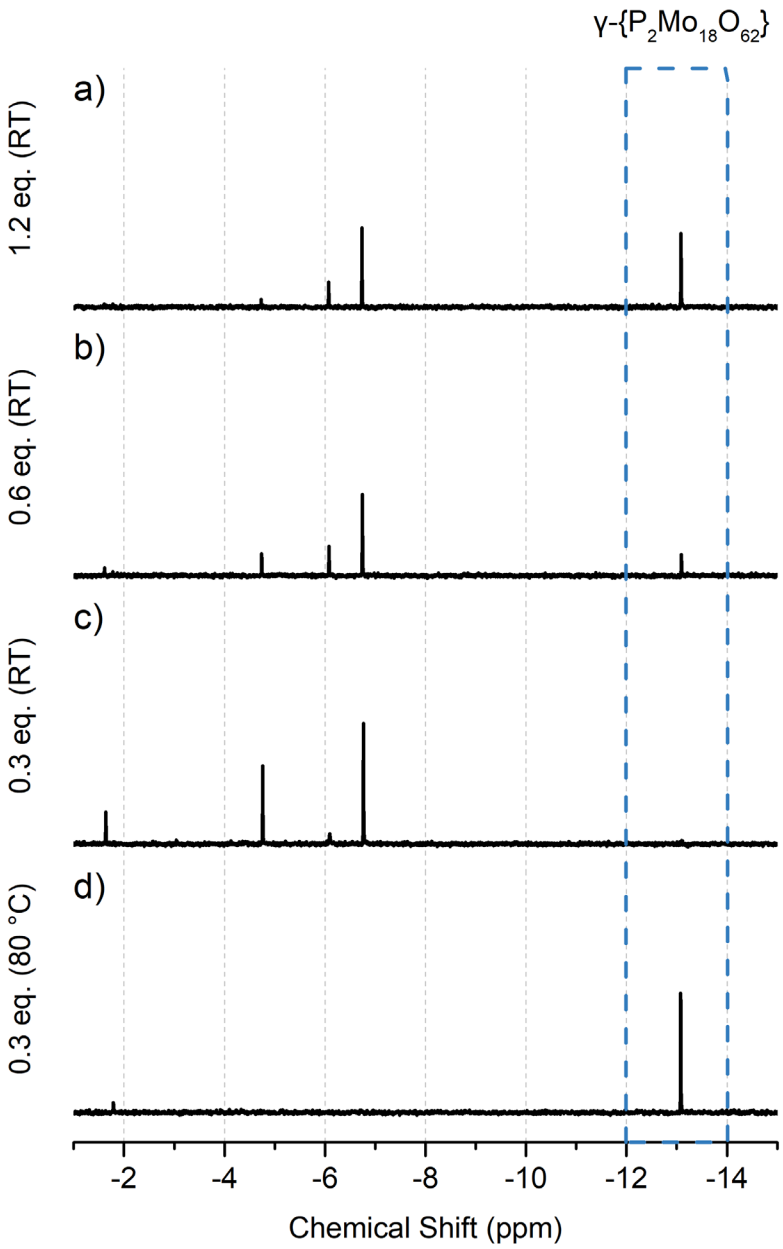

Fig. S3 ^{31}P-NMR in 50% D_2O of sodium molybdate (100 mg/mL), 1 eq. H_3PO_4, and fructose at pH 1 demonstrating reduction and γ-{P_2Mo_{18}} formation. Spectra **a** to **c**, are aliquots of reaction mixtures containing 1.2, 0.6, and 0.3 equivalents of fructose respectively and were performed at room temperature (20 °C). Spectrum **d** is a reaction mixture identical to **c** though heated for 24 hrs at 80 °C.

ESI-TWIMS-MS (Electrospray Ionization Travelling Wave Ion Mobility Separation Mass Spectrometry)

Note regarding ESI-TWIMS-MS data

In the following spectra, multiple ions of {P_2Mo_{18}} were separated and detected using electrospray ionization mass spectrometry and travelling wave ion mobility separation. Spectra of the purified

compounds demonstrate good overlap with simulated isotope patterns of the $\{P_2Mo_{18}\}$ cluster ions which were generated using ChemCalc (simulated data not shown). [8] The Wells-Dawson cluster anions are detectable near *m/z* 2800 in standard full scan mode of the ESI-MS. The full spectra reported below generally have broad continuous peak envelopes which is quite typical of ESI-MS spectra of POMs. This is attributed to a large mixture of counter ions (Na^+, H^+, NH_4^+), neutral solvent molecules (H_2O, MeCN), and aggregation (with self-aggregation evident in IMS separated species of similar m/z but with *z* greater than –1. The central values of each peak were determined with the peak analyser function of OriginPro 2016 without additional post-processing.

ESI-TWIMS-MS of γ-Dawson isomer γ-$\{P_2Mo_{18}\}$

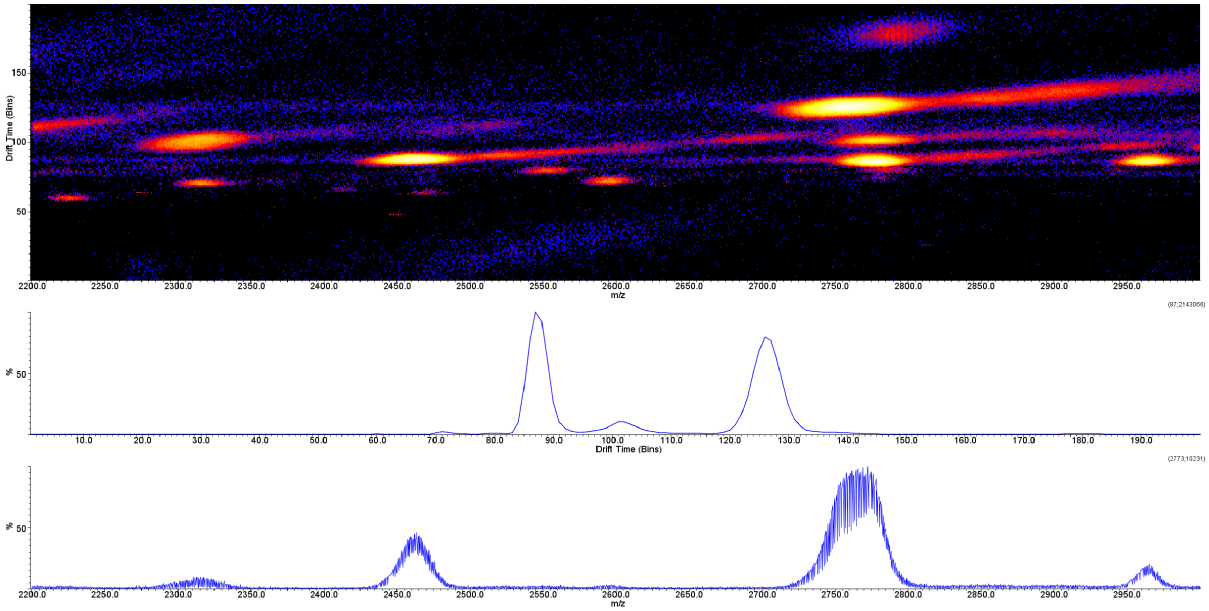

Fig. S4 Top to bottom: 2D TWIMS mobility plot, mobilogram, and mass spectrum of isolated crystals of γ-$\{P_2Mo_{18}\}$. The wide signals demonstrate multiple charge states (self-association), mixed cationization, and neutral aggregation.

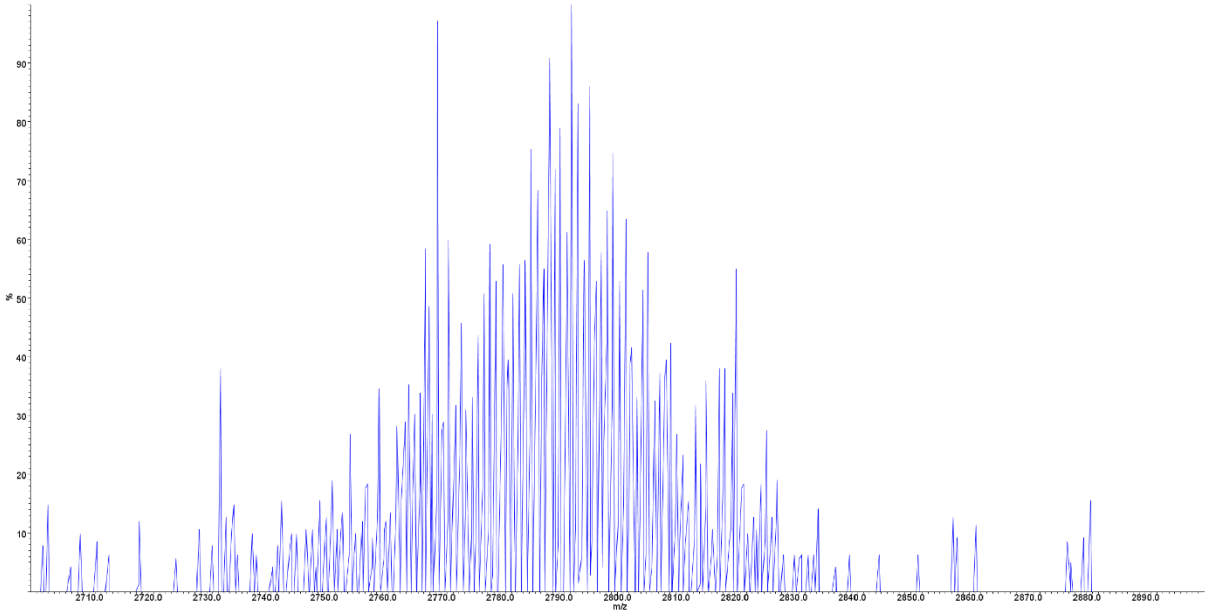

Fig S5 Drift-time selected mass spectrum of γ-{P_2Mo_{18}} demonstrating presence of singly-charged [{$P_2Mo_{18}O_{62}$}H_{11}]$^-$ anion (calcd. *m/z* 2791.9, Obs. *m/z* 2792.2) selected with a drift time (t_d) of 19.63 ms.

ESI-TWIMS-MS spectra of α-Dawson isomer α-{P_2Mo_{18}}

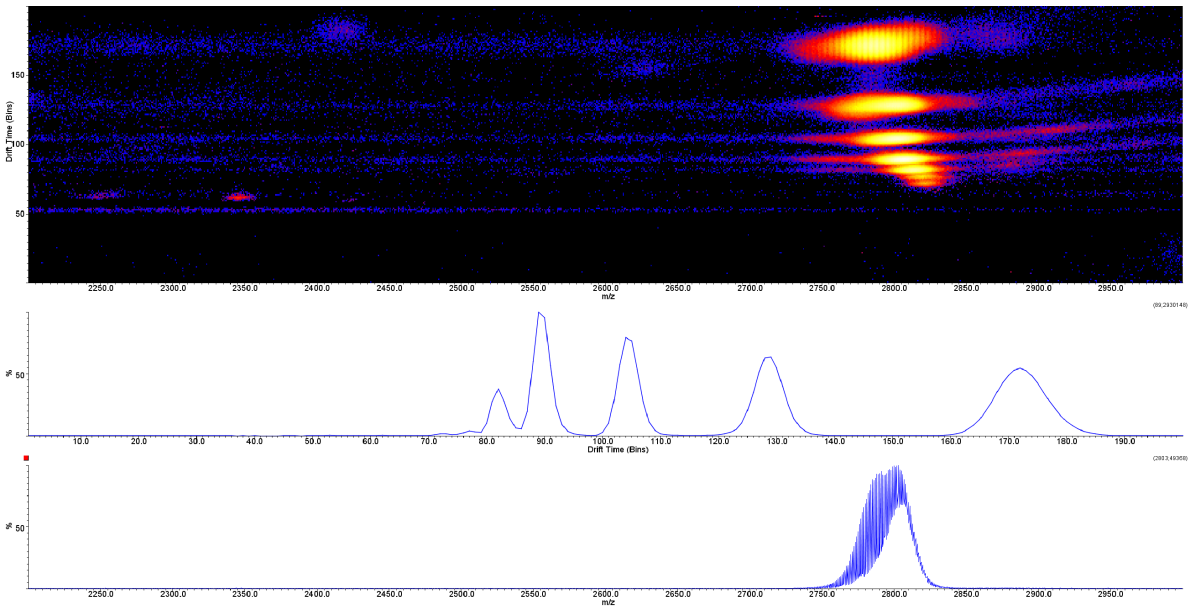

Fig. S6 Top to bottom: 2D TWIMS mobility plot, mobilogram, and mass spectrum of isolated α-{P_2Mo_{18}} crystals. The wide signal demonstrates multiple charge states (self-association), mixed cationization, and neutral aggregation.

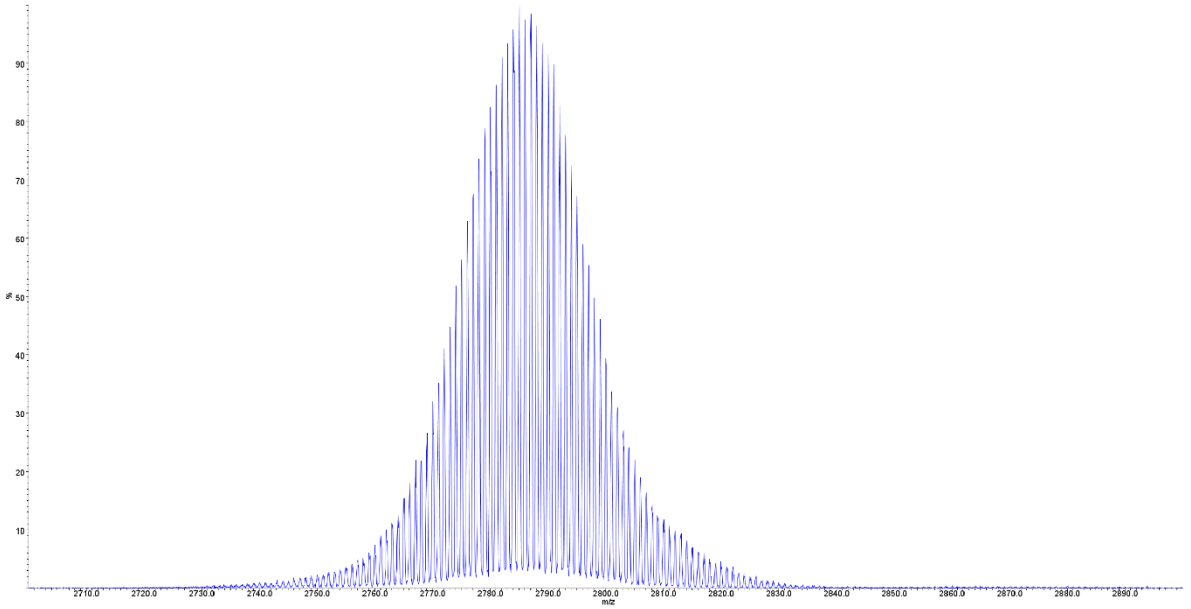

Fig S7. Drift-time selected mass spectrum of of α-{P_2Mo_{18}} demonstrating presence of singly-charged [{$P_2Mo_{18}O_{62}$}H_5]$^-$ anion (calcd. *m/z* 2785.8, Obs. *m/z* 2786.1) selected with a drift time (t_d) of 18.85 ms.

UV-VIS-NIR Spectroscopy

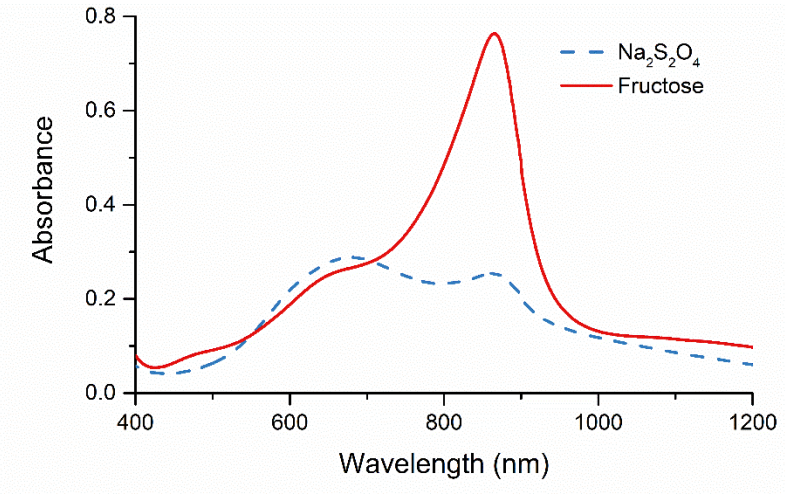

Fig. S8 UV-vis-NIR spectra of reaction products following treatment with fructose or sodium dithionite. Reactions carried out with $Na_2MoO_4{\cdot}2(H_2O)$ with 1 eq. of H_3PO_4 at pH 1 (4 M HCl) and treated with either with 0.15 eq. D-(–)-fructose (red) or 0.15 eq. $Na_2S_2O_4$ (blue) stirred overnight at 20°C. Solids were obtained from vacuum dried reaction mixture aliquots. The strong absorbance at 866 nm is indicative of the intense blue colour of the presence of Mo^V following reduction.

Cerimetric Titration

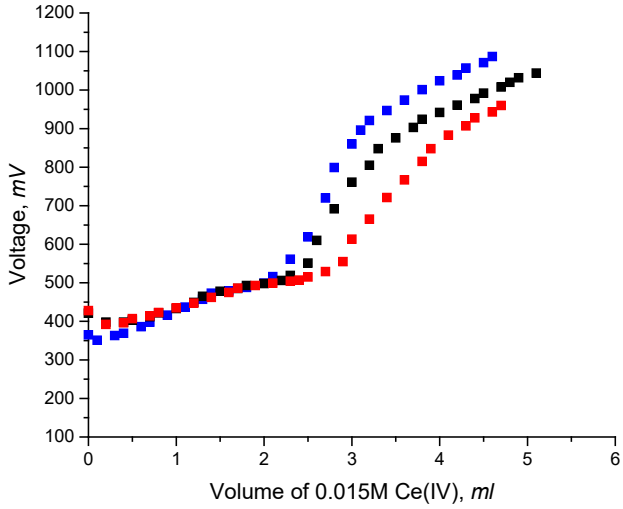

Fig. S9 Triplicate cerimetric redox titrations of γ-{P_2Mo_{18}} samples. Samples of γ-{P_2Mo_{18}} are completely oxidized following the addition of 2.5 mL (0.0375 mmol) to 3 mL (0.045 mmol) of Ce(IV) (0.015M) titrant corresponding to 6 - 8 reduced electrons in the sample. Note that the colour of solution changed from dark blue to yellow following titration.

Bulk Electrolysis

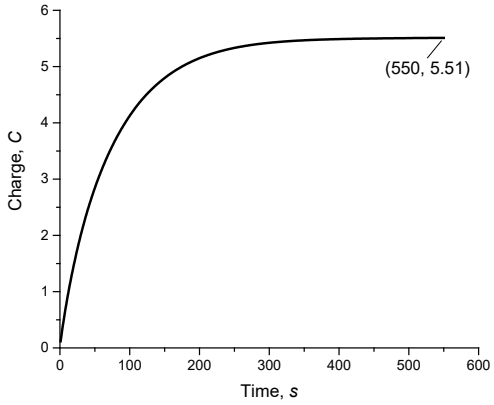

Fig. S10 Bulk electrolysis of 50 mg (0.31 mM) of isolated γ-{P_2Mo_{18}} crystals in 30.0 mL of 0.5 M H_2SO_4 following sparging with argon gas. Measurement ends at 550° C showing a 5.51 C increase which suggests approximately 6 reduced electrons present in the γ-{P_2Mo_{18}} cluster.

Cyclic Voltammetry

The redox chemistry of γ-{P_2Mo_{18}} was characterized with cyclic voltammetry. The open circuit voltage of the solution was –0.1 V. Fewer electrons in the cluster (by way of oxidation) will increase the open circuit voltage. Scanning below –0.1 volt (Fig. SX, red/black traces) resulted in additional redox processes, which indicate γ-{P_2Mo_{18}} can be further reduced.

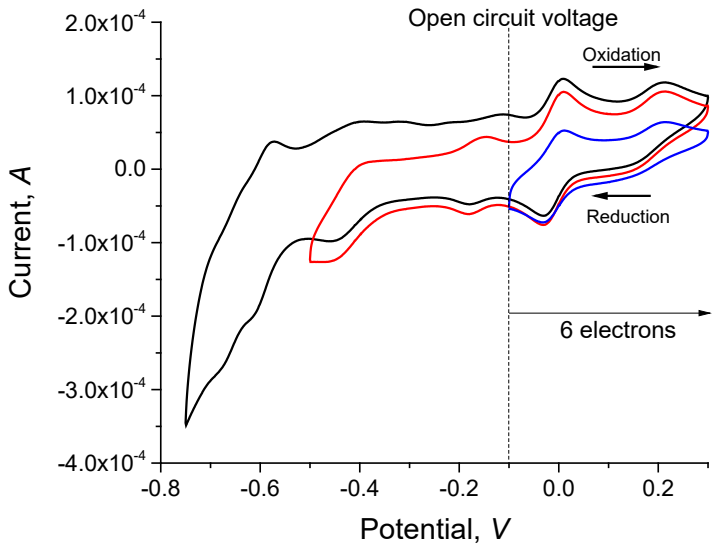

Fig. S11 Cyclic voltammetry of γ-{P_2Mo_{18}} (2 mM in 0.5M H_2SO_4) with a scan rate of 100 mV/s. **Black**: Scan between -0.7 and 0.3 volt. **Red**: Scan between -0.5 and 0.3 Volt. **Blue**: Scan between -0.1 and 0.3 Volt. (Reference electrode = Hg/Hg (SO_4) in 1M H_2SO_4. Counter electrode = carbon felt. Working electrode = glassy carbon.)

Single-crystal X-ray Diffraction (XRD) Data

Table S3. Crystal data and structure refinement details for $\{P_2Mo_{18}O_{62}\}$ isomers isolated in this work.†

Identification Code	**α-$\{P_2Mo_{18}\}$**	**γ-$\{P_2Mo_{18}\}$**
Isomer:	α-isomer	γ-isomer
Empirical formula	H52 Mo18 N6 O76 P2	H62 Mo18 N4 O81 P2
Formula weight	3134.33	3203.3
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	*P* -1	*P* -1
Unit cell dimensions	a = 12.7233(9) Å α = 101.443(4)°.	a = 13.7650(8) Å α = 82.099 (3)°.
	b = 14.4286(10) Å β = 98.500(4)°.	b = 15.5376(9) Å β = 87.537 (3)°.
	c = 19.8131(14) Å γ = 114.254(4)°.	c = 17.7625(10) Å γ = 83.277 (3)°.
Volume	3141.5(4) Å3	3735.6(4) Å3
Z	2	2
Density (calculated)	3.321 Mg/m3	2.889 Mg/m3
Absorption coefficient	3.657 mm-1	3.082 mm-1
F(000)	2976	3048
Crystal size	0.133 x 0.069 x 0.027 mm3	0.100 x 0.100 x 0.050 mm3
Theta range for data collection	1.616 to 25.713°.	1.490 to 26.000°.
Index ranges	-15<=h<=15, -14<=k<=17, -24<=l<=22	-16<=h<=16, -17<=k<=19, -21<=l<=21
Reflections collected	45024	56809
Independent reflections	11933 [R(int) = 0.0592]	14635 [R(int) = 0.0394]
Completeness to θ = 25.242°	99.90%	99.9%
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	11933 / 0 / 903	14635 / 0 / 988
Goodness-of-fit on F2	1.036	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0841	R1 = 0.0353, wR2 = 0.0860
R indices (all data)	R1 = 0.0520, wR2 = 0.0932	R1 = 0.0465, wR2 = 0.0949
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.70 and -1.05 e.Å-3	1.38 and -1.11 e.Å-3

†The X-ray crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, under deposition number CCDC-1903343-1903344.

Bond Valence Sum calculations[9]

Bond Valence Sum Analysis Report for $(NH_4)_4H_8[\gamma\text{-}P_2Mo_{18}O_{62}]\cdot 19(H_2O)$

Bond	R	EXP((R0-R)/B)	Angles
MO1 -O3	1.917	.918	MO-O
MO1 -O4	1.888	1.006	MO-O 156.6
MO1 -O5	1.873	1.056	MO-O 92.8 91.3
MO1 -O22	2.380	.210	MO-O 73.1 84.1 87.3
MO1 -O28	2.058	.586	MO-O 83.3 86.4 163.9 76.6
MO1 -O40	1.684	1.927	MO-O 99.9 102.0 100.2 170.2 95.9
***Valence sum for MO1	5.702	.000	(6 Bonds used)
MO2 -O1	1.874	1.052	MO-O
MO2 -O17	1.878	1.039	MO-O 91.9
MO2 -O30	2.386	.206	MO-O 87.1 83.8
MO2 -O32	1.922	.903	MO-O 92.4 156.2 73.0
MO2 -O34	2.062	.578	MO-O 163.8 86.3 76.7 83.1
MO2 -O42	1.679	1.958	MO-O 100.6 102.1 170.0 100.1 95.5
***Valence sum for MO2	5.737	.000	(6 Bonds used)
MO3 -O1	1.878	1.039	MO-O
MO3 -O16	2.047	.607	MO-O 164.0
MO3 -O18	1.936	.864	MO-O 92.0 82.9
MO3 -O27	1.874	1.052	MO-O 91.7 87.3 157.1
MO3 -O38	2.382	.209	MO-O 86.5 77.5 73.2 84.5
MO3 -O46	1.680	1.952	MO-O 100.1 95.7 99.2 102.4 170.2
***Valence sum for MO3	5.722	.000	(6 Bonds used)
MO4 -O2	1.867	1.076	MO-O
MO4 -O4	1.862	1.093	MO-O 92.4
MO4 -O19	2.373	.215	MO-O 87.3 83.4
MO4 -O21	1.905	.953	MO-O 91.7 156.7 73.9
MO4 -O23	2.132	.463	MO-O 166.1 84.6 78.9 85.9
MO4 -O52	1.686	1.915	MO-O 100.2 101.3 170.9 100.5 93.7
***Valence sum for MO4	5.715	.000	(6 Bonds used)
MO5 -O5	1.872	1.059	MO-O
MO5 -O7	1.881	1.029	MO-O 91.6
MO5 -O10	1.921	.906	MO-O 92.1 156.7
MO5 -O14	2.368	.218	MO-O 87.6 84.2 73.0
MO5 -O37	2.054	.593	MO-O 165.5 87.7 83.1 77.9
MO5 -O61	1.676	1.977	MO-O 101.1 101.9 99.9 169.1 93.2
***Valence sum for MO5	5.782	.000	(6 Bonds used)
MO6 -O8	1.873	1.056	MO-O
MO6 -O9	1.884	1.019	MO-O 91.9
MO6 -O11	1.684	1.927	MO-O 100.4 102.1
MO6 -O13	1.938	.858	MO-O 91.5 157.6 99.1
MO6 -O20	2.050	.601	MO-O 164.4 87.6 94.9 83.2
MO6 -O39	2.362	.222	MO-O 86.8 84.4 170.0 73.6 77.6
***Valence sum for MO6	5.684	.000	(6 Bonds used)

MO7 -O3 1.919 .912 MO-O
MO7 -O22 2.363 .222 MO-O 73.5
MO7 -O27 1.876 1.046 MO-O 157.4 84.3
MO7 -O31 1.883 1.023 MO-O 91.6 86.7 91.5
MO7 -O36 2.107 .501 MO-O 86.3 79.4 85.3 165.9
MO7 -O49 1.676 1.977 MO-O 100.0 170.8 101.5 100.2 93.9
***Valence sum for MO7 5.680 .000 (6 Bonds used)

MO8 -O2 1.881 1.029 MO-O
MO8 -O6 2.117 .485 MO-O 166.7
MO8 -O7 1.870 1.066 MO-O 91.6 84.9
MO8 -O13 1.917 .918 MO-O 92.3 86.1 157.2
MO8 -O24 1.673 1.996 MO-O 100.1 93.1 101.6 99.8
MO8 -O39 2.360 .224 MO-O 87.8 79.1 83.7 74.0 170.3
***Valence sum for MO8 5.717 .000 (6 Bonds used)

MO9 -O12 1.868 1.073 MO-O
MO9 -O15 1.862 1.093 MO-O 92.6
MO9 -O18 1.929 .883 MO-O 92.4 156.9
MO9 -O38 2.352 .230 MO-O 88.0 83.6 74.0
MO9 -O43 2.120 .481 MO-O 167.0 85.5 84.6 79.0
MO9 -O54 1.686 1.915 MO-O 100.2 102.0 99.3 169.8 92.9
***Valence sum for MO9 5.674 .000 (6 Bonds used)

MO10-O9 1.866 1.079 MO-O
MO10-O12 1.881 1.029 MO-O 91.6
MO10-O30 2.347 .233 MO-O 83.8 87.4
MO10-O32 1.912 .932 MO-O 157.4 91.8 74.1
MO10-O35 1.681 1.946 MO-O 101.5 100.0 170.7 99.8
MO10-O41 2.109 .498 MO-O 85.8 166.8 79.5 85.8 93.2
***Valence sum for MO10 5.718 .000 (6 Bonds used)

MO11-O25 1.685 1.921 MO-O
MO11-O34 1.777 1.433 MO-O 105.2
MO11-O41 2.050 .601 MO-O 99.1 86.1
MO11-O45 2.385 .207 MO-O 167.2 87.5 82.8
MO11-O48 2.023 .655 MO-O 95.5 156.7 80.3 72.2
MO11-O57 1.859 1.104 MO-O 101.2 98.8 157.1 75.1 87.2
***Valence sum for MO11 5.920 .000 (6 Bonds used)

MO12-O8 1.868 1.073 MO-O
MO12-O15 1.878 1.039 MO-O 91.1
MO12-O19 2.354 .228 MO-O 87.9 84.3
MO12-O21 1.934 .869 MO-O 93.0 157.5 73.9
MO12-O26 2.050 .601 MO-O 165.4 87.2 77.5 83.3
MO12-O29 1.691 1.885 MO-O 99.8 102.3 169.7 98.7 94.7
***Valence sum for MO12 5.694 .000 (6 Bonds used)

MO13-O6 2.035 .630 MO-O
MO13-O20 1.787 1.388 MO-O 86.4
MO13-O33 1.694 1.867 MO-O 99.6 105.1
MO13-O45 2.392 .202 MO-O 82.8 87.5 167.3
MO13-O48 1.859 1.104 MO-O 156.6 98.4 101.1 74.7

MO13-O55 2.013 .676 MO-O 80.6 157.3 95.5 72.5 86.8
***Valence sum for MO13 5.867 .000 (6 Bonds used)

MO14-O10 1.906 .950 MO-O
MO14-O14 2.358 .225 MO-O 73.5
MO14-O17 1.873 1.056 MO-O 156.7 83.9
MO14-O31 1.863 1.090 MO-O 93.0 88.2 92.0
MO14-O50 1.684 1.927 MO-O 99.9 169.6 101.6 100.3
MO14-O56 2.145 .444 MO-O 84.6 79.6 85.6 167.8 91.9
***Valence sum for MO14 5.692 .000 (6 Bonds used)

MO15-O37 1.787 1.388 MO-O
MO15-O44 1.693 1.873 MO-O 103.8
MO15-O45 2.428 .180 MO-O 86.7 169.3
MO15-O55 1.852 1.129 MO-O 98.4 101.6 74.3
MO15-O56 2.060 .582 MO-O 85.9 100.2 82.5 156.0
MO15-O57 2.005 .693 MO-O 155.3 98.4 71.7 87.5 79.6
***Valence sum for MO15 5.845 .000 (6 Bonds used)

MO16-O23 2.058 .586 MO-O
MO16-O26 1.789 1.379 MO-O 86.0
MO16-O47 2.020 .661 MO-O 80.0 156.5
MO16-O53 2.405 .194 MO-O 81.8 86.4 73.0
MO16-O59 1.686 1.915 MO-O 101.0 103.0 98.3 170.3
MO16-O60 1.855 1.118 MO-O 155.9 98.2 87.5 74.8 101.1
***Valence sum for MO16 5.853 .000 (6 Bonds used)

MO17-O28 1.789 1.379 MO-O
MO17-O36 2.044 .612 MO-O 86.0
MO17-O47 1.871 1.062 MO-O 98.7 156.3
MO17-O51 2.008 .687 MO-O 155.8 80.3 86.6
MO17-O53 2.404 .195 MO-O 85.9 81.8 75.5 72.5
MO17-O58 1.688 1.903 MO-O 103.8 99.7 101.7 98.2 170.3
***Valence sum for MO17 5.838 .000 (6 Bonds used)

MO18-O16 1.798 1.340 MO-O
MO18-O43 2.056 .589 MO-O 85.6
MO18-O51 1.860 1.100 MO-O 98.5 156.1
MO18-O53 2.407 .193 MO-O 86.8 82.0 74.8
MO18-O60 2.001 .702 MO-O 156.1 80.0 87.5 72.4
MO18-O62 1.687 1.909 MO-O 104.2 100.5 101.3 168.8 97.1
***Valence sum for MO18 5.834 .000 (6 Bonds used)

P1 -O19 1.535 1.258 P -O
P1 -O22 1.533 1.265 P -O 110.9
P1 -O38 1.537 1.251 P -O 111.5 111.2
P1 -O53 1.584 1.102 P -O 107.7 107.7 107.6
***Valence sum for P1 4.877 .000 (4 Bonds used)

P2 -O14 1.530 1.275 P -O
P2 -O30 1.537 1.251 P -O 111.7
P2 -O39 1.539 1.245 P -O 111.4 111.4
P2 -O45 1.586 1.096 P -O 107.2 107.5 107.4
***Valence sum for P2 4.868 .000 (4 Bonds used)

O1 -MO2 1.874 1.052 MO-O
O1 -MO3 1.878 1.039 MO-O 173.8
***Valence sum for O1 2.091 .000 (2 Bonds used)

O2 -MO4 1.867 1.076 MO-O
O2 -MO8 1.881 1.029 MO-O 172.5
***Valence sum for O2 2.105 .000 (2 Bonds used)

O3 -MO1 1.917 .918 MO-O
O3 -MO7 1.919 .912 MO-O 122.9
***Valence sum for O3 1.829 .000 (2 Bonds used)

O4 -MO1 1.888 1.006 MO-O
O4 -MO4 1.862 1.093 MO-O 163.5
***Valence sum for O4 2.100 .000 (2 Bonds used)

O5 -MO1 1.873 1.056 MO-O
O5 -MO5 1.872 1.059 MO-O 173.3
***Valence sum for O5 2.115 .000 (2 Bonds used)

O6 -MO8 2.117 .485 MO-O
O6 -MO13 2.035 .630 MO-O 138.0
***Valence sum for O6 1.115 .000 (2 Bonds used)

O7 -MO5 1.881 1.029 MO-O
O7 -MO8 1.870 1.066 MO-O 163.1
***Valence sum for O7 2.095 .000 (2 Bonds used)

O8 -MO6 1.873 1.056 MO-O
O8 -MO12 1.868 1.073 MO-O 173.1
***Valence sum for O8 2.128 .000 (2 Bonds used)

O9 -MO6 1.884 1.019 MO-O
O9 -MO10 1.866 1.079 MO-O 162.8
***Valence sum for O9 2.099 .000 (2 Bonds used)

O10 -MO5 1.921 .906 MO-O
O10 -MO14 1.906 .950 MO-O 122.9
***Valence sum for O10 1.856 .000 (2 Bonds used)

O11 -MO6 1.684 1.927 MO-O
***Valence sum for O11 1.927 .000 (1 Bonds used)

O12 -MO9 1.868 1.073 MO-O
O12 -MO10 1.881 1.029 MO-O 171.9
***Valence sum for O12 2.102 .000 (2 Bonds used)

O13 -MO6 1.938 .858 MO-O
O13 -MO8 1.917 .918 MO-O 121.5
***Valence sum for O13 1.776 .000 (2 Bonds used)

O14 -MO5 2.368 .218 MO-O
O14 -MO14 2.358 .225 MO-O 90.7

O14 -P2 1.530 1.275 P -O 129.2 130.2
***Valence sum for O14 1.719 .000 (3 Bonds used)

O15 -MO9 1.862 1.093 MO-O
O15 -MO12 1.878 1.039 MO-O 163.2
***Valence sum for O15 2.132 .000 (2 Bonds used)

O16 -MO3 2.047 .607 MO-O
O16 -MO18 1.798 1.340 MO-O 151.6
***Valence sum for O16 1.947 .000 (2 Bonds used)

O17 -MO2 1.878 1.039 MO-O
O17 -MO14 1.873 1.056 MO-O 163.5
***Valence sum for O17 2.095 .000 (2 Bonds used)

O18 -MO3 1.936 .864 MO-O
O18 -MO9 1.929 .883 MO-O 121.8
***Valence sum for O18 1.747 .000 (2 Bonds used)

O19 -MO4 2.373 .215 MO-O
O19 -MO12 2.354 .228 MO-O 90.4
O19 -P1 1.535 1.258 P -O 130.2 128.9
***Valence sum for O19 1.701 .000 (3 Bonds used)

O20 -MO6 2.050 .601 MO-O
O20 -MO13 1.787 1.388 MO-O 151.0
***Valence sum for O20 1.989 .000 (2 Bonds used)

O21 -MO4 1.905 .953 MO-O
O21 -MO12 1.934 .869 MO-O 121.8
***Valence sum for O21 1.823 .000 (2 Bonds used)

O22 -MO1 2.380 .210 MO-O
O22 -MO7 2.363 .222 MO-O 90.5
O22 -P1 1.533 1.265 P -O 129.0 129.6
***Valence sum for O22 1.697 .000 (3 Bonds used)

O23 -MO4 2.132 .463 MO-O
O23 -MO16 2.058 .586 MO-O 137.8
***Valence sum for O23 1.048 .000 (2 Bonds used)

O24 -MO8 1.673 1.996 MO-O
***Valence sum for O24 1.996 .000 (1 Bonds used)

O25 -MO11 1.685 1.921 MO-O
***Valence sum for O25 1.921 .000 (1 Bonds used)

O26 -MO12 2.050 .601 MO-O
O26 -MO16 1.789 1.379 MO-O 151.9
***Valence sum for O26 1.980 .000 (2 Bonds used)

O27 -MO3 1.874 1.052 MO-O
O27 -MO7 1.876 1.046 MO-O 162.3
***Valence sum for O27 2.098 .000 (2 Bonds used)

O28 -MO1 2.058 .586 MO-O
O28 -MO17 1.789 1.379 MO-O 152.6
***Valence sum for O28 1.965 .000 (2 Bonds used)

O29 -MO12 1.691 1.885 MO-O
***Valence sum for O29 1.885 .000 (1 Bonds used)

O30 -MO2 2.386 .206 MO-O
O30 -MO10 2.347 .233 MO-O 90.4
O30 -P2 1.537 1.251 P -O 129.0 130.3
***Valence sum for O30 1.691 .000 (3 Bonds used)

O31 -MO7 1.883 1.023 MO-O
O31 -MO14 1.863 1.090 MO-O 173.1
***Valence sum for O31 2.112 .000 (2 Bonds used)

O32 -MO2 1.922 .903 MO-O
O32 -MO10 1.912 .932 MO-O 122.4
***Valence sum for O32 1.835 .000 (2 Bonds used)

O33 -MO13 1.694 1.867 MO-O
***Valence sum for O33 1.867 .000 (1 Bonds used)

O34 -MO2 2.062 .578 MO-O
O34 -MO11 1.777 1.433 MO-O 151.7
***Valence sum for O34 2.011 .000 (2 Bonds used)

O35 -MO10 1.681 1.946 MO-O
***Valence sum for O35 1.946 .000 (1 Bonds used)

O36 -MO7 2.107 .501 MO-O
O36 -MO17 2.044 .612 MO-O 138.5
***Valence sum for O36 1.113 .000 (2 Bonds used)

O37 -MO5 2.054 .593 MO-O
O37 -MO15 1.787 1.388 MO-O 151.5
***Valence sum for O37 1.981 .000 (2 Bonds used)

O38 -MO3 2.382 .209 MO-O
O38 -MO9 2.352 .230 MO-O 91.0
O38 -P1 1.537 1.251 P -O 128.7 129.9
***Valence sum for O38 1.690 .000 (3 Bonds used)

O39 -MO6 2.362 .222 MO-O
O39 -MO8 2.360 .224 MO-O 90.8
O39 -P2 1.539 1.245 P -O 128.8 130.1
***Valence sum for O39 1.691 .000 (3 Bonds used)

O40 -MO1 1.684 1.927 MO-O
***Valence sum for O40 1.927 .000 (1 Bonds used)

O41 -MO10 2.109 .498 MO-O
O41 -MO11 2.050 .601 MO-O 137.7

***Valence sum for O41 1.099 .000 (2 Bonds used)

O42 -MO2 1.679 1.958 MO-O
***Valence sum for O42 1.958 .000 (1 Bonds used)

O43 -MO9 2.120 .481 MO-O
O43 -MO18 2.056 .589 MO-O 138.8
***Valence sum for O43 1.070 .000 (2 Bonds used)

O44 -MO15 1.693 1.873 MO-O
***Valence sum for O44 1.873 .000 (1 Bonds used)

O45 -MO11 2.385 .207 MO-O
O45 -MO13 2.392 .202 MO-O 90.8
O45 -MO15 2.428 .180 MO-O 89.9 89.8
O45 -P2 1.586 1.096 P -O 125.0 125.0 125.4
***Valence sum for O45 1.685 .000 (4 Bonds used)

O46 -MO3 1.680 1.952 MO-O
***Valence sum for O46 1.952 .000 (1 Bonds used)

O47 -MO16 2.020 .661 MO-O
O47 -MO17 1.871 1.062 MO-O 121.6
***Valence sum for O47 1.723 .000 (2 Bonds used)

O48 -MO11 2.023 .655 MO-O
O48 -MO13 1.859 1.104 MO-O 122.3
***Valence sum for O48 1.758 .000 (2 Bonds used)

O49 -MO7 1.676 1.977 MO-O
***Valence sum for O49 1.977 .000 (1 Bonds used)

O50 -MO14 1.684 1.927 MO-O
***Valence sum for O50 1.927 .000 (1 Bonds used)

O51 -MO17 2.008 .687 MO-O
O51 -MO18 1.860 1.100 MO-O 122.9
***Valence sum for O51 1.787 .000 (2 Bonds used)

O52 -MO4 1.686 1.915 MO-O
***Valence sum for O52 1.915 .000 (1 Bonds used)

O53 -MO16 2.405 .194 MO-O
O53 -MO17 2.404 .195 MO-O 89.9
O53 -MO18 2.407 .193 MO-O 89.6 89.9
O53 -P1 1.584 1.102 P -O 125.3 125.5 125.4
***Valence sum for O53 1.683 .000 (4 Bonds used)

O54 -MO9 1.686 1.915 MO-O
***Valence sum for O54 1.915 .000 (1 Bonds used)

O55 -MO13 2.013 .676 MO-O
O55 -MO15 1.852 1.129 MO-O 123.4
***Valence sum for O55 1.805 .000 (2 Bonds used)

O56 -MO14 2.145   .444   MO-O
O56 -MO15 2.060   .582   MO-O 137.4
***Valence sum for O56   1.026   .000   (2 Bonds used)

O57 -MO11 1.859   1.104   MO-O
O57 -MO15 2.005   .693   MO-O 123.2
***Valence sum for O57   1.797   .000   (2 Bonds used)

O58 -MO17 1.688   1.903   MO-O
***Valence sum for O58   1.903   .000   (1 Bonds used)

O59 -MO16 1.686   1.915   MO-O
***Valence sum for O59   1.915   .000   (1 Bonds used)

O60 -MO16 1.855   1.118   MO-O
O60 -MO18 2.001   .702   MO-O 123.1
***Valence sum for O60   1.820   .000   (2 Bonds used)

O61 -MO5   1.676   1.977   MO-O
***Valence sum for O61   1.977   .000   (1 Bonds used)

O62 -MO18 1.687   1.909   MO-O
***Valence sum for O62   1.909   .000   (1 Bonds used)

MEAN VALUES FOR   1 2121 ATOMS =   .000   .000   1

MEAN VALUES FOR 18 MO ATOMS =   5.760   .000   2

MEAN VALUES FOR   2 P ATOMS =   4.872   .000   3

MEAN VALUES FOR 62 O ATOMS =   1.829   .000   4

Parameter list :
  Bond   Type   R0(B)   B   R0(N)   N   R max

 MO - O   46   1.890   .314 10.000 -10.000   2.428
 P - O   63   1.620   .370 10.000 -10.000   1.586

Bond Valence Sum Analysis Report for $(NH_4)_6[\alpha\text{-}P_2Mo_{18}O_{62}]\cdot 14(H_2O)$

Bond	R	EXP((R0-R)/B)	Angles
MO1 -O1	1.699	1.837	MO-O
MO1 -O19	1.832	1.203	MO-O 102.7
MO1 -O21	2.023	.655	MO-O 98.5 88.2
MO1 -O22	1.791	1.371	MO-O 103.6 99.6 154.3
MO1 -O27	2.045	.610	MO-O 99.3 155.9 78.8 84.7
MO1 -O55	2.387	.205	MO-O 170.4 75.4 72.2 86.0 81.3
***Valence sum for MO1	5.881	.000	(6 Bonds used)
MO2 -O2	1.697	1.849	MO-O
MO2 -O19	2.035	.630	MO-O 96.4
MO2 -O20	1.823	1.238	MO-O 104.7 88.0
MO2 -O23	2.052	.597	MO-O 98.0 78.6 154.8
MO2 -O24	1.788	1.384	MO-O 104.1 155.0 100.3 84.4
MO2 -O55	2.391	.203	MO-O 168.4 72.0 75.7 79.9 87.1
***Valence sum for MO2	5.901	.000	(6 Bonds used)
MO3 -O3	1.677	1.971	MO-O
MO3 -O20	2.042	.616	MO-O 97.3
MO3 -O21	1.846	1.150	MO-O 103.7 88.0
MO3 -O25	2.045	.610	MO-O 98.6 79.7 155.7
MO3 -O26	1.785	1.397	MO-O 103.2 155.8 99.3 84.7
MO3 -O55	2.380	.210	MO-O 169.6 72.3 75.2 81.1 87.2
***Valence sum for MO3	5.955	.000	(6 Bonds used)
MO4 -O4	1.692	1.879	MO-O
MO4 -O22	2.153	.433	MO-O 89.4
MO4 -O28	1.955	.813	MO-O 96.8 80.3
MO4 -O33	1.843	1.161	MO-O 102.1 81.7 153.7
MO4 -O34	1.765	1.489	MO-O 102.9 167.1 94.4 99.0
MO4 -O56	2.321	.253	MO-O 163.5 76.8 72.2 85.1 90.5
***Valence sum for MO4	6.028	.000	(6 Bonds used)
MO5 -O5	1.691	1.885	MO-O
MO5 -O23	1.791	1.371	MO-O 101.1
MO5 -O28	1.877	1.042	MO-O 99.3 99.5
MO5 -O29	1.914	.926	MO-O 103.1 91.2 152.8
MO5 -O35	2.110	.496	MO-O 91.9 165.8 83.8 80.1
MO5 -O56	2.334	.243	MO-O 169.7 87.2 73.2 82.5 80.5
***Valence sum for MO5	5.963	.000	(6 Bonds used)
MO6 -O6	1.686	1.915	MO-O
MO6 -O24	2.135	.458	MO-O 90.7
MO6 -O29	1.882	1.026	MO-O 102.0 81.8
MO6 -O30	1.943	.845	MO-O 98.1 82.2 154.4
MO6 -O36	1.762	1.503	MO-O 101.3 167.9 96.6 94.8
MO6 -O57	2.320	.254	MO-O 166.7 78.6 84.4 72.9 89.4
***Valence sum for MO6	6.001	.000	(6 Bonds used)
MO7 -O7	1.684	1.927	MO-O
MO7 -O25	1.798	1.340	MO-O 101.5

MO7 -O30 1.902 .963 MO-O 99.7 97.0
MO7 -O31 1.884 1.019 MO-O 101.8 91.7 154.7
MO7 -O37 2.091 .527 MO-O 92.3 166.0 83.0 83.0
MO7 -O57 2.329 .247 MO-O 169.7 87.2 73.4 83.4 79.4
***Valence sum for MO7 6.024 .000 (6 Bonds used)

MO8 -O8 1.690 1.891 MO-O
MO8 -O26 2.135 .458 MO-O 90.5
MO8 -O31 1.897 .978 MO-O 101.0 80.9
MO8 -O32 1.935 .866 MO-O 98.2 82.4 154.6
MO8 -O38 1.755 1.537 MO-O 102.6 166.8 94.5 97.4
MO8 -O58 2.300 .271 MO-O 166.6 77.9 83.9 73.9 89.3
***Valence sum for MO8 6.002 .000 (6 Bonds used)

MO9 -O9 1.685 1.921 MO-O
MO9 -O27 1.811 1.286 MO-O 101.7
MO9 -O32 1.863 1.090 MO-O 101.7 98.6
MO9 -O33 1.923 .900 MO-O 102.3 89.7 152.4
MO9 -O39 2.077 .551 MO-O 94.5 162.2 85.0 79.6
MO9 -O58 2.376 .213 MO-O 171.4 86.1 73.3 81.1 78.3
***Valence sum for MO9 5.961 .000 (6 Bonds used)

MO10-O10 1.677 1.971 MO-O
MO10-O34 2.090 .529 MO-O 93.9
MO10-O40 1.917 .918 MO-O 98.8 82.6
MO10-O45 1.882 1.026 MO-O 104.6 82.0 152.7
MO10-O51 1.805 1.311 MO-O 101.1 164.7 97.4 91.7
MO10-O59 2.362 .222 MO-O 169.2 78.8 72.4 82.6 86.6
***Valence sum for MO10 5.976 .000 (6 Bonds used)

MO11-O11 1.682 1.939 MO-O
MO11-O35 1.785 1.397 MO-O 102.3
MO11-O40 1.909 .941 MO-O 97.8 95.7
MO11-O41 1.895 .984 MO-O 101.7 94.6 155.4
MO11-O46 2.107 .501 MO-O 90.2 167.4 83.4 81.7
MO11-O59 2.323 .252 MO-O 165.8 89.9 73.5 84.3 77.8
***Valence sum for MO11 6.015 .000 (6 Bonds used)

MO12-O12 1.688 1.903 MO-O
MO12-O36 2.130 .466 MO-O 90.4
MO12-O41 1.890 1.000 MO-O 102.1 80.8
MO12-O42 1.912 .932 MO-O 99.7 83.3 153.0
MO12-O47 1.770 1.465 MO-O 103.2 165.9 92.6 97.8
MO12-O60 2.341 .238 MO-O 167.7 78.9 82.5 73.1 87.9
***Valence sum for MO12 6.004 .000 (6 Bonds used)

MO13-O13 1.692 1.879 MO-O
MO13-O37 1.782 1.411 MO-O 101.4
MO13-O42 1.937 .861 MO-O 97.3 95.0
MO13-O43 1.863 1.090 MO-O 102.3 96.1 155.0
MO13-O48 2.111 .495 MO-O 91.3 167.2 82.4 81.8
MO13-O60 2.302 .269 MO-O 166.6 89.3 73.6 84.2 77.9
***Valence sum for MO13 6.004 .000 (6 Bonds used)

MO14-O14 1.687 1.909 MO-O
MO14-O38 2.119 .482 MO-O 91.6
MO14-O43 1.919 .912 MO-O 101.6 79.8
MO14-O44 1.875 1.049 MO-O 100.3 84.3 153.2
MO14-O49 1.780 1.420 MO-O 101.5 165.5 91.3 99.3
MO14-O61 2.309 .263 MO-O 169.9 79.4 81.5 74.4 88.0
***Valence sum for MO14 6.035 .000 (6 Bonds used)

MO15-O15 1.677 1.971 MO-O
MO15-O39 1.771 1.461 MO-O 103.4
MO15-O44 1.937 .861 MO-O 97.6 96.8
MO15-O45 1.874 1.052 MO-O 102.6 97.1 152.1
MO15-O50 2.174 .405 MO-O 90.8 165.9 81.0 79.7
MO15-O61 2.355 .227 MO-O 165.0 89.1 72.2 83.9 76.9
***Valence sum for MO15 5.977 .000 (6 Bonds used)

MO16-O16 1.685 1.921 MO-O
MO16-O50 1.775 1.442 MO-O 104.2
MO16-O51 2.035 .630 MO-O 100.3 85.1
MO16-O52 2.059 .584 MO-O 96.9 155.1 78.2
MO16-O54 1.841 1.169 MO-O 102.6 100.6 154.1 87.1
MO16-O62 2.386 .206 MO-O 168.7 87.1 80.3 72.1 74.8
***Valence sum for MO16 5.952 .000 (6 Bonds used)

MO17-O17 1.687 1.909 MO-O
MO17-O46 1.784 1.402 MO-O 103.7
MO17-O47 2.101 .511 MO-O 96.3 82.5
MO17-O52 1.805 1.311 MO-O 105.0 101.0 156.8
MO17-O53 2.018 .665 MO-O 97.7 152.7 78.4 89.5
MO17-O62 2.382 .209 MO-O 170.0 85.6 81.1 76.4 72.4
***Valence sum for MO17 6.006 .000 (6 Bonds used)

MO18-O18 1.691 1.885 MO-O
MO18-O48 1.780 1.420 MO-O 103.3
MO18-O49 2.068 .567 MO-O 99.2 83.3
MO18-O53 1.843 1.161 MO-O 104.2 100.1 154.9
MO18-O54 2.024 .653 MO-O 98.6 153.7 79.0 88.3
MO18-O62 2.383 .208 MO-O 170.5 86.1 80.2 75.3 71.9
***Valence sum for MO18 5.894 .000 (6 Bonds used)

P1 -O55 1.565 1.160 P -O
P1 -O56 1.531 1.272 P -O 107.5
P1 -O57 1.536 1.255 P -O 107.2 111.0
P1 -O58 1.537 1.251 P -O 107.7 111.7 111.4
***Valence sum for P1 4.939 .000 (4 Bonds used)

P2 -O59 1.526 1.289 P -O
P2 -O60 1.533 1.265 P -O 111.3
P2 -O61 1.540 1.241 P -O 110.9 111.1
P2 -O62 1.574 1.132 P -O 108.5 107.2 107.6
***Valence sum for P2 4.928 .000 (4 Bonds used)

O1 -MO1 1.699 1.837 MO-O
***Valence sum for O1 1.837 .000 (1 Bonds used)

O2 -MO2 1.697 1.849 MO-O
***Valence sum for O2 1.849 .000 (1 Bonds used)

O3 -MO3 1.677 1.971 MO-O
***Valence sum for O3 1.971 .000 (1 Bonds used)

O4 -MO4 1.692 1.879 MO-O
***Valence sum for O4 1.879 .000 (1 Bonds used)

O5 -MO5 1.691 1.885 MO-O
***Valence sum for O5 1.885 .000 (1 Bonds used)

O6 -MO6 1.686 1.915 MO-O
***Valence sum for O6 1.915 .000 (1 Bonds used)

O7 -MO7 1.684 1.927 MO-O
***Valence sum for O7 1.927 .000 (1 Bonds used)

O8 -MO8 1.690 1.891 MO-O
***Valence sum for O8 1.891 .000 (1 Bonds used)

O9 -MO9 1.685 1.921 MO-O
***Valence sum for O9 1.921 .000 (1 Bonds used)

O10 -MO10 1.677 1.971 MO-O
***Valence sum for O10 1.971 .000 (1 Bonds used)

O11 -MO11 1.682 1.939 MO-O
***Valence sum for O11 1.939 .000 (1 Bonds used)

O12 -MO12 1.688 1.903 MO-O
***Valence sum for O12 1.903 .000 (1 Bonds used)

O13 -MO13 1.692 1.879 MO-O
***Valence sum for O13 1.879 .000 (1 Bonds used)

O14 -MO14 1.687 1.909 MO-O
***Valence sum for O14 1.909 .000 (1 Bonds used)

O15 -MO15 1.677 1.971 MO-O
***Valence sum for O15 1.971 .000 (1 Bonds used)

O16 -MO16 1.685 1.921 MO-O
***Valence sum for O16 1.921 .000 (1 Bonds used)

O17 -MO17 1.687 1.909 MO-O
***Valence sum for O17 1.909 .000 (1 Bonds used)

O18 -MO18 1.691 1.885 MO-O
***Valence sum for O18 1.885 .000 (1 Bonds used)

O19 -MO1 1.832 1.203 MO-O
O19 -MO2 2.035 .630 MO-O 122.2

***Valence sum for O19 1.833 .000 (2 Bonds used)

O20 -MO2 1.823 1.238 MO-O
O20 -MO3 2.042 .616 MO-O 121.8
***Valence sum for O20 1.854 .000 (2 Bonds used)

O21 -MO1 2.023 .655 MO-O
O21 -MO3 1.846 1.150 MO-O 122.1
***Valence sum for O21 1.805 .000 (2 Bonds used)

O22 -MO1 1.791 1.371 MO-O
O22 -MO4 2.153 .433 MO-O 153.0
***Valence sum for O22 1.803 .000 (2 Bonds used)

O23 -MO2 2.052 .597 MO-O
O23 -MO5 1.791 1.371 MO-O 147.4
***Valence sum for O23 1.968 .000 (2 Bonds used)

O24 -MO2 1.788 1.384 MO-O
O24 -MO6 2.135 .458 MO-O 153.1
***Valence sum for O24 1.842 .000 (2 Bonds used)

O25 -MO3 2.045 .610 MO-O
O25 -MO7 1.798 1.340 MO-O 146.0
***Valence sum for O25 1.951 .000 (2 Bonds used)

O26 -MO3 1.785 1.397 MO-O
O26 -MO8 2.135 .458 MO-O 153.7
***Valence sum for O26 1.855 .000 (2 Bonds used)

O27 -MO1 2.045 .610 MO-O
O27 -MO9 1.811 1.286 MO-O 147.9
***Valence sum for O27 1.896 .000 (2 Bonds used)

O28 -MO4 1.955 .813 MO-O
O28 -MO5 1.877 1.042 MO-O 122.2
***Valence sum for O28 1.855 .000 (2 Bonds used)

O29 -MO5 1.914 .926 MO-O
O29 -MO6 1.882 1.026 MO-O 151.5
***Valence sum for O29 1.952 .000 (2 Bonds used)

O30 -MO6 1.943 .845 MO-O
O30 -MO7 1.902 .963 MO-O 121.3
***Valence sum for O30 1.807 .000 (2 Bonds used)

O31 -MO7 1.884 1.019 MO-O
O31 -MO8 1.897 .978 MO-O 152.2
***Valence sum for O31 1.997 .000 (2 Bonds used)

O32 -MO8 1.935 .866 MO-O
O32 -MO9 1.863 1.090 MO-O 122.0
***Valence sum for O32 1.956 .000 (2 Bonds used)

O33 -MO4 1.843 1.161 MO-O
O33 -MO9 1.923 .900 MO-O 154.2
***Valence sum for O33 2.062 .000 (2 Bonds used)

O34 -MO4 1.765 1.489 MO-O
O34 -MO10 2.090 .529 MO-O 159.8
***Valence sum for O34 2.018 .000 (2 Bonds used)

O35 -MO5 2.110 .496 MO-O
O35 -MO11 1.785 1.397 MO-O 162.4
***Valence sum for O35 1.893 .000 (2 Bonds used)

O36 -MO6 1.762 1.503 MO-O
O36 -MO12 2.130 .466 MO-O 160.4
***Valence sum for O36 1.969 .000 (2 Bonds used)

O37 -MO7 2.091 .527 MO-O
O37 -MO13 1.782 1.411 MO-O 159.5
***Valence sum for O37 1.938 .000 (2 Bonds used)

O38 -MO8 1.755 1.537 MO-O
O38 -MO14 2.119 .482 MO-O 163.8
***Valence sum for O38 2.019 .000 (2 Bonds used)

O39 -MO9 2.077 .551 MO-O
O39 -MO15 1.771 1.461 MO-O 164.1
***Valence sum for O39 2.012 .000 (2 Bonds used)

O40 -MO10 1.917 .918 MO-O
O40 -MO11 1.909 .941 MO-O 122.6
***Valence sum for O40 1.859 .000 (2 Bonds used)

O41 -MO11 1.895 .984 MO-O
O41 -MO12 1.890 1.000 MO-O 150.6
***Valence sum for O41 1.984 .000 (2 Bonds used)

O42 -MO12 1.912 .932 MO-O
O42 -MO13 1.937 .861 MO-O 120.8
***Valence sum for O42 1.793 .000 (2 Bonds used)

O43 -MO13 1.863 1.090 MO-O
O43 -MO14 1.919 .912 MO-O 151.6
***Valence sum for O43 2.002 .000 (2 Bonds used)

O44 -MO14 1.875 1.049 MO-O
O44 -MO15 1.937 .861 MO-O 122.0
***Valence sum for O44 1.910 .000 (2 Bonds used)

O45 -MO10 1.882 1.026 MO-O
O45 -MO15 1.874 1.052 MO-O 154.4
***Valence sum for O45 2.078 .000 (2 Bonds used)

O46 -MO11 2.107 .501 MO-O
O46 -MO17 1.784 1.402 MO-O 156.7

***Valence sum for O46 1.903 .000 (2 Bonds used)

O47 -MO12 1.770 1.465 MO-O
O47 -MO17 2.101 .511 MO-O 146.0
***Valence sum for O47 1.976 .000 (2 Bonds used)

O48 -MO13 2.111 .495 MO-O
O48 -MO18 1.780 1.420 MO-O 155.3
***Valence sum for O48 1.914 .000 (2 Bonds used)

O49 -MO14 1.780 1.420 MO-O
O49 -MO18 2.068 .567 MO-O 147.1
***Valence sum for O49 1.987 .000 (2 Bonds used)

O50 -MO15 2.174 .405 MO-O
O50 -MO16 1.775 1.442 MO-O 154.0
***Valence sum for O50 1.847 .000 (2 Bonds used)

O51 -MO10 1.805 1.311 MO-O
O51 -MO16 2.035 .630 MO-O 146.0
***Valence sum for O51 1.941 .000 (2 Bonds used)

O52 -MO16 2.059 .584 MO-O
O52 -MO17 1.805 1.311 MO-O 121.5
***Valence sum for O52 1.895 .000 (2 Bonds used)

O53 -MO17 2.018 .665 MO-O
O53 -MO18 1.843 1.161 MO-O 121.9
***Valence sum for O53 1.827 .000 (2 Bonds used)

O54 -MO16 1.841 1.169 MO-O
O54 -MO18 2.024 .653 MO-O 122.6
***Valence sum for O54 1.822 .000 (2 Bonds used)

O55 -MO1 2.387 .205 MO-O
O55 -MO2 2.391 .203 MO-O 90.3
O55 -MO3 2.380 .210 MO-O 90.5 90.2
O55 -P1 1.565 1.160 P -O 124.8 125.7 124.6
***Valence sum for O55 1.778 .000 (4 Bonds used)

O56 -MO4 2.321 .253 MO-O
O56 -MO5 2.334 .243 MO-O 92.3
O56 -P1 1.531 1.272 P -O 130.2 125.3
***Valence sum for O56 1.769 .000 (3 Bonds used)

O57 -MO6 2.320 .254 MO-O
O57 -MO7 2.329 .247 MO-O 92.3
O57 -P1 1.536 1.255 P -O 130.9 124.8
***Valence sum for O57 1.756 .000 (3 Bonds used)

O58 -MO8 2.300 .271 MO-O
O58 -MO9 2.376 .213 MO-O 90.5
O58 -P1 1.537 1.251 P -O 131.8 125.4
***Valence sum for O58 1.735 .000 (3 Bonds used)

O59 -MO10 2.362   .222   MO-O
O59 -MO11 2.323   .252   MO-O   91.5
O59 -P2   1.526   1.289   P -O 124.4 130.1
***Valence sum for O59   1.763   .000   (3 Bonds used)

O60 -MO12 2.341   .238   MO-O
O60 -MO13 2.302   .269   MO-O   92.2
O60 -P2   1.533   1.265   P -O 125.2 130.5
***Valence sum for O60   1.772   .000   (3 Bonds used)

O61 -MO14 2.309   .263   MO-O
O61 -MO15 2.355   .227   MO-O   91.2
O61 -P2   1.540   1.241   P -O 125.6 130.5
***Valence sum for O61   1.732   .000   (3 Bonds used)

O62 -MO16 2.386   .206   MO-O
O62 -MO17 2.382   .209   MO-O   90.1
O62 -MO18 2.383   .208   MO-O   90.7 90.3
O62 -P2   1.574   1.132   P -O 124.8 125.1 125.2
***Valence sum for O62   1.755   .000   (4 Bonds used)

MEAN VALUES FOR   1 2929 ATOMS =   .000   .000   1

MEAN VALUES FOR 18 MO ATOMS =   5.977   .000   2

MEAN VALUES FOR   2 P ATOMS =   4.933   .000   3

MEAN VALUES FOR 62 O ATOMS =   1.894   .000   4

Parameter list :

Bond	Type	R0(B)	B	R0(N)	N	R max
MO - O	46	1.890	.314	10.000	-10.000	2.391
P - O	63	1.620	.370	10.000	-10.000	1.574

5. References

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

2 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

3 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

4 L. E. Briand, G. M. Valle and H. J. Thomas, *J. Mater. Chem.*, 2002, **12**, 299–304.

5 S. R. Matkovic, G. M. Valle, L. A. Gambaro and L. E. Briand, *Catal. Today*, 2008, **133**–**135**, 192–199.

6 L. E. Briand, G. T. Baronetti and H. J. Thomas, *Appl. Catal. A Gen.*, 2003, **256**, 37–50.

7 R. I. Maksimovskaya, G. M. Maksimov and G. S. Litvak, *Russ. Chem. Bull.*, 2003, **52**, 103–108.

8 L. Patiny and A. Borel, *J. Chem. Inf. Model.*, 2013, **53**, 1223–1228.

9 http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/