Oxidation Reactions Catalyzed by Polyoxomolybdate Salts

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1. Crystallographic data of compounds 1, 3 and 4

Table S1. Crystallographic details of **1**, **3** and **4**.

	1	**3**	**4**
Formula	$C_{32}H_{72}PO_{19}Mo_6$	$C_{16}H_{30}N_4O_{19}Mo_6$	$C_{18}H_{34}N_4O_{19}Mo_6$
M_r	1398.48	1158.08	1186.13
Cryst. size, mm^3	0.25 × 0.26 × 0.47	0.10 × 0.20 × 0.22	0.24 × 0.41 × 0.46
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1/c$	$P2_1/n$
a, Å	16.0547(3)	8.5458(16)	11.0074(2)
b, Å	16.0680(3)	17.085(3)	10.7827(2)
c, Å	19.7281(4)	11.075(2)	13.5900(3)
α, deg	90	90	90
β, deg	106.2476(7)	108.937(8)	91.045(1)
γ, deg	90	90	90
V, Å^3	4885.94(16)	1529.5(5)	1612.72(5)
Z	4	2	2
D_{calcd}, g cm^{-3}	1.901	2.515	2.443
$\mu(MoK_\alpha)$, mm^{-1}	1.625	2.471	2.347
F(000), e	2792	1116	1148
hkl range	$-19 \le h \le +19$	$-10 \le h \le +10$	$-13 \le h \le +13$
	$-19 \le k \le +19$	$-20 \le k \le +20$	$-13 \le k \le +13$
	$-21 \le l \le +23$	$-13 \le l \le +13$	$-16 \le l \le +16$
$\theta_{min/max}$, deg	1.8, 25.4	2.4, 25.6	2.4, 25.5
Refl. measured	15516	48445	40353
Refl. unique	4475	2836	2928
R_{int}	0.017	0.048	0.82
Param. refined	414	208	218
$R(F)/wR(F^2)$[a] (all reflexions)	0.0177, 0.0370	0.0196, 0.0395	0.0264, 0.0660
GoF (F^2)[b]	1.05	1.06	1.16
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.34, -0.34	0.34, -0.27	1.36, -0.58

[a] $R_1 = ||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$; [b] GoF = $[\Sigma w(F_o^2-F_c^2)^2/(n_{obs}-n_{param})]^{1/2}$

2. Experimental details, bond distances and angles of compounds 1, 3 and 4

2.1. Experimental details, bond distances and angles of **1**

$C_{32}H_{72}PMo_6O_{19}$ (**1**): a clear pale yellow fragment-like specimen of $C_{32}H_{72}Mo_6O_{19}P_2$, approximate dimensions 0.252 mm x 0.260 mm x 0.469 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2592 frames were collected. The total exposure time was 7.20 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 42081 reflections to a maximum θ angle of 25.35° (0.83 Å resolution). The final cell

constants of a = 16.0547(3) Å, b = 16.0680(3) Å, c = 19.7281(4) Å, β = 106.2476(7)°, volume = 4885.94(16) Å^3, are based upon the refinement of the XYZ-centroids of 216 reflections above 20 σ(I) with 3.605° < 2θ < 66.77°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.909. Bond distances and angles of **1** are shown in Table S2 and Table S3.

Table S2. Bond distances (Å) in compound **1**.

Mo1	-O2	1.6779(18)	C14	-C15	1.518(3)
Mo1	-O7	1.9284(13)	C15	-C16	1.520(3)
Mo1	-O9	1.9298(13)	C1	-H1B	0.93(2)
Mo1	-O7_a	1.9284(13)	C1	-H1A	0.94(2)
Mo1	-O9_a	1.9298(13)	C2	-H2A	0.95(3)
Mo1	-O1	2.3177(16)	C1	-H2B	0.90(3)
Mo2	-O1	2.3135(16)	C3	-H3A	0.99(3)
Mo2	-O11_a	1.9308(13)	C3	-H3B	0.91(2)
Mo2	-O8_a	1.9269(13)	C4	-H4A	0.97(3)
Mo2	-O11	1.9308(13)	C4	-H4B	0.95(3)
Mo2	-O3	1.6800(19)	C4	-H4C	0.93(3)
Mo2	-O8	1.9269(13)	C5	-H5A	0.95(2)
Mo3	-O4	1.6833(13)	C5	-H5B	0.92(2)
Mo3	-O9	1.9287(13)	C6	-H6A	0.96(2)
Mo3	-O10	2.0020(13)	C6	-H6B	0.94(2)
Mo3	-O11	1.9227(13)	C7	-H7B	0.98(2)
Mo3	-O1	2.3188(2)	C7	-H7A	0.94(2)
Mo3	-O6_a	1.8610(13)	C8	-H8A	0.99(3)
Mo4	-O6	1.9902(13)	C8	-H8B	0.92(3)
Mo4	-O8	1.9193(13)	C8	-H8C	0.94(3)
Mo4	-O10	1.8681(14)	C9	-H9A	0.92(2)
Mo4	-O7	1.9282(13)	C9	-H9B	0.89(2)
Mo4	-O1	2.3177(2)	C10	-H10A	0.91(2)
Mo4	-O5	1.6879(14)	C10	-H10B	0.92(2)
P1	-C1	1.804(2)	C11	-H11A	0.95(2)
P1	-C5	1.801(2)	C11	-H11B	0.93(2)
P1	-C9	1.803(2)	C12	-H12A	0.96(2)
P1	-C13	1.800(2)	C12	-H12B	0.92(2)
C1	-C2	1.528(3)	C12	-H12C	0.90(3)
C2	-C3	1.517(3)	C13	-H13B	0.92(2)
C3	-C4	1.514(4)	C13	-H13A	0.92(2)
C5	-C6	1.528(3)	C14	-H14A	0.94(2)
C6	-C7	1.524(3)	C14	-H14B	0.94(2)
C7	-C8	1.518(3)	C15	-H15B	0.96(2)
C9	-C10	1.527(3)	C15	-H15A	0.93(2)
C10	-C11	1.518(3)	C16	-H16C	0.92(3)
C11	-C12	1.519(3)	C16	-H16A	0.94(2)
C13	-C14	1.528(3)	C16	-H16B	0.95(3)

Table S3. Bond angles (°) in compound **1**.

O2	-Mo1	-O7_a	103.17(4)	O5	-Mo4	-O6	102.04(6)
O2	-Mo1	-O9_a	103.42(4)	O7	-Mo4	-O8	152.87(6)
O7	-Mo1	-O9	86.94(6)	O6	-Mo4	-O8	84.47(5)
O7	-Mo1	-O7_a	153.67(6)	O6	-Mo4	-O10	153.85(6)
O7	-Mo1	-O9_a	87.00(6)	C1	-P1	-C13	105.02(10)

O7_a	-Mo1	-O9	87.00(6)	C5	-P1	-C9	110.02(10)
O9	-Mo1	-O9_a	153.16(6)	C5	-P1	-C13	112.35(10)
O7_a	-Mo1	-O9_a	86.94(6)	C9	-P1	-C13	108.48(9)
O1	-Mo1	-O2	180.00(1)	C1	-P1	-C5	108.37(9)
O1	-Mo1	-O7	76.83(4)	C1	-P1	-C9	112.55(9)
O1	-Mo1	-O9	76.58(4)	Mo1	-O1	-Mo2	180.00(1)
O1	-Mo1	-O7_a	76.83(4)	Mo1	-O1	-Mo3	90.13(4)
O1	-Mo1	-O9_a	76.58(4)	Mo1	-O1	-Mo4	89.92(4)
O2	-Mo1	-O7	103.17(4)	Mo1	-O1	-Mo3_a	90.13(4)
O2	-Mo1	-O9	103.42(4)	Mo3	-O1	-Mo3_a	179.74(8)
O8	-Mo2	-O8_a	152.87(6)	Mo1	-O1	-Mo4_a	89.92(4)
O8	-Mo2	-O11_a	87.00(6)	Mo2	-O1	-Mo3	89.87(4)
O8_a	-Mo2	-O11	87.00(6)	Mo2	-O1	-Mo4	90.08(4)
O11	-Mo2	-O11_a	153.71(6)	Mo2	-O1	-Mo3_a	89.87(4)
O8_a	-Mo2	-O11_a	86.89(6)	Mo2	-O1	-Mo4_a	90.08(4)
O1	-Mo2	-O11_a	76.86(4)	Mo3	-O1	-Mo4	90.20(1)
O3	-Mo2	-O8	103.56(4)	Mo4	-O1	-Mo4_a	179.85(8)
O3	-Mo2	-O11	103.14(4)	Mo3	-O1	-Mo4_a	89.81(1)
O1	-Mo2	-O3	180.00(1)	Mo3_a	-O1	-Mo4	89.81(1)
O1	-Mo2	-O8	76.44(4)	Mo3_a	-O1	-Mo4_a	90.20(1)
O1	-Mo2	-O11	76.86(4)	Mo3_a	-O6	-Mo4	116.35(7)
O1	-Mo2	-O8_a	76.44(4)	Mo1	-O7	-Mo4	116.28(7)
O3	-Mo2	-O8_a	103.56(4)	Mo2	-O8	-Mo4	116.86(7)
O3	-Mo2	-O11_a	103.14(4)	Mo1	-O9	-Mo3	116.57(7)
O8	-Mo2	-O11	86.89(6)	Mo3	-O10	-Mo4	116.07(7)
O1	-Mo3	-O4	176.62(5)	Mo2	-O11	-Mo3	116.22(7)
O1	-Mo3	-O9	76.57(6)	P1	-C1	-C2	118.17(15)
O1	-Mo3	-O10	75.61(4)	C1	-C2	-C3	111.72(19)
O10	-Mo3	-O11	84.58(5)	C2	-C3	-C4	113.6(2)
O6_a	-Mo3	-O10	153.70(6)	P1	-C5	-C6	115.66(14)
O6_a	-Mo3	-O11	90.42(6)	C5	-C6	-C7	111.66(17)
O4	-Mo3	-O11	102.94(6)	C6	-C7	-C8	111.34(18)
O4	-Mo3	-O6_a	105.28(6)	P1	-C9	-C10	116.21(14)
O9	-Mo3	-O10	83.81(5)	C9	-C10	-C11	111.75(17)
O1	-Mo3	-O11	76.88(6)	C10	-C11	-C12	112.81(17)
O1	-Mo3	-O6_a	78.10(4)	P1	-C13	-C14	118.12(15)
O4	-Mo3	-O9	103.25(6)	C13	-C14	-C15	110.66(17)
O4	-Mo3	-O10	101.00(6)	C14	-C15	-C16	112.63(19)
O9	-Mo3	-O11	152.92(6)	P1	-C1	-H1A	105.0(13)
O6_a	-Mo3	-O9	89.26(6)	C2	-C1	-H1A	108.7(14)
O1	-Mo4	-O7	76.84(6)	C2	-C1	-H1B	110.7(14)
O1	-Mo4	-O5	177.38(5)	P1	-C1	-H1B	108.1(14)
O1	-Mo4	-O6	75.74(4)	H1A	-C1	-H1B	105(2)
O7	-Mo4	-O10	89.21(6)	C3	-C2	-H2A	111.4(15)
O8	-Mo4	-O10	89.99(6)	C3	-C2	-H2B	109.4(17)
O5	-Mo4	-O7	101.66(6)	H2A	-C2	-H2B	106(2)
O5	-Mo4	-O8	104.82(6)	C1	-C2	-H2B	109.0(17)
O5	-Mo4	-O10	104.09(6)	C1	-C2	-H2A	108.9(16)
O6	-Mo4	-O7	84.40(5)	C4	-C3	-H3A	109.3(16)
O1	-Mo4	-O8	76.47(6)	C2	-C3	-H3A	107.6(15)
O1	-Mo4	-O10	78.11(4)	C2	-C3	-H3B	112.2(15)
H3A	-C3	-H3B	104(2)	C9	-C10	-H10B	110.3(16)
C4	-C3	-H3B	109.4(16)	C11	-C10	-H10B	111.0(15)
C3	-C4	-H4B	109.7(19)	C9	-C10	-H10A	109.7(16)
C3	-C4	-H4A	110.2(17)	C10	-C11	-H11A	106.9(15)
H4A	-C4	-H4C	111(3)	C12	-C11	-H11B	108.2(15)
C3	-C4	-H4C	108.8(19)	H11A	-C11	-H11B	110(2)
H4A	-C4	-H4B	110(2)	C10	-C11	-H11B	108.1(14)
H4B	-C4	-H4C	108(3)	C12	-C11	-H11A	110.7(15)
P1	-C5	-H5A	108.3(13)	C11	-C12	-H12A	109.8(14)
P1	-C5	-H5B	106.7(14)	H12A	-C12	-H12B	105(2)
C6	-C5	-H5A	109.0(13)	C11	-C12	-H12B	112.1(15)

C6	-C5	-H5B	111.3(13)	C11	-C12	-H12C	111.9(17)
H5A	-C5	-H5B	105.4(19)	H12B	-C12	-H12C	108(2)
C5	-C6	-H6A	108.6(13)	H12A	-C12	-H12C	110(2)
C5	-C6	-H6B	111.3(13)	P1	-C13	-H13B	104.7(14)
C7	-C6	-H6A	109.7(13)	P1	-C13	-H13A	103.5(15)
C7	-C6	-H6B	108.6(13)	H13A	-C13	-H13B	107.3(19)
H6A	-C6	-H6B	106.9(19)	C14	-C13	-H13A	110.4(13)
C6	-C7	-H7A	108.3(13)	C14	-C13	-H13B	112.0(13)
C6	-C7	-H7B	109.4(12)	C15	-C14	-H14B	109.7(15)
C8	-C7	-H7A	111.0(13)	H14A	-C14	-H14B	108(2)
C8	-C7	-H7B	110.4(11)	C15	-C14	-H14A	108.6(14)
H7A	-C7	-H7B	106.4(18)	C13	-C14	-H14A	111.1(13)
H8A	-C8	-H8B	109(2)	C13	-C14	-H14B	108.9(14)
H8A	-C8	-H8C	107(2)	C14	-C15	-H15A	110.9(14)
H8B	-C8	-H8C	105(2)	C14	-C15	-H15B	109.6(13)
C7	-C8	-H8B	111.0(17)	C16	-C15	-H15A	109.5(13)
C7	-C8	-H8C	113.1(15)	C16	-C15	-H15B	109.0(13)
C7	-C8	-H8A	112.1(15)	H15A	-C15	-H15B	104.9(18)
P1	-C9	-H9A	106.1(15)	C15	-C16	-H16C	111.9(15)
P1	-C9	-H9B	104.9(16)	H16A	-C16	-H16C	108(2)
C10	-C9	-H9A	110.5(16)	H16B	-C16	-H16C	107(2)
C10	-C9	-H9B	112.0(16)	H16A	-C16	-H16B	107(2)
H9A	-C9	-H9B	107(2)	C15	-C16	-H16A	111.2(14)
C11	-C10	-H10A	110.6(16)	C15	-C16	-H16B	111.4(14)
H10A	-C10	-H10B	103(2)				

2.2. Experimental details, bond distances and angles of **3**

$C_{16}H_{30}$ N_4 Mo_6O_{19} (**3**): a clear light yellow fragment-like specimen of Mo_6 O_{19}, 2(C_8 H_{15} N_2), approximate dimensions 0.104 x 0.196 x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 3967 frames were collected. The total exposure time was 5.51 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 48484 reflections to a maximum θ angle of 25.62° (0.82 Å resolution), of which 2838 were independent (average redundancy 17.084, completeness = 98.2%, R_{int} = 4.83%, R_{sig} = 1.79%) and 2586 (91.12%) were greater than 2σ(F2). The final cell constants of a = 8.5458(16) Å, b = 17.085(3) Å, c = 11.075(2) Å, β = 108.937(8)°, volume = 1529.5(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 61 reflections above 20 σ(I) with 4.568° < 2θ < 56.01°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.894. Bond distances and angles of **3** are shown in Table S4 and Table S5.

Table S4. Bond distances (Å) in compound **3**.

Mo1	-O2	2.3206(5)	N2	-C3	1.373(4)
Mo1	-O5	1.8507(18)	N2	-C8	1.470(4)
Mo1	-O8	1.9738(17)	C2	-C3	1.343(4)
Mo1	-O9	1.6815(18)	C4	-C5	1.509(3)
Mo1	-O1_a	2.0149(18)	C5	-C6	1.532(4)
Mo1	-O6_a	1.8877(17)	C6	-C7	1.504(5)
Mo2	-O1	1.8620(18)	C1	-H1	0.9500
Mo2	-O2	2.3286(5)	C2	-H2	0.9500
Mo2	-O3	1.9229(17)	C3	-H3	0.9500
Mo2	-O5	2.0052(18)	C4	-H4A	0.9900
Mo2	-O10	1.6784(18)	C4	-H4B	0.9900
Mo2	-O4_a	1.9333(18)	C5	-H5A	0.9900
Mo3	-O2	2.3178(5)	C5	-H5B	0.9900
Mo3	-O3	1.9318(18)	C6	-H6A	0.9900
Mo3	-O4	1.9356(18)	C6	-H6B	0.9900
Mo3	-O6	1.9661(18)	C7	-H7A	0.9800
Mo3	-O7	1.6812(19)	C7	-H7B	0.9800
Mo3	-O8	1.8835(17)	C7	-H7C	0.9800
N1	-C1	1.330(3)	C8	-H8A	0.9800
N1	-C2	1.373(3)	C8	-H8B	0.9800
N1	-C4	1.476(3)	C8	-H8C	0.9800
N2	-C1	1.333(3)			

Table S5. Bond angles (°) in compound **3**.

O2	-Mo1	-O5	78.25(6)	Mo2_a	-O2	-Mo3	89.94(1)
O2	-Mo1	-O8	75.66(5)	Mo3	-O2	-Mo3_a	180.00
O2	-Mo1	-O9	175.56(6)	Mo1_a	-O2	-Mo2_a	89.82(1)
O1_a	-Mo1	-O2	75.48(5)	Mo1_a	-O2	-Mo3_a	90.10(1)
O2	-Mo1	-O6_a	77.38(5)	Mo2_a	-O2	-Mo3_a	90.06(1)
O5	-Mo1	-O8	88.26(7)	Mo2	-O3	-Mo3	117.03(9)
O5	-Mo1	-O9	105.62(8)	Mo2_a	-O4	-Mo3	116.16(9)
O1_a	-Mo1	-O5	153.54(7)	Mo1	-O5	-Mo2	116.64(9)
O5	-Mo1	-O6_a	92.29(7)	Mo1_a	-O6	-Mo3	116.48(8)
O8	-Mo1	-O9	102.06(8)	Mo1	-O8	-Mo3	116.64(8)
O1_a	-Mo1	-O8	82.32(7)	C1	-N1	-C2	108.4(2)
O6_a	-Mo1	-O8	152.33(7)	C1	-N1	-C4	127.2(2)
O1_a	-Mo1	-O9	100.53(8)	C2	-N1	-C4	124.41(19)
O6_a	-Mo1	-O9	104.41(8)	C1	-N2	-C3	108.2(2)
O1_a	-Mo1	-O6_a	85.06(7)	C1	-N2	-C8	125.1(2)
O1	-Mo2	-O2	78.09(5)	C3	-N2	-C8	126.7(2)
O1	-Mo2	-O3	89.57(7)	N1	-C1	-N2	108.7(2)
O1	-Mo2	-O5	153.31(7)	N1	-C2	-C3	107.3(2)
O1	-Mo2	-O10	103.93(8)	N2	-C3	-C2	107.5(2)
O1	-Mo2	-O4_a	90.31(7)	N1	-C4	-C5	112.8(2)
O2	-Mo2	-O3	76.39(5)	C4	-C5	-C6	111.1(2)
O2	-Mo2	-O5	75.22(5)	C5	-C6	-C7	113.0(3)
O2	-Mo2	-O10	177.82(6)	N1	-C1	-H1	126.00
O2	-Mo2	-O4_a	76.60(5)	N2	-C1	-H1	126.00
O3	-Mo2	-O5	83.89(7)	N1	-C2	-H2	126.00
O3	-Mo2	-O10	104.34(8)	C3	-C2	-H2	126.00
O3	-Mo2	-O4_a	152.41(7)	N2	-C3	-H3	126.00
O5	-Mo2	-O10	102.77(8)	C2	-C3	-H3	126.00
O4_a	-Mo2	-O5	83.92(7)	N1	-C4	-H4A	109.00
O4_a	-Mo2	-O10	102.45(8)	N1	-C4	-H4B	109.00
O2	-Mo3	-O3	76.50(5)	C5	-C4	-H4A	109.00
O2	-Mo3	-O4	76.83(5)	C5	-C4	-H4B	109.00
O2	-Mo3	-O6	76.01(5)	H4A	-C4	-H4B	108.00

O2	-Mo3	-O7	177.35(7)	C4	-C5	-H5A	109.00
O2	-Mo3	-O8	77.38(5)	C4	-C5	-H5B	109.00
O3	-Mo3	-O4	153.12(7)	C6	-C5	-H5A	109.00
O3	-Mo3	-O6	85.08(7)	C6	-C5	-H5B	109.00
O3	-Mo3	-O7	102.21(8)	H5A	-C5	-H5B	108.00
O3	-Mo3	-O8	88.76(7)	C5	-C6	-H6A	109.00
O4	-Mo3	-O6	85.40(7)	C5	-C6	-H6B	109.00
O4	-Mo3	-O7	104.31(8)	C7	-C6	-H6A	109.00
O4	-Mo3	-O8	88.59(7)	C7	-C6	-H6B	109.00
O6	-Mo3	-O7	101.63(8)	H6A	-C6	-H6B	108.00
O6	-Mo3	-O8	153.39(7)	C6	-C7	-H7A	109.00
O7	-Mo3	-O8	104.97(8)	C6	-C7	-H7B	109.00
Mo1_a	-O1	-Mo2	116.21(8)	C6	-C7	-H7C	109.00
Mo1	-O2	-Mo2	89.82(1)	H7A	-C7	-H7B	109.00
Mo1	-O2	-Mo3	90.10(1)	H7A	-C7	-H7C	110.00
Mo1	-O2	-Mo1_a	180.00	H7B	-C7	-H7C	109.00
Mo1	-O2	-Mo2_a	90.18(1)	N2	-C8	-H8A	109.00
Mo1	-O2	-Mo3_a	89.90(1)	N2	-C8	-H8B	110.00
Mo2	-O2	-Mo3	90.06(1)	N2	-C8	-H8C	109.00
Mo1_a	-O2	-Mo2	90.18(1)	H8A	-C8	-H8B	109.00
Mo2	-O2	-Mo2_a	180.00	H8A	-C8	-H8C	109.00
Mo2	-O2	-Mo3_a	89.94(1)	H8B	-C8	-H8C	109.00
Mo1_a	-O2	-Mo3	89.90(1)				

2.3. Experimental details, bond distances and angles of **4**

$C_{18}H_{34}N_4$ Mo_6O_{19} (**4**): a clear light yellow fragment-like specimen of 2(C_9 H_{17} N_2), Mo_6 O_{19}, approximate dimensions 0.240 mm x 0.410 mm x 0.460 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 3797 frames were collected. The total exposure time was 5.28 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 40353 reflections to a maximum θ angle of 25.47° (0.83 Å resolution), of which 2989 were independent (average redundancy 13.501, completeness = 99.9%, R_{int} = 8.15%, R_{sig} = 2.24%) and 2902 (97.09%) were greater than 2σ(F2). The final cell constants of a = 11.0074(2) Å, b = 10.7827(2) Å, c = 13.5900(3) Å, β = 91.0450(10)°, volume = 1612.72(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 179 reflections above 20 σ(I) with 3.027° < 2θ < 65.42°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.788. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4091 and 0.5983. Bond distances and angles of **4** are shown in Table S6 and Table S7.

Table S6. Bond distances (Å) in compound **4**.

Mo1	-O5	1.967(2)	N2	-C8	1.434(6)
Mo1	-O9	1.937(3)	C1	-C9	1.451(6)
Mo1	-O10	1.681(3)	C2	-C3	1.305(6)
Mo1	-O1	1.903(2)	C4	-C5	1.527(5)
Mo1	-O2	2.3162(3)	C5	-C6	1.519(6)
Mo1	-O4	1.891(2)	C6	-C7	1.524(6)
Mo2	-O1	1.944(3)	C2	-H2	0.9500
Mo2	-O2	2.3157(3)	C3	-H3	0.9500
Mo2	-O6	1.898(2)	C4	-H4A	0.9900
Mo2	-O9_a	1.906(3)	C4	-H4B	0.9900
Mo2	-O8	1.678(3)	C5	-H5A	0.9900
Mo2	-O7_a	1.969(2)	C5	-H5B	0.9900
Mo3	-O2	2.3243(3)	C6	-H6A	0.9900
Mo3	-O3	1.686(2)	C6	-H6B	0.9900
Mo3	-O4	1.971(2)	C7	-H7A	0.9800
Mo3	-O6	1.971(2)	C7	-H7B	0.9800
Mo3	-O5_a	1.888(2)	C7	-H7C	0.9800
Mo3	-O7	1.874(2)	C8	-H8C	0.9800
N1	-C2	1.425(6)	C8	-H8A	0.9800
N1	-C1	1.327(5)	C8	-H8B	0.9800
N1	-C4	1.476(6)	C9	-H9A	0.9800
N2	-C3	1.421(6)	C9	-H9B	0.9800
N2	-C1	1.308(6)	C9	-H9C	0.9800

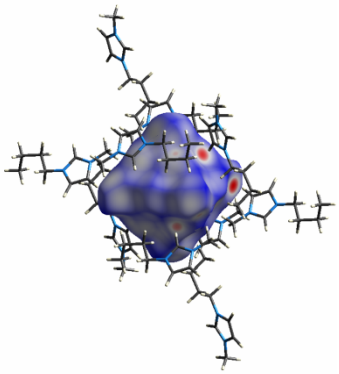
Table S7. Bond angles (°)in compound **4**.

O5	-Mo1	-O9	84.56(11)	Mo2_a	-O2	-Mo3	89.98(1)
O5	-Mo1	-O10	101.76(13)	Mo3	-O2	-Mo3_a	180.00
O9	-Mo1	-O10	102.61(13)	Mo1_a	-O2	-Mo3	89.94(1)
O2	-Mo1	-O4	77.59(7)	Mo1_a	-O2	-Mo3_a	90.06(1)
O2	-Mo1	-O5	76.03(7)	Mo1_a	-O2	-Mo2_a	89.84(1)
O1	-Mo1	-O2	77.13(7)	Mo1	-O4	-Mo3	116.40(12)
O1	-Mo1	-O4	89.00(10)	Mo1	-O5	-Mo3_a	116.59(12)
O1	-Mo1	-O5	86.48(10)	Mo2	-O6	-Mo3	116.01(11)
O1	-Mo1	-O9	153.05(10)	Mo2_a	-O7	-Mo3	117.15(12)
O1	-Mo1	-O10	104.09(13)	Mo1	-O9	-Mo2_a	117.18(13)
O2	-Mo1	-O10	177.46(11)	C1	-N1	-C4	127.4(4)
O4	-Mo1	-O5	153.59(10)	C1	-N1	-C2	107.7(4)
O2	-Mo1	-O9	76.05(7)	C2	-N1	-C4	124.5(3)
O4	-Mo1	-O10	104.59(13)	C1	-N2	-C3	107.9(3)
O4	-Mo1	-O9	87.84(11)	C1	-N2	-C8	131.4(4)
O1	-Mo2	-O6	87.73(10)	C3	-N2	-C8	120.5(4)
O1	-Mo2	-O2	76.39(7)	N2	-C1	-C9	124.7(4)
O7_a	-Mo2	-O9_a	85.71(11)	N1	-C1	-C9	125.5(4)
O2	-Mo2	-O7_a	75.67(7)	N1	-C1	-N2	109.7(4)
O2	-Mo2	-O9_a	76.62(8)	N1	-C2	-C3	106.9(4)
O1	-Mo2	-O8	104.08(12)	N2	-C3	-C2	107.8(4)
O1	-Mo2	-O7_a	84.68(10)	N1	-C4	-C5	109.3(3)
O1	-Mo2	-O9_a	152.83(10)	C4	-C5	-C6	111.5(3)
O2	-Mo2	-O6	77.70(7)	C5	-C6	-C7	111.5(3)
O2	-Mo2	-O8	178.73(10)	C3	-C2	-H2	126.00
O6	-Mo2	-O7_a	153.33(10)	N1	-C2	-H2	127.00
O6	-Mo2	-O9_a	89.57(11)	N2	-C3	-H3	126.00
O6	-Mo2	-O8	103.48(12)	C2	-C3	-H3	126.00
O8	-Mo2	-O9_a	102.84(12)	N1	-C4	-H4A	110.00
O7_a	-Mo2	-O8	103.17(12)	N1	-C4	-H4B	110.00
O2	-Mo3	-O4	75.92(6)	H4A	-C4	-H4B	108.00
O2	-Mo3	-O3	177.79(8)	C5	-C4	-H4B	110.00
O5_a	-Mo3	-O7	90.38(11)	C5	-C4	-H4A	110.00
O3	-Mo3	-O6	102.12(10)	C6	-C5	-H5A	109.00
O3	-Mo3	-O7	104.46(11)	C4	-C5	-H5B	109.00

O3	-Mo3	-O5_a	104.08(11)	C4	-C5	-H5A	109.00
O2	-Mo3	-O6	76.15(6)	C6	-C5	-H5B	109.00
O2	-Mo3	-O7	77.19(7)	H5A	-C5	-H5B	108.00
O2	-Mo3	-O5_a	77.29(7)	C5	-C6	-H6A	109.00
O3	-Mo3	-O4	102.59(11)	H6A	-C6	-H6B	108.00
O5_a	-Mo3	-O6	86.79(10)	C5	-C6	-H6B	109.00
O4	-Mo3	-O7	87.25(10)	C7	-C6	-H6A	109.00
O4	-Mo3	-O5_a	152.96(9)	C7	-C6	-H6B	109.00
O4	-Mo3	-O6	83.35(10)	C6	-C7	-H7A	109.00
O6	-Mo3	-O7	153.15(9)	C6	-C7	-H7B	110.00
Mo1	-O1	-Mo2	116.44(11)	C6	-C7	-H7C	110.00
Mo1	-O2	-Mo3	90.06(1)	H7B	-C7	-H7C	109.00
Mo1	-O2	-Mo2	89.84(1)	H7A	-C7	-H7B	109.00
Mo2_a	-O2	-Mo3_a	90.03(1)	H7A	-C7	-H7C	109.00
Mo2	-O2	-Mo2_a	180.00	N2	-C8	-H8B	109.00
Mo2	-O2	-Mo3_a	89.98(1)	H8A	-C8	-H8C	109.00
Mo1	-O2	-Mo1_a	180.00	N2	-C8	-H8C	110.00
Mo1	-O2	-Mo2_a	90.16(1)	H8A	-C8	-H8B	109.00
Mo1	-O2	-Mo3_a	89.94(1)	N2	-C8	-H8A	109.00
Mo2	-O2	-Mo3	90.03(1)	H8B	-C8	-H8C	110.00
Mo1_a	-O2	-Mo2	90.16(1)	C1	-C9	-H9C	109.00
H9A	-C9	-H9C	109.00	C1	-C9	-H9A	109.00
H9B	-C9	-H9C	109.00	C1	-C9	-H9B	110.00
H9A	-C9	-H9B	110.00				

2.4. Hirshfeld Surface Analysis

$[Bmim]_2[Mo_6O_{19}]$



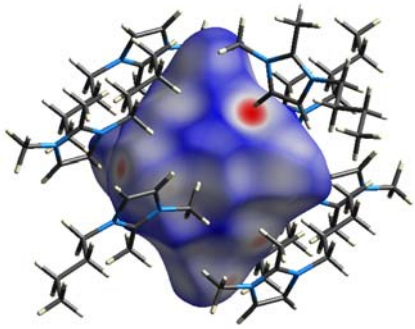
(**3**)

d_{norm}:

Min	-0.2863
Max	10.435
Mean	0.3811
Mean+	0.3951
Mean-	**-0.0860**

all contacts:

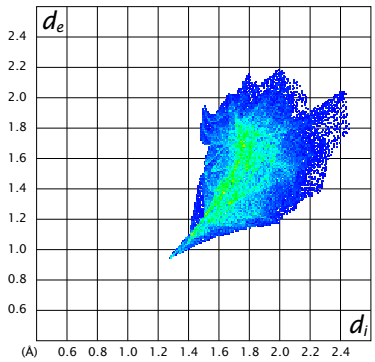
$Dmbim]_2[Mo_6O_{19}]$ (**4**)

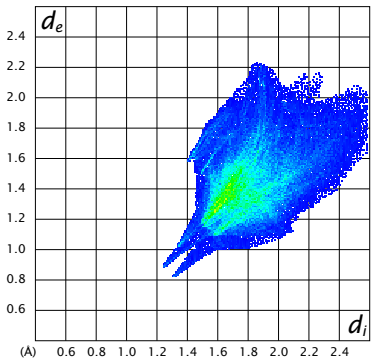


d_{norm}:

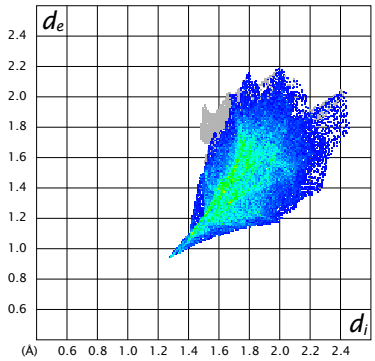
Min	-0.3784
Max	11.577
Mean	0.4164
Mean+	0.4333
Mean-	**-0.1021**

all contacts:

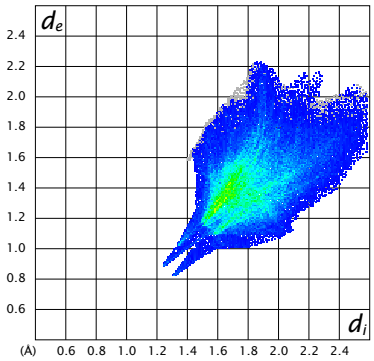




O-H interaction: (**84.7%** of all)



O-H interaction: (**93.7%** of all)



3. Characterization data of sulfoxides

1) Dimethyl sulfoxide: colorless liquid. IR (cm^{-1}): 1015. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t. ppm): δ = 2.47 (s, 6H). ^{13}C NMR ($CDCl_3$, 100Hz, r.t., ppm): δ = 41.30.

2) Dibutyl sulfoxide: white solid. M. p.: 30-32 ^{o}C. IR (cm^{-1}): 1023. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 0.98-1.01 (t, 6H), 1.48-1.52 (m, 4H), 1.83-1.87 (m, 4H), 2.94-2.99 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 13.53, 21.78, 23.95, 52.50.

3) Methyl phenyl sulfoxide: pale yellow oil. IR (cm^{-1}): 1032. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 2.60 (s, 3H), 7.39-7.40 (d, 3H), 7.53-7.55 (t, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 43.75, 123.29, 129.17, 130.81, 145.62.

4) Ethyl phenyl sulfoxide: yellow oil. IR (cm^{-1}): 1018. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 1.03 - 1.07 (t, 3H), 2.58-2.67 (m, 1H), 2.73-2.82 (m, 1H), 7.33 -7.40 (m, 3H), 7.47-7.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 6.06, 50.49, 124.38, 129.33, 131.08, 143.78.

5) Phenyl isopropyl sulfoxide: yellow oil. IR (cm^{-1}): 1020. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 1.04-1.06 (d, 3H), 1.14-1.15 (d, 3H), 2.73 - 2.77 (m, 3H), 7.41-7.44 (m, 3H), 7.50-7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 13.82, 15.84, 54.45, 124.91, 128.83, 130.93, 141.68.

6) Phenyl allyl sulfoxide: yellow oil. IR (cm^{-1}): 1037. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 3.39-3.52 (m, 2H), 5.08-5.13 (d, 1H), 5.22-5.25 (d, 1H), 5.51-5.59 (m, 1H), 7.41 - 7.45 (m, 3H), 7.51-7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 59.76, 122.85, 123.27, 124.19, 128.01, 130.06, 141.85

7) 2-(Phenylsulfinyl)ethanol: pale yellow oil. IR (cm^{-1}): 3343, 1018. ^{1}H NMR (d_6-DMSO, 400 MHz, r.t., ppm): δ = 2.83-2.98 (m, 1H), 2.99-3.04 (m, 1H), 3.64-3.70 (m, 1H), 3.80-3.88 (m, 1H), 5.08 - 5.12 (t, 1H), 7.50-7.58 (m, 3H), 7.588-7.67 (m, 2H). ^{13}C NMR (d_6-DMSO, 100 MHz, r.t., ppm): δ = 54.32, 59.92, 123.78, 129.20, 130.65, 144.66

8) Methoxymethyl phenyl sulfoxide: pale yellow oil. IR (cm^{-1}):1015. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 3.68 (s, 3H), 4.53 (s, 2H), 7.58-7.62 (m, 2H), 7.64-7.70 (m, 1H), 7.94 - 7.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 61.19, 87.78, 128.74, 129.23, 134.07, 137.39

9) Methyl 2-(pheylsulfinyl) acetate: pale yellow oil. IR (cm^{-1}): 1043. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 3.54 (s, 3H), 3.58-3.62 (d, 1H), 3.69-3.72 (d, 1H), 7.39-7.40 (d, 3H), 7.54-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 52.63, 61.34, 124.03, 129.37, 131.73, 142.92, 165.17.

10) Diphenyl sulfoxide: colorless crystals. M.p.: 70-72 °C. IR (cm^{-1}): 1034. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 7.34-7.41 (m, 6H), 7.55-7.59 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 123.80, 128.31, 130.02, 144.69.

11) Benzyl phenyl sulfoxide: white solid. M.p.: 234-237 °C. IR (cm^{-1}): 1027. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 4.03-4.06 (d, 1H), 4.13-4.16 (d, 1H), 7.02 - 7.03 (d, 2H), 7.27-7.41 (m, 3H), 7.41-7.53 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 63.57, 124.47, 128.26, 128.46, 128.86, 129.13, 130.37, 131.19, 142.72.

12) Dibenzyl sulfoxide: white solid. M.p.: 136-138 °C. IR (cm^{-1}): 1028. ^{1}H NMR ($CDCl_3$, 400 MHz, r.t., ppm): δ = 3.94 – 4.01 (q, 4H), 7.31-7.38 (m, 4H), 7.40-7.45

(m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, r.t., ppm): δ = 57.18, 128.42, 128.99, 130.16, 130.86.