# Electronic Supplementary Information

## Unprecedented Fullercage-like and Heterometallic $[Mo^{IV}_3O_4]$-Polyoxomolybdate Hybrid

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### Crystallographic Analysis

The intensity data were collected on a Rigaku Mercury CCD diffractometer for **1** and **2**, with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the multi-scan program. The structure were solved by direct methods and refined by full-matrix least squares on $F^2$ with the SHELXTL-97 program. CCDC-1575809 (**1**) and CCDC-1575810 (**2**) contain the supplementary crystallographic data for this paper, these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

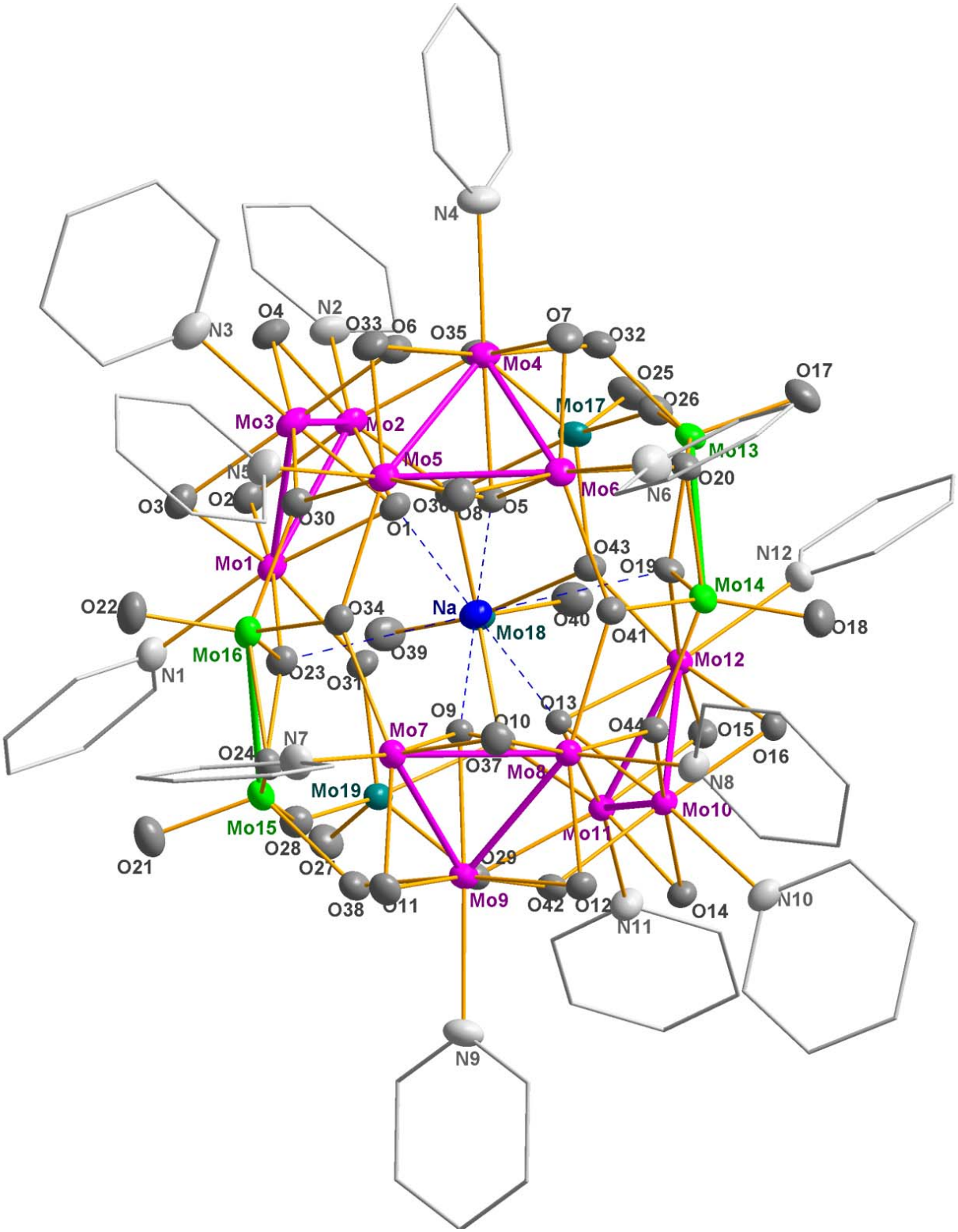
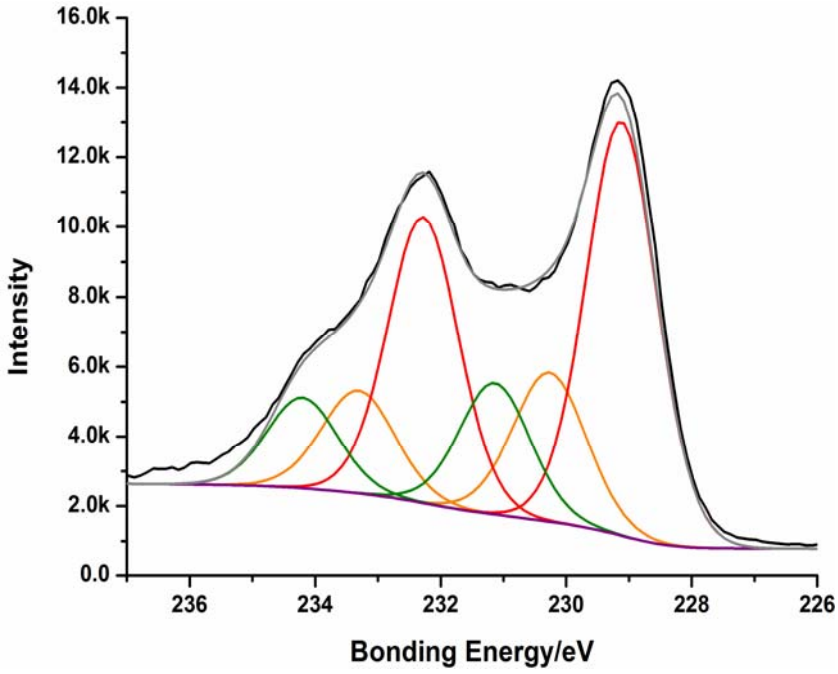



**Fig. S1** Structure of **1** with 50% probability thermal ellipsoids for non-carbon atoms ($Mo^{4+}$, pink, $Mo^{V}$, green, $Mo^{VI}$, black green).




Binding energies of Mo 3d from the literature[16-22] and the binding energies of peaks used to assign species from the present measurements of **1**.

| **Oxidation state** | **Mo $3d_{5/2}$** | **Mo $3d_{3/2}$** |
|---|---|---|
| $Mo^{IV}$- $MoO_2$ | 228. 8-229.3 | 231.7-232.6 |
| $Mo^{IV}$-**3** | 230.0 | 233.2 |
| $Mo^{V}$-$MoCl_5$ | 230.9-231.1 | 234.3-235.4 |
| $Mo^{VI}$-$Na_2MoO_4$ | 231.9-232.3 | 235-235.4 |
| $Mo^{VI}$ **-3** | 231.9 | 235.05 |
| $Mo^{IV}$-**1** | 229.12 | 232.28 |
| $Mo^{V}$-**1** | 230.26 | 233.30 |
| $Mo^{VI}$-**1** | 231.14 | 234.20 |

**Fig. S2** XPS of **1** shows an approximate 12:4:3 ratio of $Mo^{IV}$:$Mo^{V}$:$Mo^{VI}$ (the binding energies of all of the peaks are referenced to a C 1s value of 284.6 eV).

Reference

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17. F. Werfel and E. Minni, *J. Phys. C: Solid State Phys*. 1983, **16**, 6094.

18. B. Brox and I. Olefjord, *Surf. Interface Anal*. 1988, **13**, 3.

19. C. R. Clayton and Y. C. Lu, *Surf. Interface Anal.* 1989,**14**, 66.

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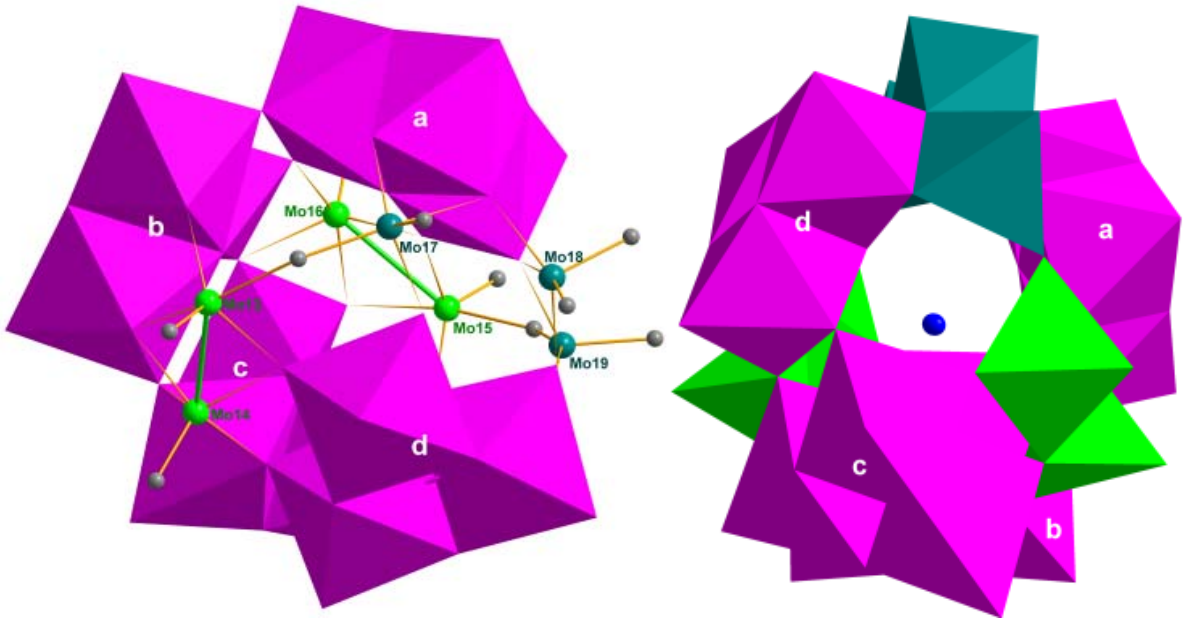
21. I. A. Okonkwo, J. Doff, A. Baron-Wiecheć, G. Jones, E. V. Koroleva, P. Skeldon and G. E. Thompson, *Thin Solid Films,* 2012,**520**, 6318–6327.

22. http://srdata.nist.gov/xps/DataDefinition.aspx(26/08/2009).




**(a)** **(b)**

**Fig. S3** (**a**) Four 2-corner shared $Mo^{IV}_3O_{13}$ sets (a→d pink polyhedra) linked together by two $Mo^{V}_2$ dimmers (green) and three $Mo^{VI}$ (black green) (**b**)$Na^{+}$-incorporated channel formed by the four $Mo^{IV}_3O_{13}$ sets (a→d), four $Mo^{V}$ and three $Mo^{VI}$ mono-capped squares.

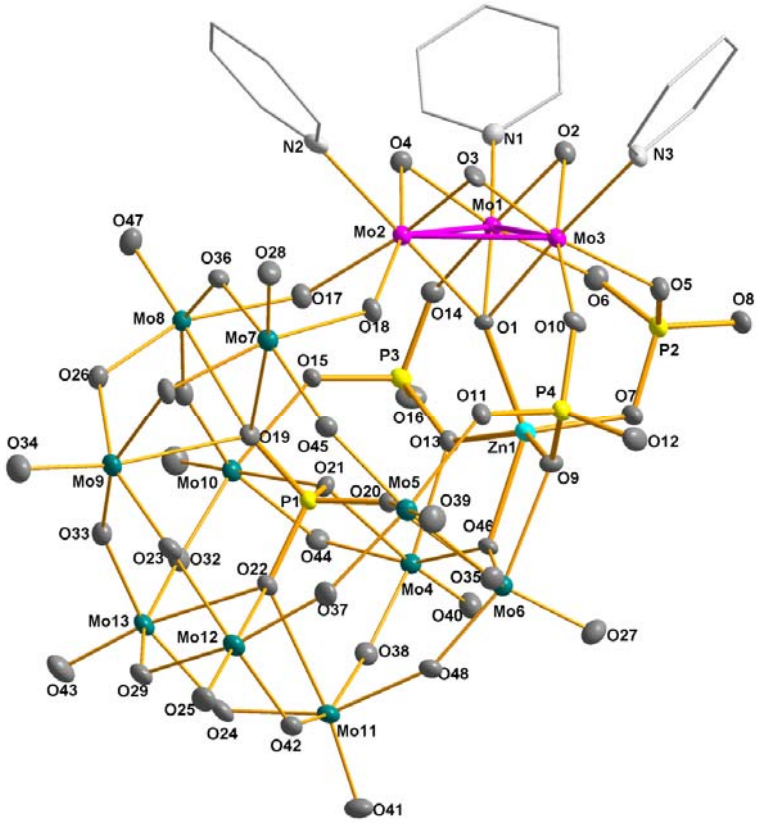



**Fig. S4** Structure of **2** with 30% probability thermal ellipsoids for non-carbon atoms ($Mo^{4+}$, pink; $Mo^{VI}$, black green; $P^{5+}$, yellow; $Zn^{2+}$, aqua)

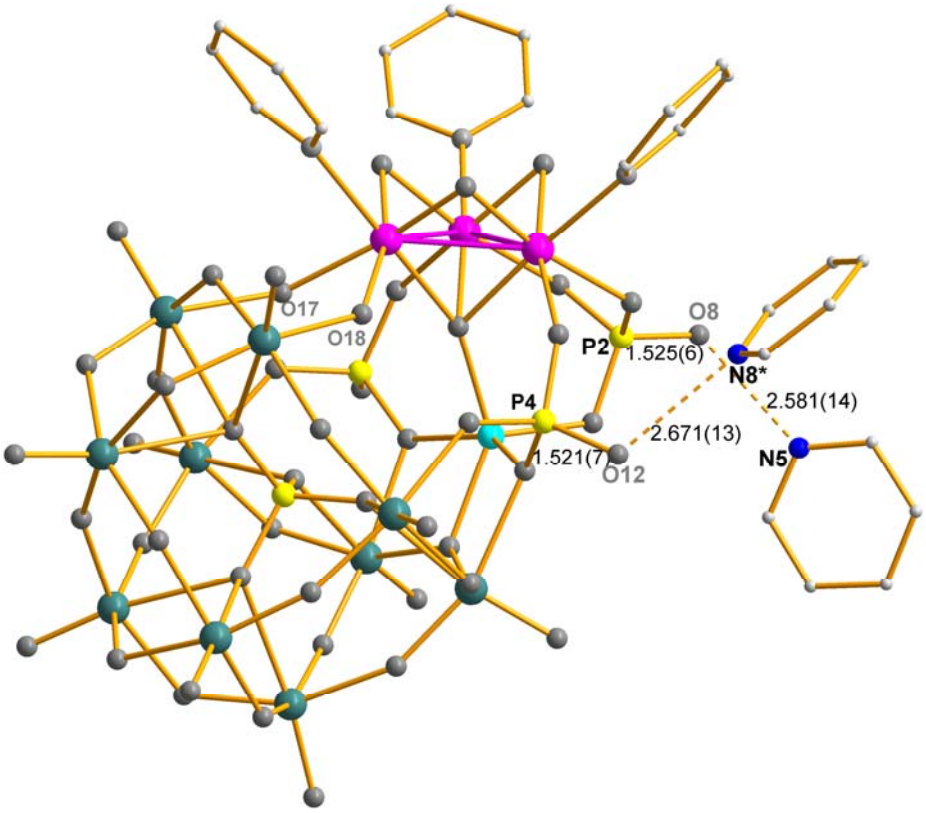
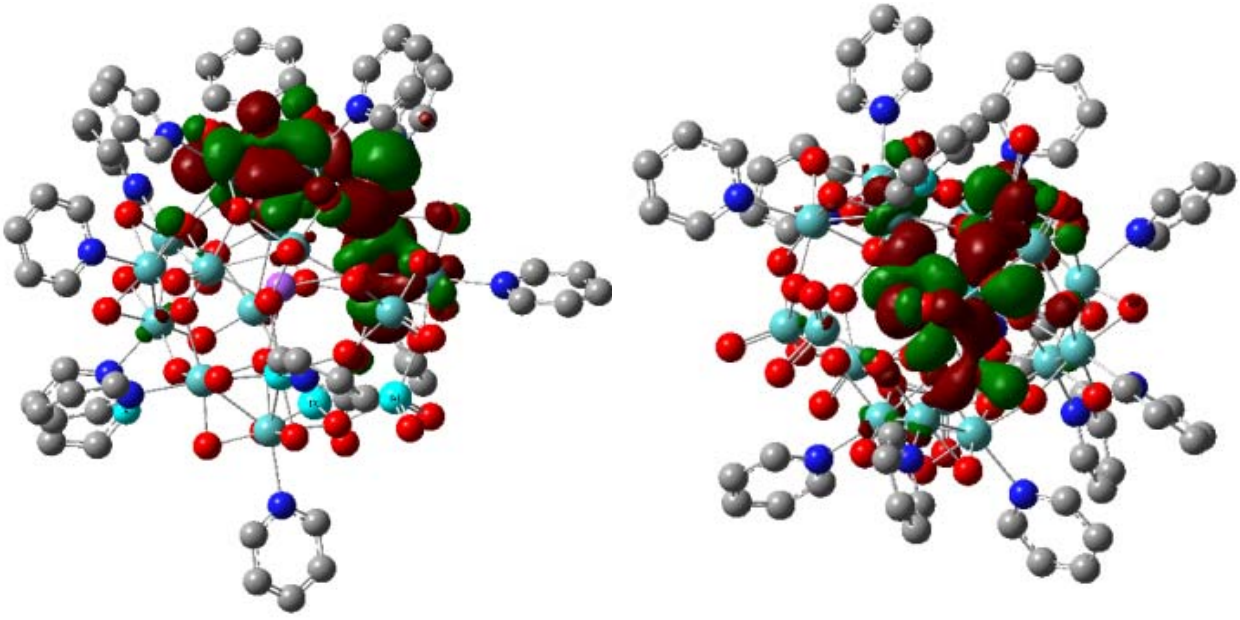



**Fig. S5** Hydrogen bonds between $PO_4$ and protonated pyridine [N8* is at equivalent position (1/2+x, -1/2-y, 1/2+z)].



HOMO LUMO

**Fig. S6** HOMO and LUMO of **1**.

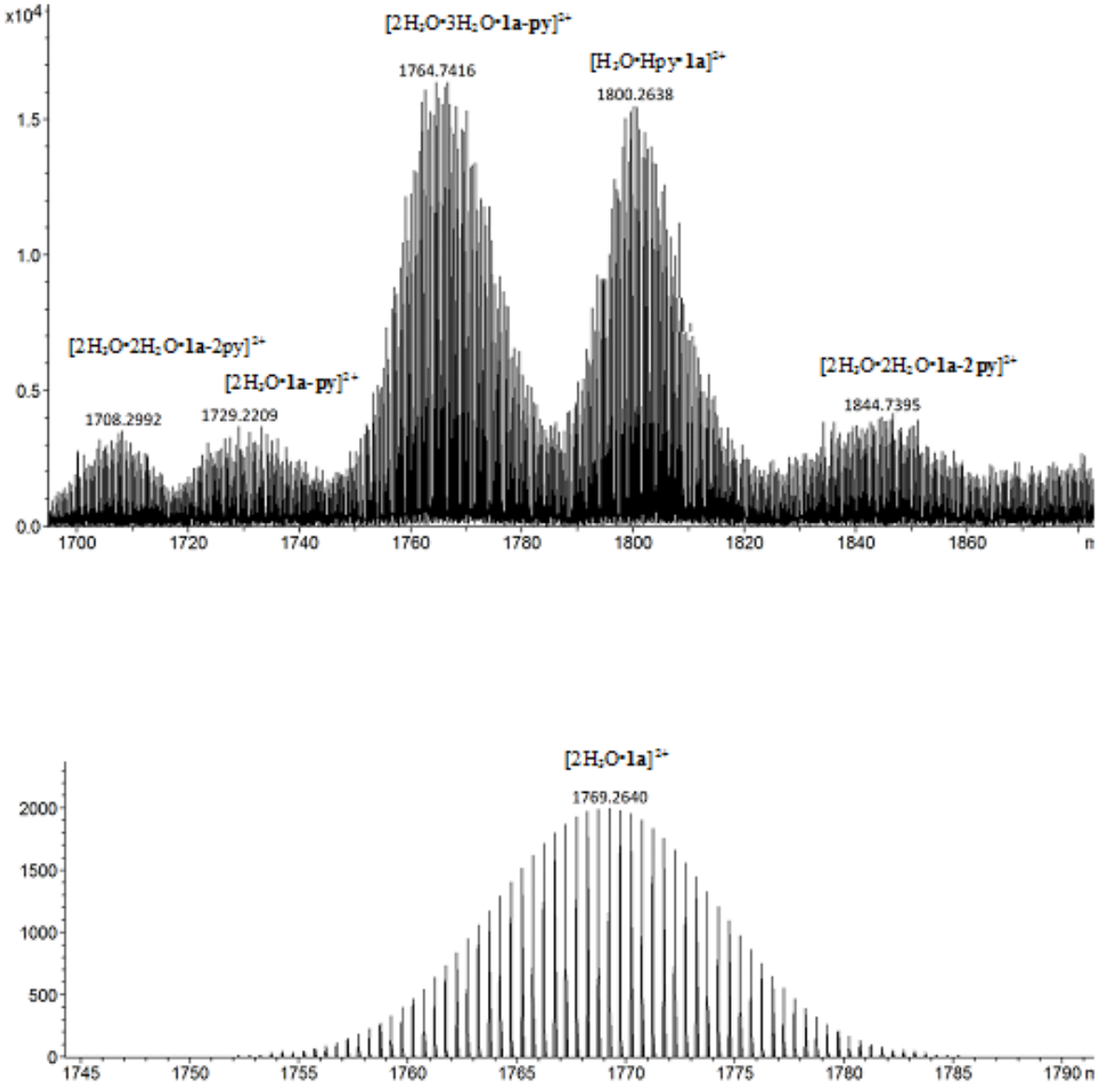





**Fig. S7** Mass spectroscopy of $Na[Mo^{IV}_{12}Mo^{V}_{4}Mo^{VI}_{3}O_{43}(OH)Py_{12}]\bullet 11H_2O$ (**1a**•$11H_2O$) in DMF solution.

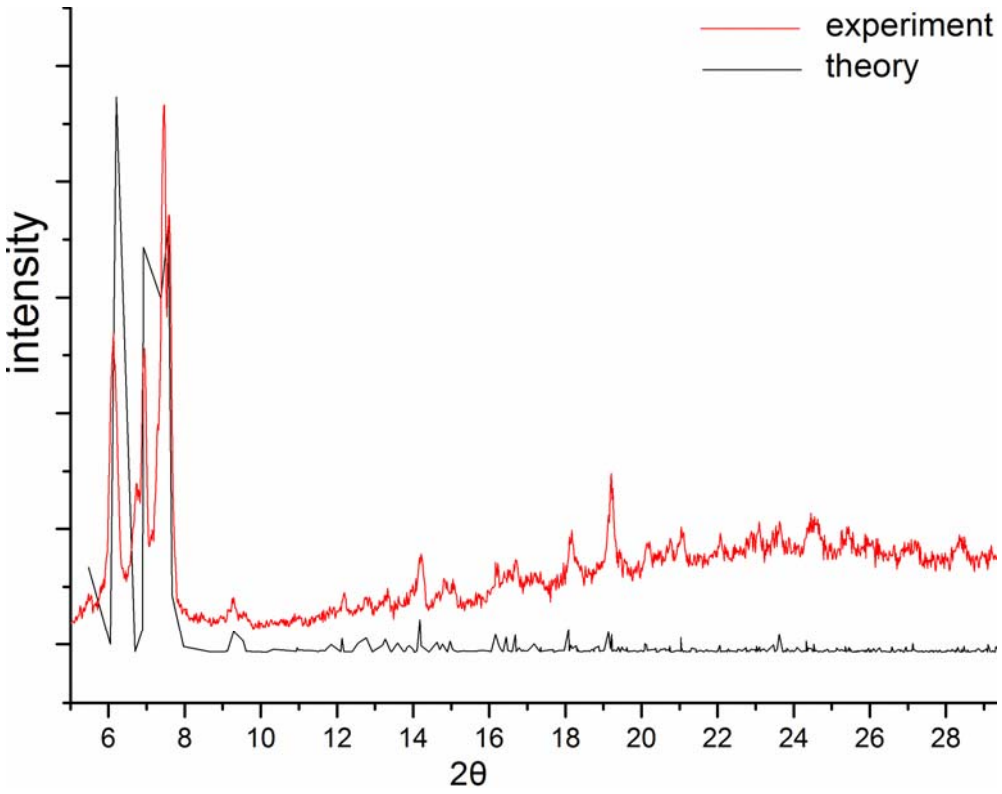



**Fig. S8** P-XRD of $Na[Mo^{IV}_{12}Mo^{V}_{4}Mo^{VI}_{3}O_{43}(OH)Py_{12}]\bullet 11H_2O$ (**1a**•$11H_2O$)

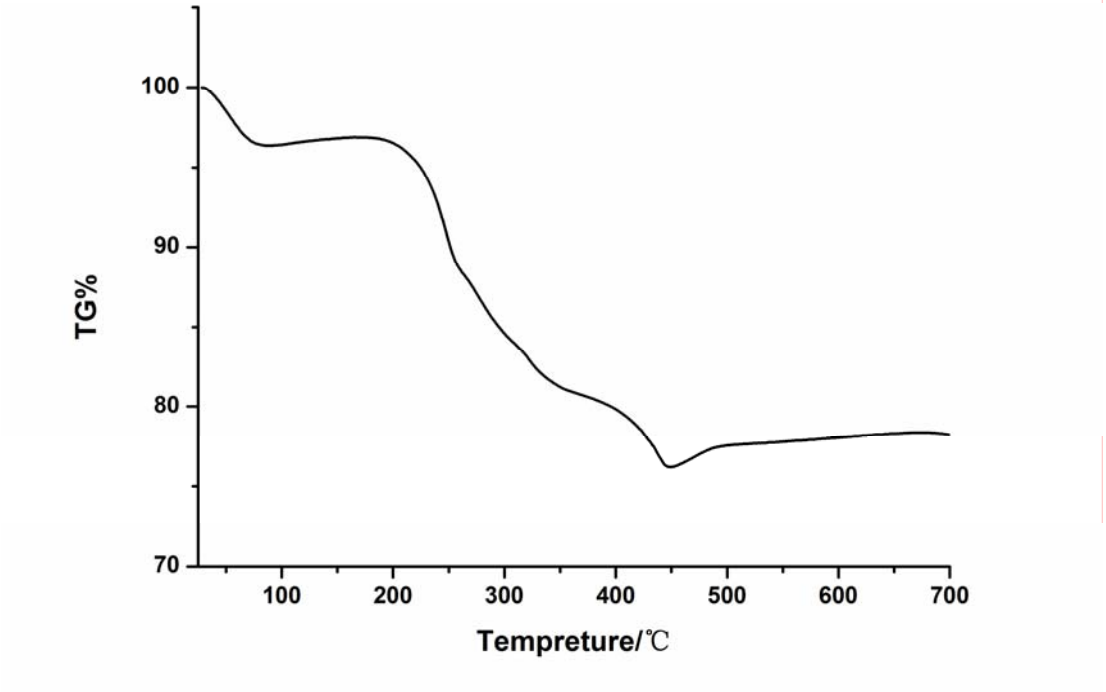



**Fig. S9** TGA of **1**

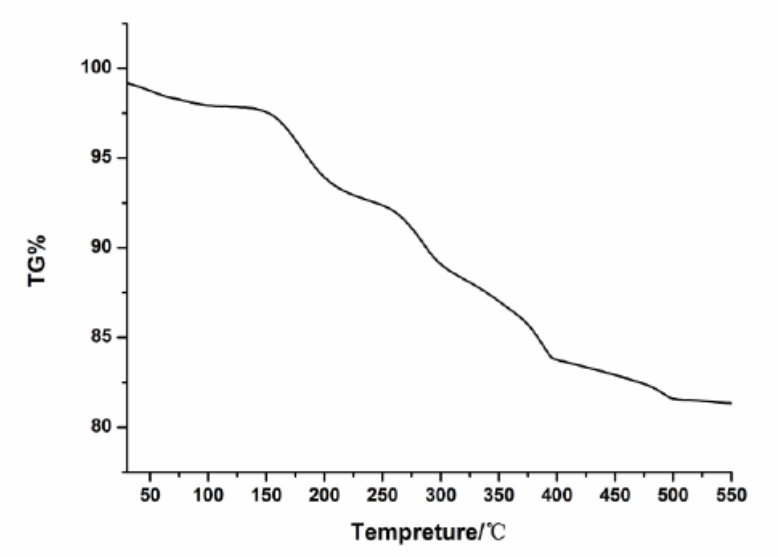



**Fig. S10** TGA of **2**

**Table S1** Bond valance sum analyses for **1**

| Atom | Coord | D_aver | Sigm | Distort(x10-4) | Valence | BVSum(Sigma) |
|---|---|---|---|---|---|---|
| Mo1 | 6.00 | 2.0612( | 14) | 32.613 | 4.000 | 4.141( 17) |
| Mo2 | 6.00 | 2.0525( | 15) | 26.885 | 4.000 | 4.184( 17) |
| Mo3 | 6.00 | 2.0485( | 15) | 30.298 | 4.000 | 4.239( 17) |
| Mo4 | 6.00 | 2.0360( | 14) | 14.944 | 4.000 | 4.308( 17) |
| Mo5 | 6.00 | 2.0538( | 14) | 30.590 | 4.000 | 4.216( 16) |
| Mo6 | 6.00 | 2.0503( | 15) | 32.132 | 4.000 | 4.256( 18) |
| Mo7 | 6.00 | 2.0525( | 14) | 31.841 | 4.000 | 4.214( 17) |
| Mo8 | 6.00 | 2.0533( | 13) | 30.034 | 4.000 | 4.207( 16) |
| Mo9 | 6.00 | 2.0480( | 14) | 21.987 | 4.000 | 4.210( 16) |
| Mo10 | 6.00 | 2.0521( | 13) | 22.743 | 4.000 | 4.183( 15) |
| Mo11 | 6.00 | 2.0388( | 13) | 23.802 | 4.000 | 4.336( 15) |
| Mo12 | 6.00 | 2.0500( | 12) | 25.881 | 4.000 | 4.232( 15) |
| Mo13 | 5.00 | 1.9155( | 16) | 45.077 | 5.000 | 5.219( 25) |
| Mo14 | 5.00 | 1.9268( | 16) | 39.748 | 5.000 | 5.044( 25) |
| Mo15 | 5.00 | 1.9159( | 16) | 45.514 | 5.000 | 5.221( 26) |
| Mo16 | 5.00 | 1.9221( | 16) | 37.894 | 5.000 | 5.092( 26) |

| | | | | | |
|---|---|---|---|---|---|
| Mo17 | 5.00 | 1.8742( 17) | 76.001 | 6.000 | 5.947( 30) |
| Mo18 | 6.00 | 2.0291( 15) | 276.066 | 6.000 | 5.989( 30) |
| Mo19 | 5.00 | 1.8765( 16) | 70.941 | 6.000 | 5.879( 28) |
| Na | 6.00 | 2.4887( 15) | 84.380 | 1.000 | 1.104( 5) |
| O1 | 4.00 | 2.1055( 17) | 25.481 | -2.000 | 2.225( 10) |
| O2 | 2.00 | 1.9269( 25) | 0.681 | -2.000 | 1.792( 12) |
| O3 | 2.00 | 1.9545( 28) | 2.008 | -2.000 | 1.667( 13) |
| O4 | 2.00 | 1.9297( 26) | 0.372 | -2.000 | 1.778( 13) |
| O5 | 4.00 | 2.1273( 17) | 32.714 | -2.000 | 2.125( 10) |
| O6 | 2.00 | 1.9327( 26) | 8.788 | -2.000 | 1.784( 12) |
| O7 | 2.00 | 1.9468( 26) | 5.770 | -2.000 | 1.711( 12) |
| O8 | 2.00 | 1.9243( 26) | 0.786 | -2.000 | 1.805( 13) |
| O9 | 4.00 | 2.1363( 17) | 47.874 | -2.000 | 2.125( 10) |
| O10 | 2.00 | 1.9274( 25) | 0.202 | -2.000 | 1.789( 12) |
| O11 | 2.00 | 1.9304( 26) | 0.580 | -2.000 | 1.775( 12) |
| O12 | 2.00 | 1.9237( 24) | 3.202 | -2.000 | 1.814( 12) |
| O13 | 4.00 | 2.1049( 16) | 27.732 | -2.000 | 2.237( 10) |
| O14 | 2.00 | 1.9210( 23) | 0.451 | -2.000 | 1.821( 11) |
| O15 | 2.00 | 1.9267( 23) | 0.018 | -2.000 | 1.792( 11) |
| O16 | 2.00 | 1.9346( 23) | 0.000 | -2.000 | 1.754( 11) |
| O17 | 1.00 | 1.6863( 39) | 0.000 | -2.000 | 1.816( 19) |
| O18 | 1.00 | 1.6853( 42) | 0.000 | -2.000 | 1.821( 21) |
| O19 | 4.00 | 2.2398( 17) | 219.065 | -2.000 | 2.111( 10) |
| O20 | 3.00 | 2.0241( 20) | 11.841 | -2.000 | 2.193( 12) |
| O21 | 1.00 | 1.6789( 41) | 0.000 | -2.000 | 1.852( 21) |
| O22 | 1.00 | 1.6856( 43) | 0.000 | -2.000 | 1.819( 21) |
| O23 | 4.00 | 2.2472( 18) | 227.161 | -2.000 | 2.098( 11) |
| O24 | 3.00 | 2.0319( 19) | 14.269 | -2.000 | 2.155( 11) |
| O25 | 1.00 | 1.6925( 42) | 0.000 | -2.000 | 1.785( 20) |
| O26 | 2.00 | 1.9176( 27) | 47.989 | -2.000 | 2.070( 16) |

| | | | | | |
|---|---|---|---|---|---|
| O27 | 1.00 | 1.7010( 38) | 0.000 | -2.000 | 1.745( 18) |
| O28 | 2.00 | 1.9105( 26) | 47.126 | -2.000 | 2.107( 16) |
| O29 | 2.00 | 1.9496( 25) | 29.276 | -2.000 | 1.819( 13) |
| O30 | 3.00 | 2.0749( 19) | 11.418 | -2.000 | 1.879( 10) |
| O31 | 3.00 | 2.1574( 19) | 141.940 | -2.000 | 1.839( 11) |
| O32 | 2.00 | 1.9367( 25) | 12.015 | -2.000 | 1.834( 13) |
| O33 | 2.00 | 1.9530( 25) | 0.793 | -2.000 | 1.670( 11) |
| O34 | 3.00 | 2.0570( 19) | 7.417 | -2.000 | 1.957( 10) |
| O35 | 2.00 | 1.9395( 28) | 41.321 | -2.000 | 1.901( 15) |
| O36 | 3.00 | 2.0580( 20) | 31.823 | -2.000 | 2.068( 12) |
| O37 | 3.00 | 2.0526( 19) | 28.466 | -2.000 | 2.084( 11) |
| O38 | 2.00 | 1.9397( 24) | 8.467 | -2.000 | 1.809( 12) |
| O39 | 1.00 | 1.6886( 39) | 0.000 | -2.000 | 1.804( 19) |
| O40 | 1.00 | 1.7022( 41) | 0.000 | -2.000 | 1.739( 19) |
| O41 | 3.00 | 2.0631( 19) | 9.047 | -2.000 | 1.932( 10) |
| O42 | 2.00 | 2.1089( 23) | -0.002 | -2.000 | 1.095( 7) |
| O43 | 3.00 | 2.1413( 19) | 128.255 | -2.000 | 1.871( 11) |
| O44 | 3.00 | 2.0615( 19) | 3.630 | -2.000 | 1.920( 10) |
| N1 | 1.00 | 2.2212( 36) | 0.000 | -3.000 | 0.618( 6) |
| N2 | 1.00 | 2.2392( 34) | 0.000 | -3.000 | 0.588( 5) |
| N3 | 1.00 | 2.2434( 37) | 0.000 | -3.000 | 0.582( 6) |
| N4 | 1.00 | 2.2018( 35) | 0.000 | -3.000 | 0.651( 6) |
| N5 | 1.00 | 2.2161( 33) | 0.000 | -3.000 | 0.626( 6) |
| N6 | 1.00 | 2.2221( 41) | 0.000 | -3.000 | 0.616( 7) |
| N7 | 1.00 | 2.2407( 36) | 0.000 | -3.000 | 0.586( 6) |
| N8 | 1.00 | 2.2282( 27) | 0.000 | -3.000 | 0.606( 4) |
| N9 | 1.00 | 2.2216( 37) | 0.000 | -3.000 | 0.617( 6) |
| N10 | 1.00 | 2.2111( 27) | 0.000 | -3.000 | 0.635( 5) |
| N11 | 1.00 | 2.2046( 28) | 0.000 | -3.000 | 0.646( 5) |
| N12 | 1.00 | 2.1958( 24) | 0.000 | -3.000 | 0.662( 4) |

**Table S2** Bond valance sum analyses for **2.**

| Atom | Coord | D_aver | Sigm | Distort(x10-4) | Valence | BVSum(Sigma) |
|---|---|---|---|---|---|---|
| Zn | 5.00 | 2.0477( | 24) | 15.886 | 2.000 | 2.023( 13) |
| Mo1 | 6.00 | 2.0463( | 23) | 24.533 | 4.000 | 4.243( 27) |
| Mo2 | 6.00 | 2.0752( | 24) | 29.786 | 4.000 | 3.989( 26) |
| Mo3 | 6.00 | 2.0552( | 23) | 19.503 | 4.000 | 4.125( 26) |
| Mo4 | 6.00 | 1.9904( | 22) | 124.198 | 6.000 | 5.618( 40) |
| Mo5 | 6.00 | 1.9885( | 22) | 99.818 | 6.000 | 5.514( 37) |
| Mo6 | 6.00 | 1.9846( | 24) | 135.314 | 6.000 | 5.779( 49) |
| Mo7 | 6.00 | 1.9910( | 23) | 161.635 | 6.000 | 5.750( 44) |
| Mo8 | 6.00 | 1.9938( | 23) | 166.130 | 6.000 | 5.723( 44) |
| Mo9 | 6.00 | 1.9871( | 22) | 171.502 | 6.000 | 5.800( 38) |
| Mo10 | 6.00 | 1.9802( | 22) | 106.372 | 6.000 | 5.668( 38) |
| Mo11 | 6.00 | 1.9827( | 24) | 140.228 | 6.000 | 5.752( 51) |
| Mo12 | 6.00 | 1.9797( | 22) | 126.270 | 6.000 | 5.753( 40) |
| Mo13 | 6.00 | 1.9830( | 23) | 127.464 | 6.000 | 5.721( 42) |
| P1 | 4.00 | 1.5481( | 28) | 1.002 | 5.000 | 4.824( 37) |
| P2 | 4.00 | 1.5405( | 29) | 0.510 | 5.000 | 4.921( 39) |
| P3 | 4.00 | 1.5430( | 30) | 1.967 | 5.000 | 4.894( 40) |
| P4 | 4.00 | 1.5501( | 30) | 1.634 | 5.000 | 4.800( 39) |
| O1 | 4.00 | 2.0674( | 28) | 2.942 | -2.000 | 2.185( 16) |
| O2 | 2.00 | 1.9513( | 35) | 0.261 | -2.000 | 1.677( 16) |
| O3 | 2.00 | 1.9230( | 39) | 0.000 | -2.000 | 1.810( 19) |
| O4 | 2.00 | 1.9311( | 39) | 0.212 | -2.000 | 1.771( 19) |
| O5 | 2.00 | 1.8161( | 42) | 217.122 | -2.000 | 1.790( 22) |
| O6 | 2.00 | 1.8218( | 46) | 216.706 | -2.000 | 1.763( 24) |
| O7 | 2.00 | 1.7361( | 36) | 136.211 | -2.000 | 1.783( 19) |
| O8 | 1.00 | 1.5264( | 52) | 0.000 | -2.000 | 1.278( 18) |
| O9 | 3.00 | 1.9641( | 32) | 195.765 | -2.000 | 1.905( 20) |

| | | | | | |
|---|---|---|---|---|---|
| O10 | 2.00 | 1.8026( 38) | 201.468 | -2.000 | 1.837( 20) |
| O11 | 2.00 | 1.8159( 34) | 204.686 | -2.000 | 1.813( 18) |
| O12 | 1.00 | 1.5212( 69) | 0.001 | -2.000 | 1.295( 24) |
| O13 | 3.00 | 1.9529( 32) | 190.933 | -2.000 | 1.968( 20) |
| O14 | 2.00 | 1.7852( 38) | 174.590 | -2.000 | 1.895( 20) |
| O15 | 2.00 | 1.8073( 34) | 218.430 | -2.000 | 1.867( 19) |
| O16 | 1.00 | 1.5111( 70) | 0.000 | -2.000 | 1.331( 25) |
| O17 | 2.00 | 2.1116( 33) | 1.580 | -2.000 | 1.124( 10) |
| O18 | 2.00 | 2.1107( 33) | 1.602 | -2.000 | 1.127( 10) |
| O19 | 2.00 | 1.9007( 42) | 3.798 | -2.000 | 2.045( 23) |
| O20 | 2.00 | 1.9222( 40) | 0.248 | -2.000 | 1.920( 21) |
| O21 | 2.00 | 1.9181( 34) | 1.691 | -2.000 | 1.945( 17) |
| O22 | 2.00 | 1.9197( 40) | 1.431 | -2.000 | 1.936( 21) |
| O23 | 2.00 | 1.8940( 32) | 2.097 | -2.000 | 2.077( 18) |
| O24 | 4.00 | 2.2110( 26) | 277.986 | -2.000 | 1.869( 16) |
| O25 | 1.00 | 1.6828( 59) | 0.000 | -2.000 | 1.833( 29) |
| O26 | 2.00 | 1.9225( 34) | 1.438 | -2.000 | 1.922( 17) |
| O27 | 1.00 | 1.6859( 83) | 0.000 | -2.000 | 1.818( 41) |
| O28 | 1.00 | 1.6878( 71) | 0.000 | -2.000 | 1.808( 34) |
| O29 | 2.00 | 2.0776( 36) | 0.005 | -2.000 | 1.261( 12) |
| O30 | 4.00 | 2.2719( 28) | 340.514 | -2.000 | 1.794( 22) |
| O31 | 3.00 | 2.0877( 33) | 353.804 | -2.000 | 1.836( 20) |
| O32 | 1.00 | 1.6783( 64) | 0.000 | -2.000 | 1.856( 32) |
| O33 | 2.00 | 1.9146( 42) | 0.243 | -2.000 | 1.960( 22) |
| O34 | 1.00 | 1.6932( 49) | 0.000 | -2.000 | 1.782( 24) |
| O35 | 2.00 | 1.9151( 41) | 13.039 | -2.000 | 1.991( 22) |
| O36 | 2.00 | 1.9110( 39) | 0.000 | -2.000 | 1.978( 21) |
| O37 | 2.00 | 1.8987( 32) | 3.391 | -2.000 | 2.054( 18) |
| O38 | 2.00 | 1.9032( 32) | 7.515 | -2.000 | 2.041( 18) |
| O39 | 1.00 | 1.6775( 55) | 0.000 | -2.000 | 1.859( 28) |

| | | | | | |
|---|---|---|---|---|---|
| O40 | 1.00 | 1.6950( 71) | 0.000 | -2.000 | 1.773( 34) |
| O41 | 1.00 | 1.6813( 89) | 0.000 | -2.000 | 1.840( 44) |
| O42 | 3.00 | 2.0843( 33) | 341.660 | -2.000 | 1.826( 20) |
| O43 | 2.00 | 1.9091( 44) | 0.288 | -2.000 | 1.989( 24) |
| O44 | 2.00 | 1.9074( 41) | 1.516 | -2.000 | 2.002( 22) |
| O45 | 2.00 | 1.8965( 42) | 1.348 | -2.000 | 2.061( 23) |
| O46 | 3.00 | 1.9967( 30) | 0.091 | -2.000 | 2.028( 17) |
| O47 | 1.00 | 1.6903( 64) | 0.000 | -2.000 | 1.796( 31) |
| O48 | 2.00 | 1.9127( 33) | 16.939 | -2.000 | 2.014( 18) |
| O49 | 1.00 | 1.6676( 55) | 0.000 | -2.000 | 1.910( 28) |
| N1 | 1.00 | 2.2254( 68) | 0.000 | -3.000 | 0.611( 11) |
| N2 | 1.00 | 2.2207( 91) | 0.000 | -3.000 | 0.619( 15) |
| N3 | 1.00 | 2.2173( 67) | 0.000 | -3.000 | 0.624( 11) |