Supporting Information

Structure directing role of amines and water molecules in the self-assembly of polyoxomolybdates

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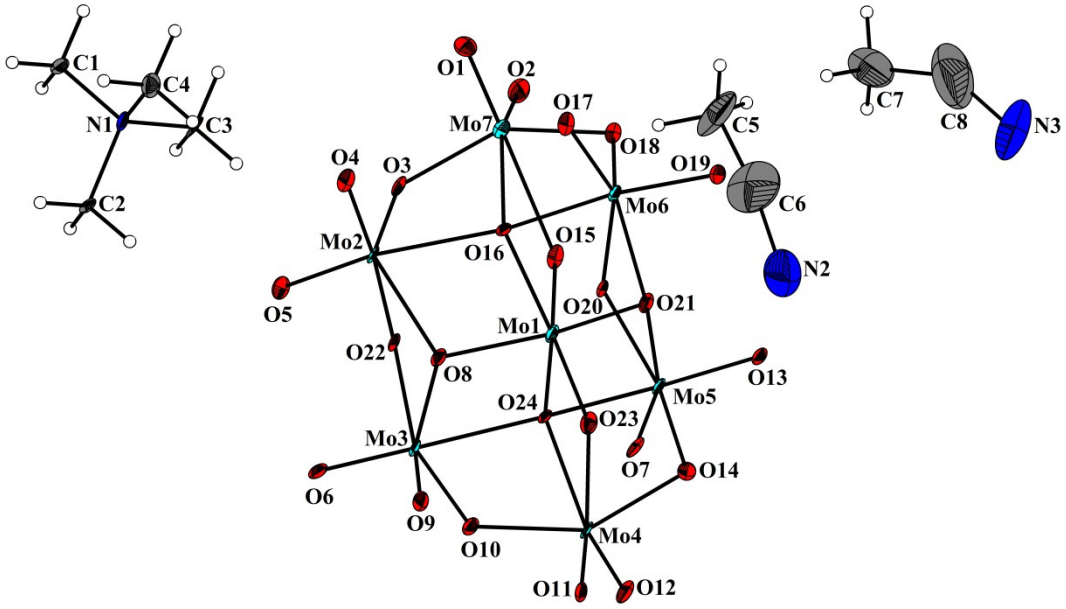

Fig S1. Showing ORTEP of asymmetric unit of complex (**I**) (with 30% probability), where oxygen atoms of water and hydroxonium ions are omitted for the clarity.

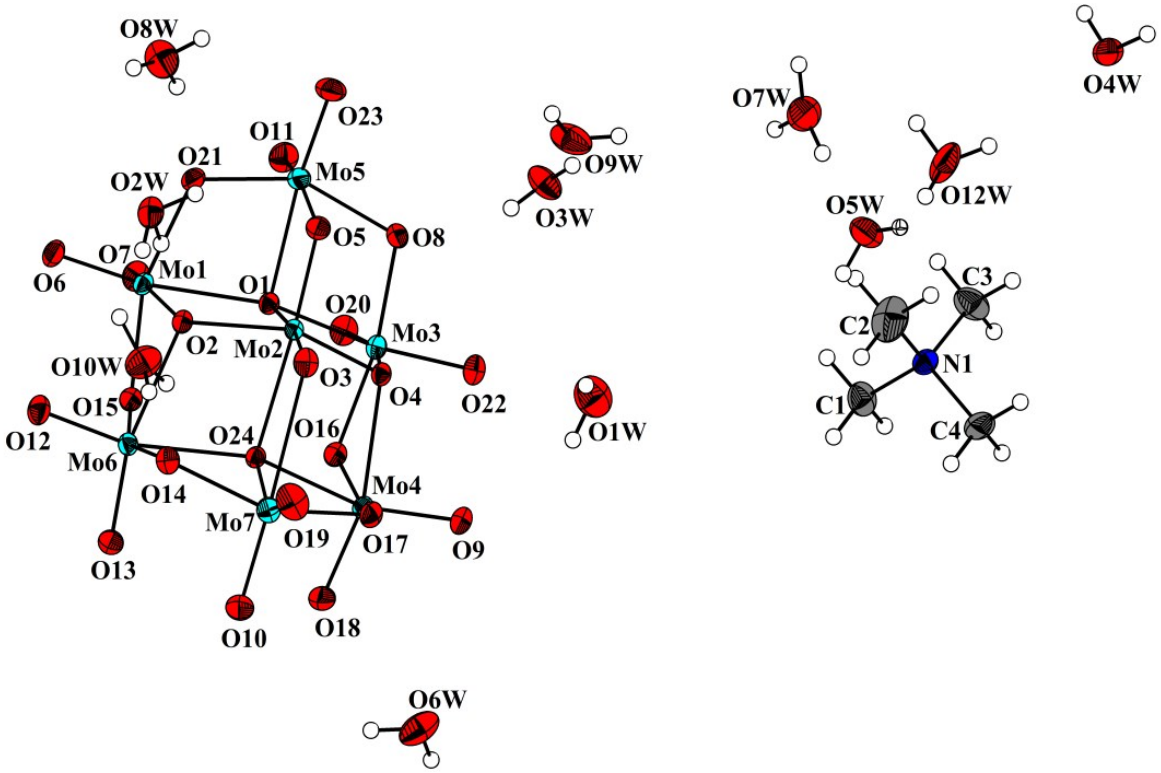

Fig S2. Showing ORTEP of asymmetric unit of complex (**II**) (with 30% probability), where isotropic oxygen atoms of water are omitted for the clarity.

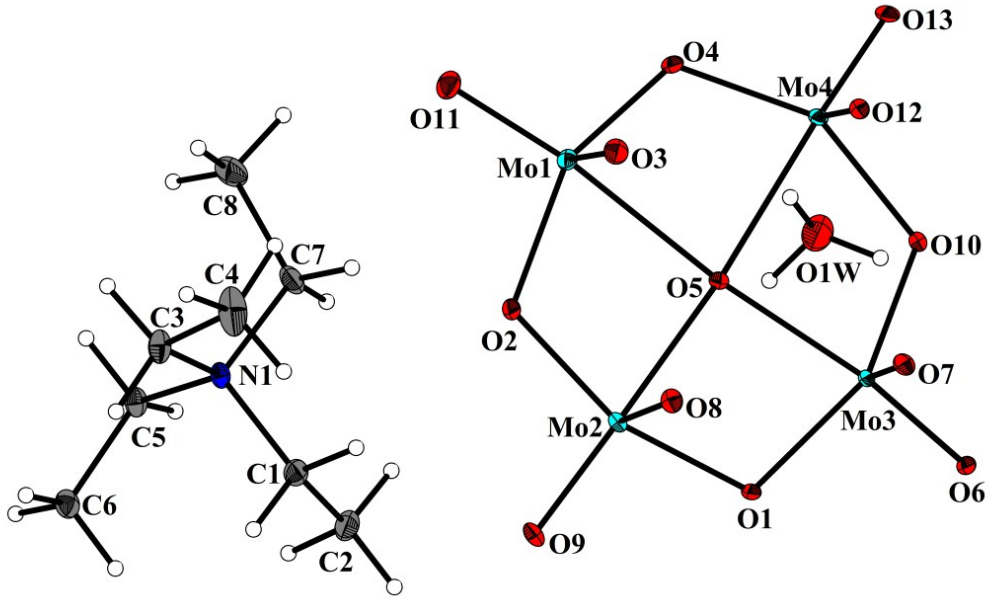

Fig S3. Showing ORTEP of asymmetric unit of complex (**III**) (with 30% probability).

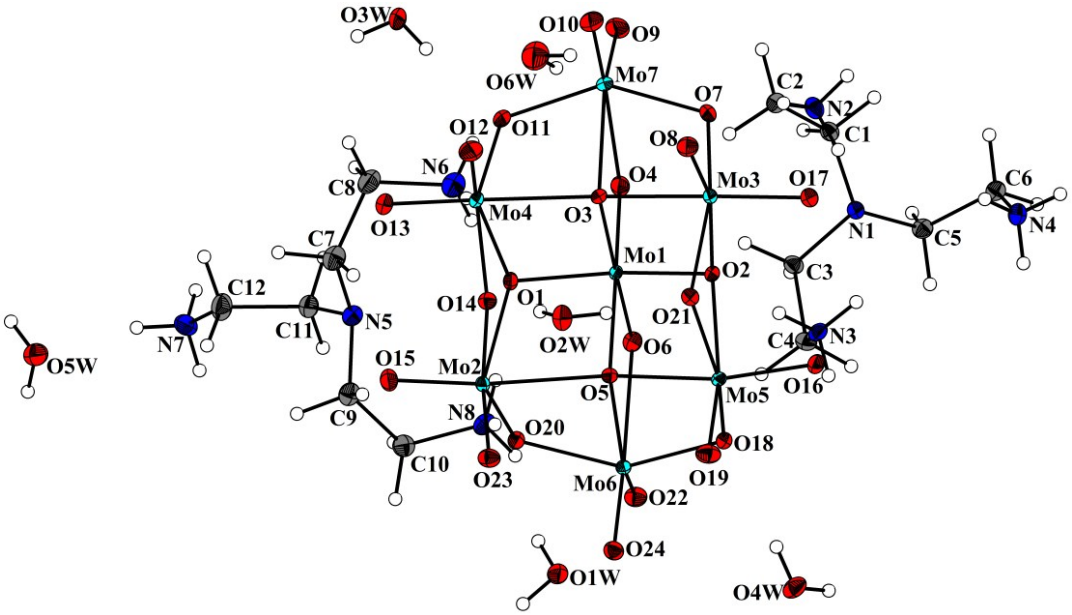

Fig S4. Showing ORTEP of asymmetric unit of complex (**IV**) (with 50% probability).

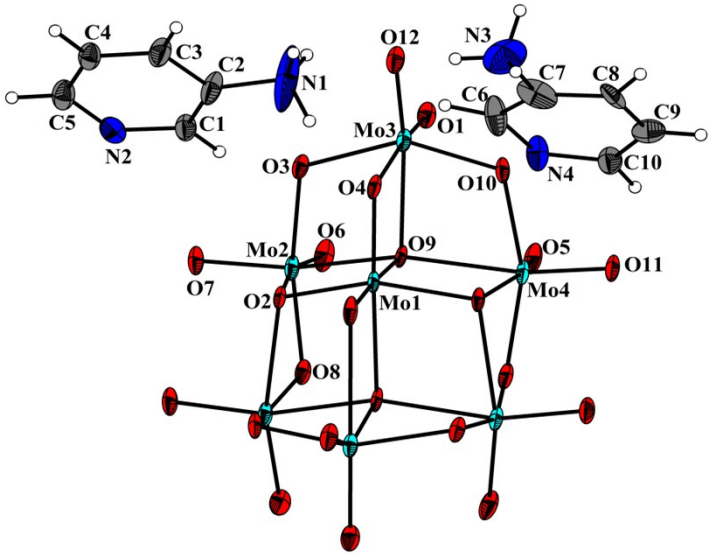

Fig S5. Showing ORTEP of asymmetric unit of complex (**V**) (with 20% probability).

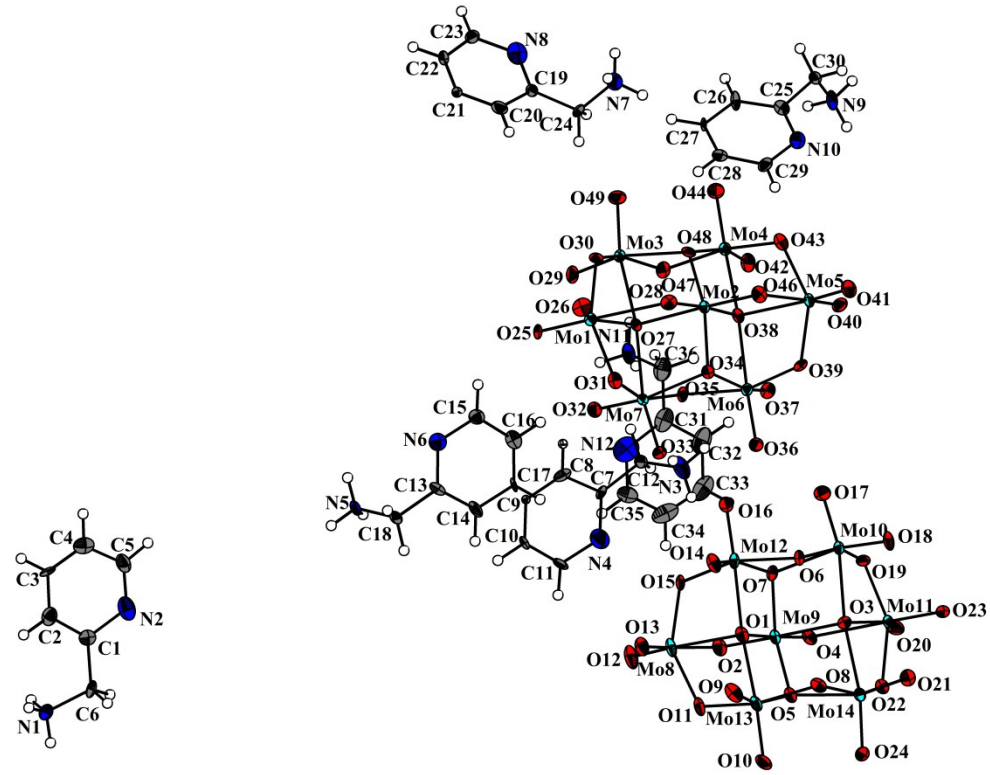

Fig S6. Showing ORTEP of asymmetric unit of complex (**VI**) (with 50% probability), where isotropic oxygen atoms of water are omitted for the clarity.

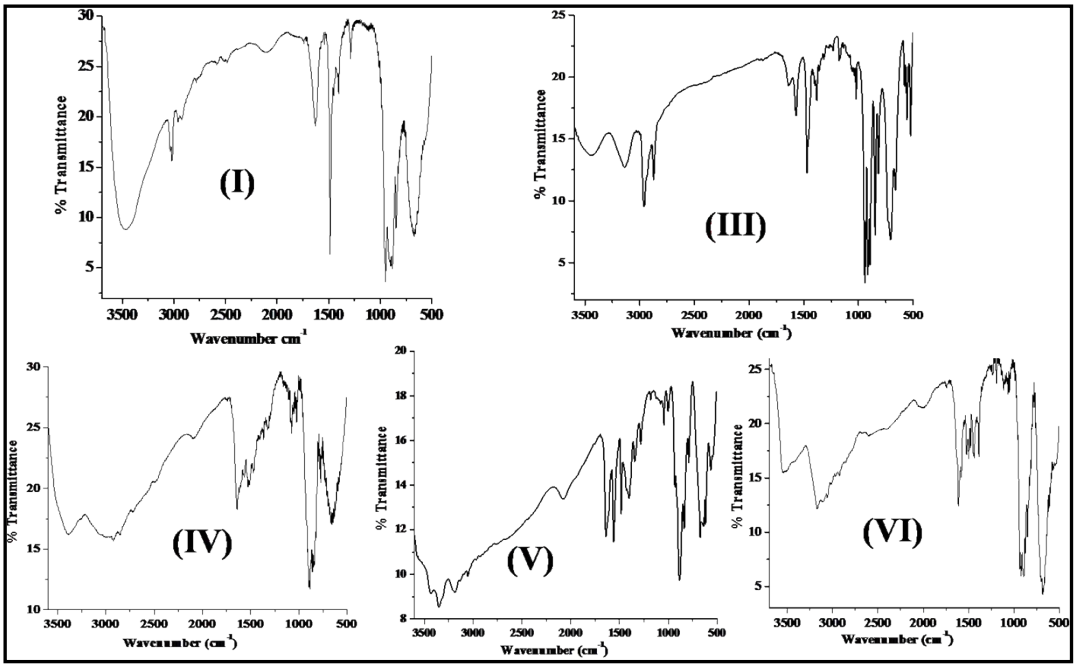

Fig S7. IR spectra of complexes (**I-VI**).

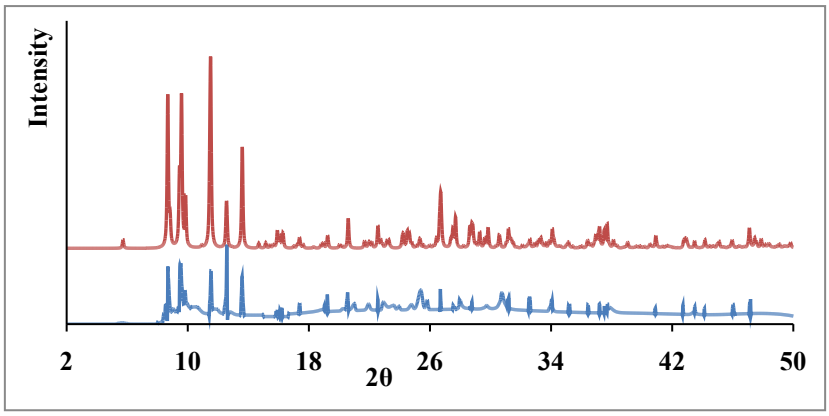

Fig S8. Generated (red) and experimental (blue) PXRD of complex (**I**)

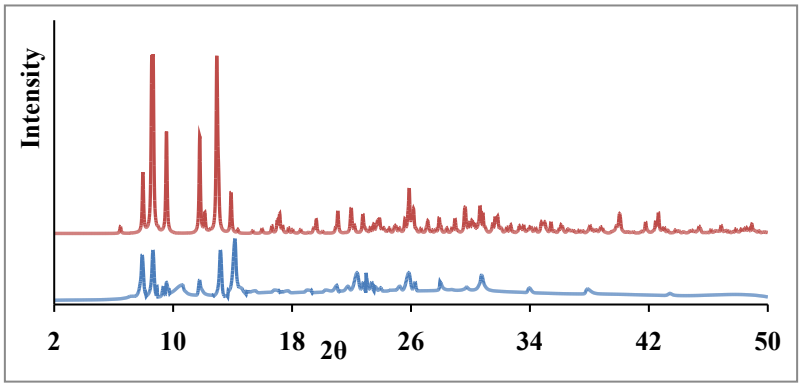

Fig S9. Generated (red) and experimental (blue) PXRD of complex (**II**)

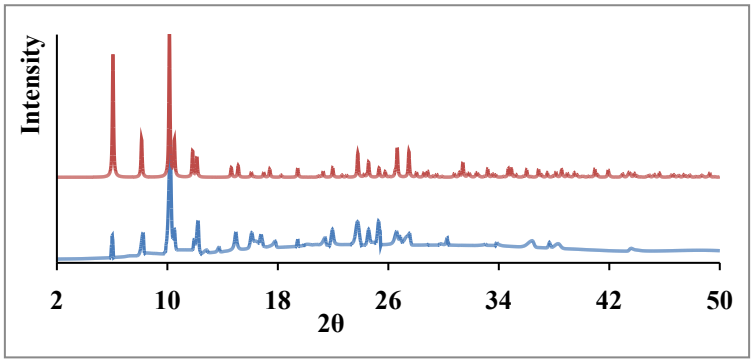

Fig S10. Generated (red) and experimental (blue) PXRD of complex (**III**)

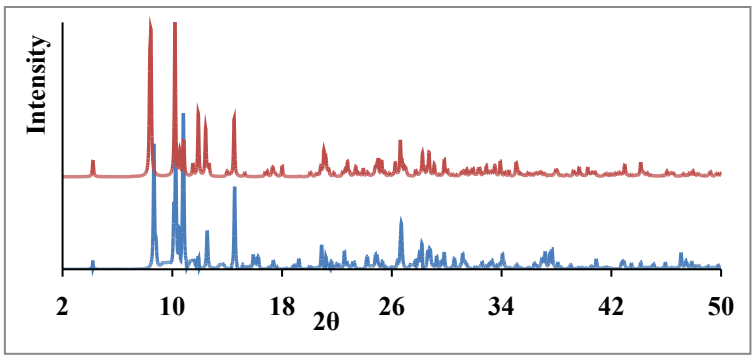

Fig S11. Generated (red) and experimental (blue) PXRD of complex (**IV**)

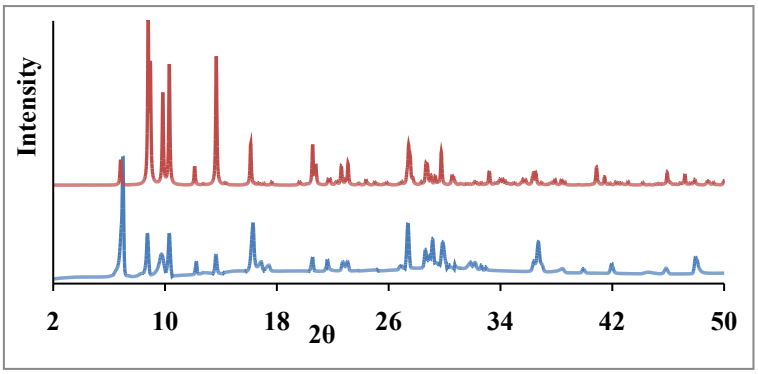

Fig S12. Generated (red) and experimental (blue) PXRD of complex (**V**)

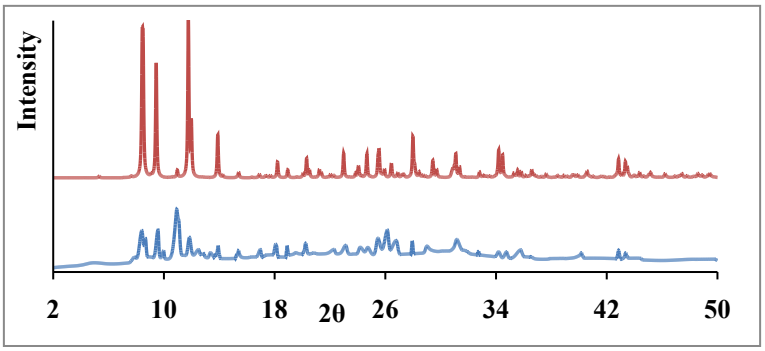

Fig S13. Generated (red) and experimental (blue) PXRD of complex (**VI**)

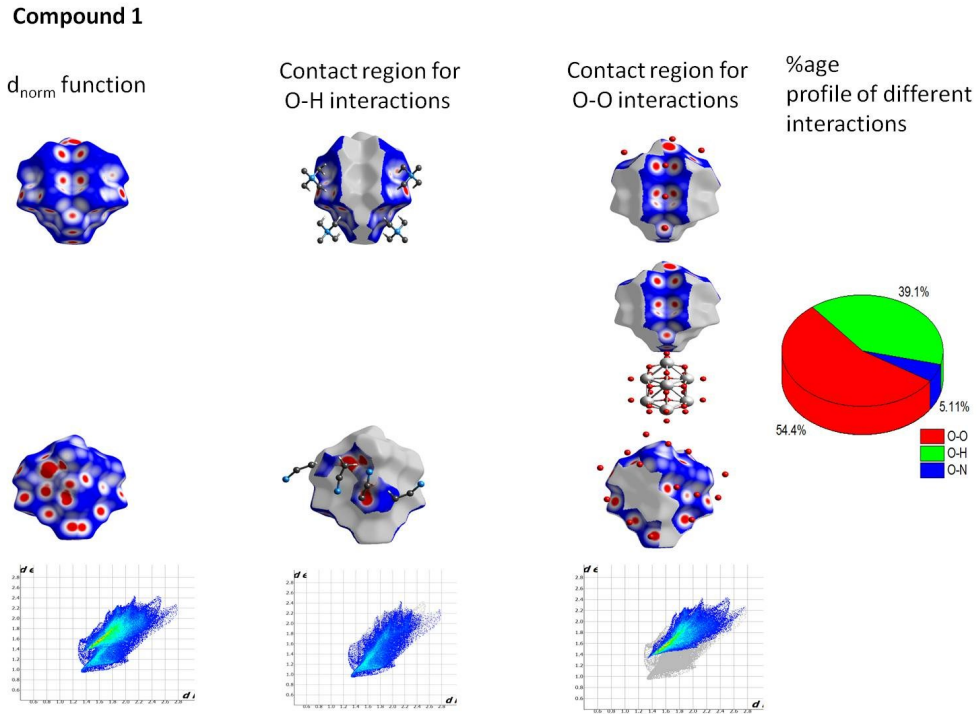

Fig S14. Front and back views of the Hirshfeld surface for POMo unit in complex (**I**), mapped with d_{norm}. Neighboring molecules associated with O···H, O···O close contacts are shown together with the features of respective interactions in the 2D fingerprint plots. Percentage contributions to the Hirshfeld surface area for the close intermolecular contacts between POMo tecton and the surrounding molecules are shown in a pie chart diagram. Isolated red balls indicate water molecules

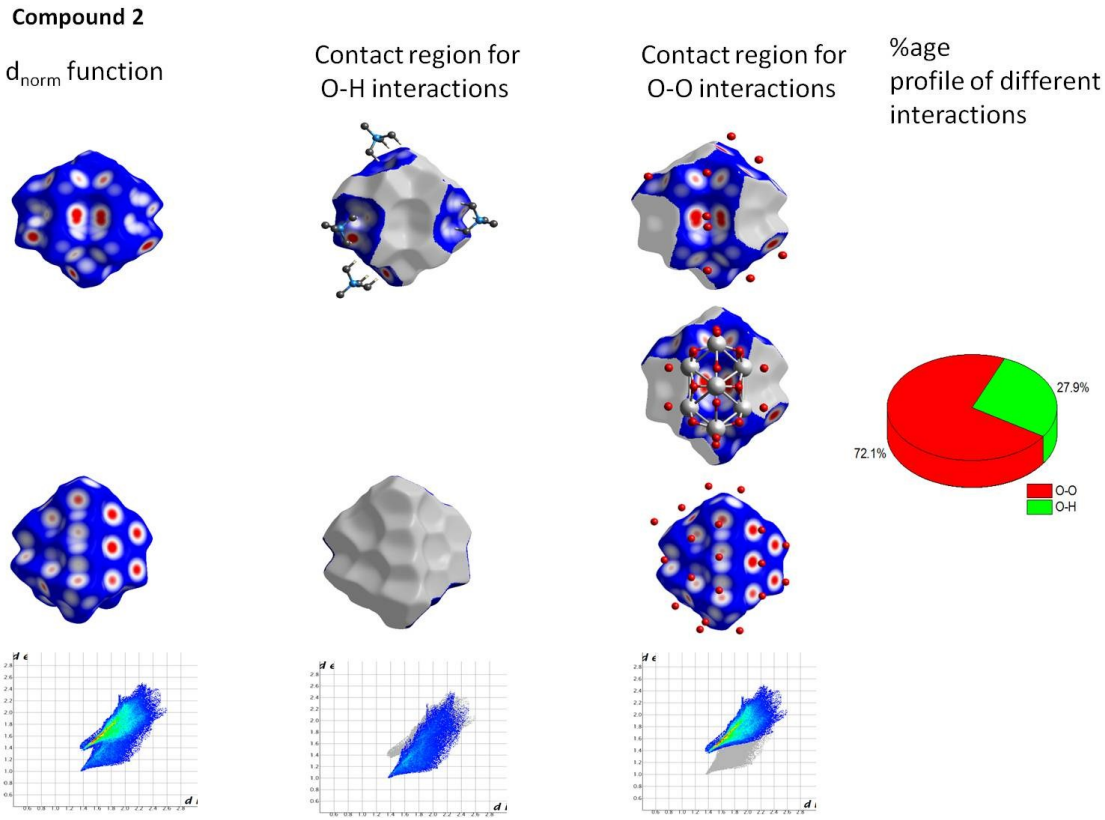

Fig S15. Front and back views of the Hirshfeld surface for POMo unit in complex (**II**), mapped with d_{norm}. Neighboring molecules associated with O···H, O···O close contacts are shown together with the features of respective interactions in the 2D fingerprint plots. Percentage contributions to the Hirshfeld surface area for the close intermolecular contacts between POMo tecton and the surrounding molecules are shown in a pie chart diagram. Isolated red balls indicate water molecules.

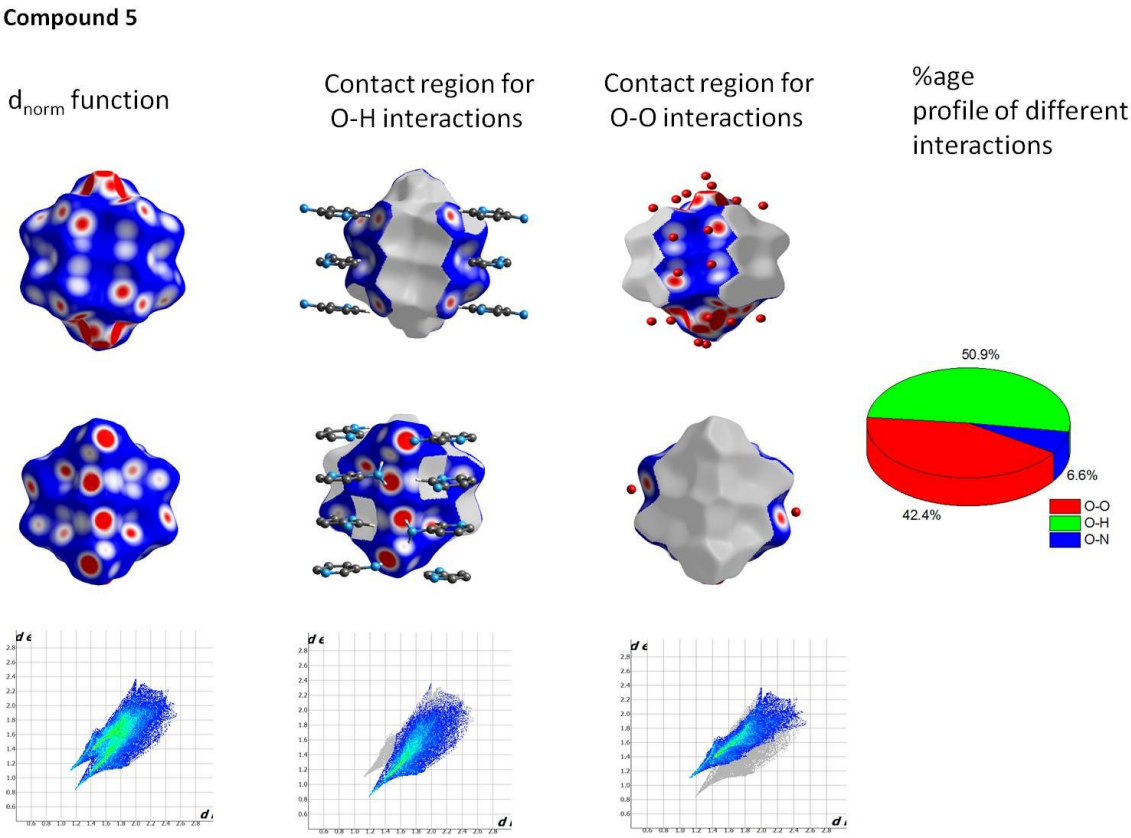

Fig S16. Front and back views of the Hirshfeld surface for molybdate unit in complex (**V**), mapped with d_{norm}. Neighboring molecules associated with O···H, O···O close contacts are shown together with the features of respective interactions in the 2D fingerprint plots. Percentage contributions to the Hirshfeld surface area for the close intermolecular contacts between POMo tecton and the surrounding molecules are shown in a pie chart diagram. Isolate red balls indicate water molecules.

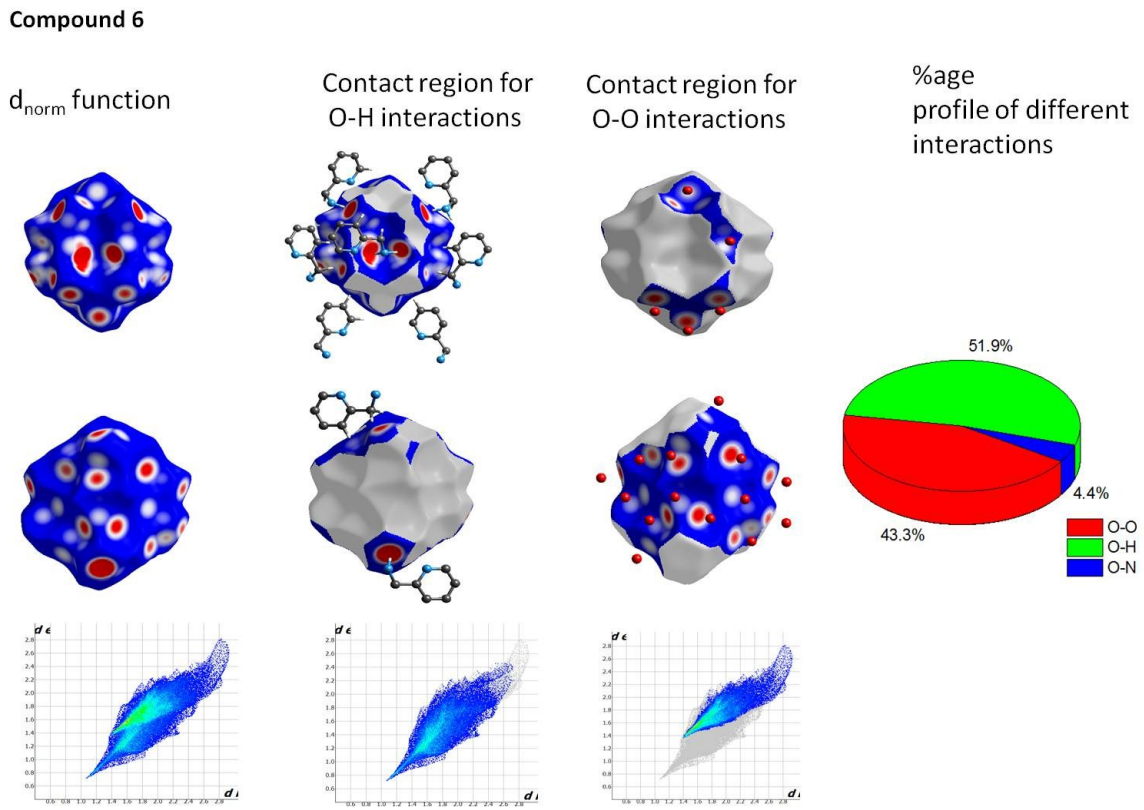

Fig S17. Front and back views of the Hirshfeld surface for POMo unit in complex (**VI**), mapped with d_{norm}. Neighboring molecules associated with O···H, O···O close contacts are shown together with the features of respective interactions in the 2D fingerprint plots. Percentage contributions to the Hirshfeld surface area for the close intermolecular contacts between POMo tecton and the surrounding molecules are shown in a pie chart diagram. Isolated red balls indicate water molecules.

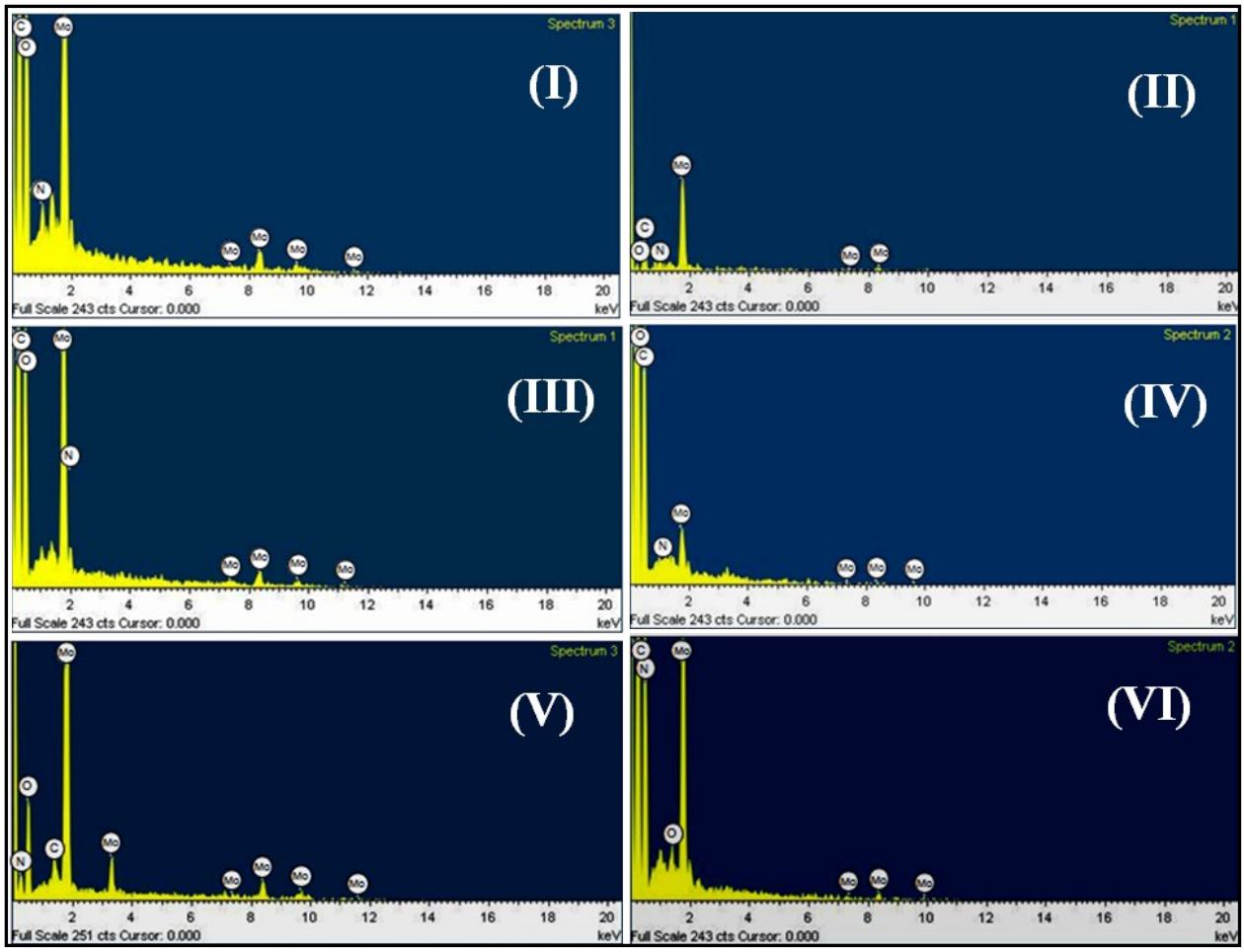

Fig S18. Showing EDS spectra of complexes (**I-VI**).

Table TS1. Important H-bonding interactions in complexes **(I-VI)**

Complex (**I**)

X-H···Y	**X···Y**	**X···H**	**∠X-H···Y**
Cation···anion			
C1-H1A···O10[1]	3.636(2)	2.78	147
C3-H3B···O10[1]	3.541(2)	2.64	154
C4-H4C···O9[1]	3.208(3)	2.41	150
C4-H4C···O10[1]	3.757(2)	2.92	143
C4-H4C···O11[1]	3.435(2)	2.74	128
C1-H1A···O6[1]	3.434(2)	2.54	152
C1-H1B···O6[2]	3.584(2)	2.77	141
C4-H4B···O6[2]	3.377(2)	2.48	151
C1-H1B···O9[2]	3.473(2)	2.56	154
C2-H2C···O5[2]	3.508(2)	2.71	139
C2-H2C···O6[2]	3.487(2)	2.63	146
C2-H2C···O22[2]	3.499(2)	2.72	137
C3-H3C···O13[3]	3.308(3)	2.39	155
C2-H2B···O13[3]	3.579(2)	2.77	140
C1-H1C···O13[3]	3.532(2)	2.68	145
C1-H1C···O19[3]	3.378(2)	2.61	135
C1-H1C···O20[3]	3.462(3)	2.64	142
C2-H2B···O7[3]	3.597(2)	2.67	158
C4-H4A···O12[4]	3.824(3)	2.93	152
C4-H4A···O14[4]	3.568(2)	2.70	148
C3-H3A···O7[4]	3.382(2)	2.52	147
C3-H3A···O11[4]	3.495(3)	2.74	135
C3-H3A···O14[4]	3.729(2)	2.90	143
C2-H2A···O14[4]	3.508(2)	2.63	149
C2-H2A···O13[4]	3.384(2)	2.52	146

Cation··· water			
C4-H4B···O4W[5]	3.475(2)	2.74	132
Anion···acetonitrile			
C7-H7B···O2	3.229(4)	2.33	152
C7-H7B···O15	3.503(4)	2.75	134
C5-H5B···O19[3]	3.834(4)	2.94	153
C7-H7C···O15[4]	3.208(3)	2.55	125
C7-H7C···O23[4]	3.238(3)	2.34	151
Water···acetonitrile			
C5-H5B···O3W	2.761(4)	2.07	126
C5-H5C···O1W	3.036(3)	2.39	123
C7-H7A···O6W	3.398(3)	2.49	153
C7-H7A···O9W[5]	3.554(5)	2.86	128
O9W···N2[3]	1.984(3)	*	*
O8W···N3[9]	2.701(3)	*	*
O10W···N3[3]	2.385(4)	*	*
Acetonitrile···acetonitrile			
C7-H7B···N3[4]	2.799(1)	2.28	112
C5-H5A···N2[6]	3.851(5)	2.88	172
C5-H5B···N2[4]	2.808(5)	2.28	113
Water··· Water			
O1W···O10W[1]	3.098(3)	*	*
O6W···O7W[5]	2.936(3)	*	*
O6W···O9W[5]	2.820(4)	*	*
O7W···O6W[5]	2.936(3)	*	*
O9W···O6W[5]	2.820(4)	*	*
O3W···O7W[6]	3.023(2)	*	*

O4W···O7W[7]	2.966(2)	*	*
O7W···O4W[7]	2.966(2)	*	*
O6W···O6W[8]	2.889(3)	*	*
O7W···O3W[6]	3.023(2)	*	*
O10W···O1W[9]	3.098(3)	*	*
Anion··· water			
O5W···O12[1]	2.807(2)	*	*
O9W···O12[1]	2.765(3)	*	*
O8W···O14[1]	2.853(2)	*	*
O3W···O10[1]	2.785(2)	*	*
O2W···O20[2]	2.851(1)	*	*
O2W···O22[2]	2.869(1)	*	*
O2W···O9[2]	2.954(1)	*	*
O2W···O7[2]	2.964(1)	*	*
O3W···O19[3]	2.758(2)	*	*
O2W···O7[3]	2.964(1)	*	*
O2W···O9[3]	2.954(1)	*	*
O5W···O7[4]	3.033(2)	*	*
O5W···O11[4]	2.896(2)	*	*
O8W···O2[5]	3.024(2)	*	*
O6W···O1[8]	3.034(2)	*	*
O3W···O19[9]	2.759(2)	*	*
O2W···O20[9]	2.851(1)	*	*
O2W···O22[9]	2.869(1)	*	*
O2W···O7[9]	2.964(1)	*	*
O2W···O9[9]	2.954(1)	*	*
O4W···O17[10]	2.821(2)	*	*
O5W···O17[10]	2.852(2)	*	*
O9W···O1[10]	2.641(3)	*	*
O7W···O2[10]	3.006(2)	*	*

O1W···O3[10]	2.827(2)	*	*
O5W···O4[10]	2.819(2)	*	*
O1W···O3[11]	2.827(2)	*	*
O4W···O17[11]	2.821(2)	*	*
O5W···O4[11]	2.819(2)	*	*
O5W···O17[11]	2.852(2)	*	*
O7W···O2[11]	3.006(2)	*	*
O9W···O1[11]	2.641(3)	*	*
O1W···O15[12]	2.805(2)	*	*
O7W···O8[12]	2.949(2)	*	*
O5W···O12[13]	2.807(2)	*	*
O9W···O12[13]	2.765(3)	*	*
O8W···O14[13]	2.853(2)	*	*
O3W···O10[13]	2.785(2)	*	*
O10W···O4[14]	2.921(4)	*	*
O10W···O4[15]	2.921(4)	*	*
O4W···O5[16]	3.021(2)	*	*
O4W···O6[16]	2.880(2)	*	*
O4W···O5[17]	3.021(2)	*	*
O4W···O6[17]	2.880(2)	*	*

(1) x,+y+1,+z-1 (2) -x,-y,-z+2 (3) x,+y,+z-1 (4) -x+1,-y,-z+2 (5) -x+1,-y+1,-z+1 (6) -x+1,-y+1,-z (7) –x+2,-y+1,-z (8) -x,-y+1,-z+2 (9) x,+y,+z+1 (10) x-1,+y,+z+1 (11) x+1, +y,+z-1 (12) –x+1,-y,-z+1 (13) x,+y-1,+z+1 (14) x+1,+y,+z (15) x-1,+y,+z (16) x-1,+y-1,+z+1 (17) x+1,+y+1,+z-1

Complex (**II**)

X-H···Y	**X···Y**	**X···H**	**∠X-H···Y**
Cation···anion			
C2-H2C···O13[1]	3.682(9)	2.84	147
C4-H4B···O10[1]	3.718(6)	2.89	144

C1-H1B···O10[1]	3.461(6)	2.56	157
C2-H2C···O10[1]	3.694(8)	2.86	145
C1-H1C···O9[2]	3.512(6)	2.62	154
C3-H3B···O9[2]	3.618(7)	2.77	148
C3-H3B···O18[2]	3.766(7)	2.88	154
C4-H4A···O16[2]	3.667(6)	2.73	164
C4-H4A···O22[2]	3.600(6)	2.85	136
C3-H3A···O6[3]	3.567(6)	2.84	133
C3-H3A···O21[3]	3.498(7)	2.58	160
C2-H2A···O11[3]	3.429(8)	2.51	160
C4-H4C···O12[4]	3.481(7)	2.72	137
C4-H4C···O15[4]	3.402(5)	2.63	137
C2-H2B···O6[4]	3.677(7)	2.88	142
C3-H3C···O6[4]	3.229(3)	2.46	156
C3-H3C···O7[4]	3.561(6)	2.87	130
C4-H4C···O6[4]	3.536(5)	2.69	147
Cation··· water			
C2-H2B···O5W	3.245(9)	2.79	109
C4-H4B···O12W[5]	3.647(6)	2.93	133
C4-H4B···O5W[5]	3.591(7)	2.83	137
Anion··· water			
O1W-H11W···O9	3.023(5)	2.33(5)	150
O2W-H21W···O2	2.735(4)	1.91(5)	176
O3W-H31W···O8	2.889(4)	2.13(3)	158
O6W-H62W···O18	2.870(5)	2.51(5)	107
O8W-H81W···O21	2.851(5)	2.02(6)	162
O10W-H13W···O14	2.765(5)	1.98(6)	151
O5W-H51W···O13[1]	2.911(4)	2.12(4)	165
O7W-H71W···O11[3]	3.024(6)	2.39(4)	157

O7W-H71W···O20[3]	3.037(5)	2.53(6)	123
O7W···O7[3]	2.970(6)	*	*
O3W-H32W···O8[6]	2.955(5)	2.21(4)	154
O9W-H91W···O20[6]	2.963(5)	2.44(6)	122
O4W-H42W···O17[7]	2.942(4)	2.17(3)	159
O9W-H92W···O12[8]	2.781(6)	1.97(6)	169
O8W-H82W···O19[8]	2.864(5)	2.07(4)	156
O10W-H14W···O23[8]	2.914(6)	2.35(7)	123
O2W-H22W···O3[8]	2.970(4)	2.29(4)	140
O10W···O5[8]	3.016(5)	*	*
O7W-H73W···O13[9]	2.919(5)	2.12(5)	154
O12W-H24W···O10[9]	2.710(4)	1.93(6)	157
O4W-H41W···O17[9]	2.847(4)	2.06(4)	163
O7W···O13[9]	2.919(5)	*	*
O6W···O6[10]	2.786(5)	*	*
O6W-H61W···O6[10]	2.786(5)	1.96(5)	172
O12W-H26W···O22[11]	2.739(6)	1.96(1)	156
O12W···O10[9]	2.709(6)	*	*
O12W···O22[11]	2.739(6)	*	*
O13W···O19[11]	3.005(4)	*	*
O8W···O9[12]	2.966(5)	*	*
O14W···O15[13]	2.790(1)	*	*
O14W···O16[13]	2.776(1)	*	*
O13W···O19[14]	3.005(4)	*	*
O7W···O18[14]	2.892(5)	*	*
O4W···O17[14]	2.847(4)	*	*
water··· water			
O7W-H72W···O5W	2.801(6)	1.97(7)	170
O8W-H83W···O2W	3.037(6)	2.56(6)	113
O12W-H25W···O11W	2.295(4)	1.64(7)	135
O13W···O1W[1]	2.993(9)	*	*

O11W···O2W[4]	2.306(4)	*	*
O1W···O1W[6]	2.819(7)	*	*
O9W···O11W[7]	2.364(4)	*	*
O11W···O6W[9]	2.387(6)	*	*
O11W···O3W[11]	2.386(4)	*	*
O8W-H83W···O4W[15]	3.027(7)	2.28(6)	157
O10W-H15W···O3W[16]	3.022(6)	2.37(4)	142
O8W-H83W···O6W[12]	3.025(6)	2.62(6)	112
O6W···O6W[12]	2.786(5)	*	*

(1) -x+1/2,+y+1/2,-z+1/2 (2) -x+1/2,-y+1/2+1,-z+1 (3) -x+1/2,-y+1/2,-z+1
(4) x,+y+1,+z+1 (5) -x+1/2,+y+1/2,-z+1/2+1 (6) -x+1,+y,-z+1/2 (7) -x+1,-y+1,-z+1 (8) -x+1,-y,-z (9) x,+y,+z+1 (10) x,+y+1,+z (11) x,-y+1,+z+1/2 (12) x,+y-1,+z (13) –x+1/2,-y+1/2.-z (14) x,+y,+z-1 (15) x,+y-1,+z-1 (16) x,-y,+z-1/2

Complex (**III**)

X-H···Y	**X···Y**	**X···H**	**∠X-H···Y**
Cation···anion			
C1-H1A···O2	3.578(7)	2.66	155
C1-H1A···O9	3.434(6)	2.64	137
C7-H7A···O2	3.465(6)	2.52	160
C7-H7A···O11	3.677(7)	2.88	138
C1-H1B···O8[1]	3.268(5)	2.29	168
C6-H6B···O9[1]	3.371(5)	2.67	129
C6-H6C···O8[1]	3.461(5)	2.78	127
C7-H7A···O6[2]	3.229(7)	2.60	121
C2-H2B···O10[2]	3.269(7)	2.70	117
C7-H7B···O4[3]	3.572(4)	2.69	148
C8-H8A···O11[3]	3.478(5)	2.87	121
C2-H2B···O13[3]	3.248(5)	2.55	128

C5-H5B···O1[4]	3.322(4)	2.36	164
C8-H8C···O6[4]	3.590(6)	2.77	142
C5-H5B···O7[4]	3.359(6)	2.99	103
C6-H6A···O7[4]	3.481(5)	2.76	131
C6-H6A···O8[4]	3.579(5)	2.98	121
C2-H2C···O9[4]	3.653(5)	2.95	129
C8-H8B···O11[5]	3.399(6)	2.83	117
C6-H6B···O3[5]	3.219(4)	2.53	127
C3-H3B···O11[5]	3.455(5)	2.47	172

Anion·· water

O1W-H11W···O3	2.981(5)	2.64(5)	103
O1W-H11W···O8	2.957(6)	2.06(5)	174
O1W-H12W···O9[6]	2.869(4)	1.99(3)	173
O1W-H13W···O12[7]	2.903(5)	2.02(4)	173
O1W-H13W···O13[7]	3.031(5)	2.77(4)	114

(1) y+1/3,-x+y+2/3,-z+2/3 (2) -x+1,-y,-z (3) y+1/3,-x+y+2/3,-z-1/3
(4) -y+1/3,+x-y-1/3,+z-1/3 (5) -x+y+1,-x+1,+z (6) x-y+1/3,+x-1/3,-z+2/3
(7) -y+2/3,+x-y-2/3,+z+1/3

Complex (**IV**)

X-H···Y	**X···Y**	**X···H**	**∠X-H···Y**
Cation···anion			
C2-H2B···O4	3.287(3)	2.37	153
C4-H4A···O6	3.258(3)	2.67	118
C7-H7A···O13	3.515(3)	2.75	134
C7-H7A···O15	3.725(3)	2.80	156
C9-H9B···O15	3.477(3)	2.49	173
N2-H21A···O7	2.659(3)	1.82(2)	167
N3-H31A···O2	2.745(2)	1.91(2)	163
N3-H31C···O16	3.069(3)	2.70(3)	107

N3-H31C···O18	2.882(3)	2.41(3)	115
N6-H16B···O1	3.059(3)	2.28(2)	154
N6-H16B···O4	3.171(3)	2.75(2)	112
N6-H16B···O11	3.119(3)	2.50(2)	130
N8-H18A···O20	2.775(3)	1.92(2)	172
C3-H3A···O16[1]	3.862(3)	2.89	167
C8-H8A···O12[1]	3.597(3)	2.84	133
C3-H3A···O17[1]	3.659(3)	2.93	131
C3-H3A···O21[1]	3.405(3)	2.74	125
C10-H10B···O23[1]	3.289(3)	2.45	141
C11-H11B···O14[1]	3.350(3)	2.82	114
C1-H1A···O17[1]	3.380(3)	2.45	157
C1-H1A···O8[1]	3.530(3)	2.74	137
N4-H41C···O24[2]	3.085(2)	2.59(3)	118
N2-H21C···O23[2]	3.034(2)	2.43(2)	131
N2-H21C···O24[2]	2.899(3)	2.23(3)	140
C6-H6B···O22[2]	3.363(3)	2.38	172
C6-H6B···O24[2]	3.356(2)	2.74	121
C1-H1B···O22[2]	3.683(3)	2.69	176
C1-H1B···O24[2]	3.556(3)	2.89	125
C2-H2A···O20[2]	3.272(3)	2.70	117
C1-H1B···O20[2]	3.591(2)	2.98	121
C4-H4B···O16[3]	3.225(3)	2.85	103
C4-H4B···O19[3]	3.694(3)	2.97	131
N3-H31C···O16[3]	2.771(2)	2.04(3)	143
N4-H41A···O19[3]	2.812(3)	1.96(2)	165
C5-H5B···O19[3]	3.458(3)	2.74	130
C6-H6A···O22[4]	3.352(3)	2.57	136
C12-H12B···O12[5]	3.696(3)	2.73	167
C7-H7B···O12[5]	3.700(3)	2.92	136
C8-H8B···O13[5]	3.413(3)	2.48	158

C10-H10A···O8[6]	3.390(3)	2.56	142
N7-H17C···O10[6]	2.840(3)	2.08(3)	145
Cation··· water			
C8-H8B···O3W	3.552(3)	2.74	140
N6-H16A···O6W	2.823(3)	1.98(3)	169
N7-H17A···O5W	2.736(3)	1.90(3)	162
N8-H18B···O2W[1]	2.758(2)	1.94(3)	174
N6-H16C···O2W[1]	2.819(2)	1.98(2)	167
N4-H41B···O1W[3]	2.786(3)	2.35(3)	112
C6-H6A···O1W[3]	3.172(3)	2.62	115
C9-H9A···O5W[6]	3.201(3)	2.73	109
C9-H9B···O5W[6]	3.201(3)	2.83	103
N7-H17B···O3W[7]	2.783(3)	1.94(3)	168
C12-H12B···O6W[7]	3.386(3)	2.77	121
Water···anion			
O1W-H11W···O23	2.785(2)	1.97(3)	175
O2W-H21W···O21	2.834(2)	2.11(3)	150
O2W-H22W···O14	2.653(2)	1.87(2)	178
O3W-H31W···O11	2.680(2)	1.91(2)	175
O4W-H41W···O18	2.878(2)	2.09(2)	171
O6W-H62W···O9	2.871(3)	2.12(2)	153
O6W-H61W···O8[1]	3.013(3)	2.28(3)	153
O4W-H42W···O17[3]	2.848(2)	2.08(2)	164
O3W-H32W···O13[5]	2.702(3)	1.93(3)	166
O5W-H51W···O9[7]	2.861(3)	2.10(3)	156
O1W-H12W···O17[8]	2.807(2)	2.00(2)	167
Water··· water			
O5W-H52W···O3W[6]	2.776(3)	1.95(2)	178

(1) x-1,+y,+z (2) x,+y+1,+z (3) -x+1,-y+1,-z (4) -x,-y+1,-z (5) -x+1,-y+1,-z+1 (6) x-1,+y-1,+z (7) -x,-y+1,-z+1 (8) x,+y-1,+z

Complex (**V**)

X-H···Y	**X···Y**	**X···H**	**∠X-H···Y**
Cation···anion			
C1-H1···O2	3.722(3)	2.95	141
C1-H1···O3	3.378(3)	2.51	155
C1-H1···O4	3.523(2)	2.88	128
C6-H6···N1	3.838(4)	2.91	175
C6-H6···O4	3.228(3)	2.73	115
N1-H1B···O12	3.422(4)	2.64	147
N1-H1C···O4	2.863(3)	2.19	132
N1-H1A···O12[1]	2.976(3)	2.13	159
N3-H3A···O12[1]	3.460(4)	2.73	140
C5-H5···O5[3]	3.274(3)	2.54	136
C4-H4···O11[3]	3.229(3)	2.58	127
C5-H5···O6[4]	3.218(3)	2.52	132
C8-H8···O8[5]	3.601(3)	2.76	151
C8-H8···O11[5]	3.580(3)	2.86	135
C8-H8···O7[5]	3.547(4)	2.76	142
N3-H3C···O11[5]	3.657(4)	2.92	142
C10-H10···O11[8]	3.446(3)	2.66	143
Cation··· water			
C3-H3···O6W[1]	3.457(3)	2.74	134
N3-H3B···O7W[1]	3.214(4)	2.75	114
C4-H4···O6W[2]	3.671(3)	2.81	154
C9-H9···O3W[6]	3.646(3)	2.93	135
C10-H10···O6W[6]	3.448(3)	2.85	123
C9-H9···O9W[7]	3.465(6)	2.60	155
C10-H10···O7W[7]	3.445(3)	2.90	118
Water···anion			
O7W···O7[4]	2.824(2)	*	*

O3W····O5[8]	2.643(2)	*	*
O4W····O5[8]	2.789(5)	*	*
O1W····O1[9]	2.949(3)	*	*
O2W····O1[9]	2.595(2)	*	*
O9W····O1[9]	2.949(9)	*	*
Water··· water			
O6W···O6W[6]	2.709(2)	*	*
O1W···O8W[9]	2.265(4)	*	*
O2W···O1W[9]	2.367(2)	*	*
O2W···O3W[9]	2.929(1)	*	*
O2W···O4W[9]	2.504(7)	*	*
O2W···O5W[9]	2.845(2)	*	*
O2W···O8W[9]	2.557(3)	*	*
O2W···O9W[9]	2.173(5)	*	*
O3W···O8W[9]	2.245(3)	*	*
O3W···O9W[9]	2.095(4)	*	*
O4W···O9W[9]	2.443(9)	*	*
O6W···O8W[9]	2.768(3)	*	*

(1) -x,-y+1,-z+1 (2) x+1/2,+y+1/2,+z (3) -x+1/2,+y+1/2,-z+1/2 (4) -x+1/2,-y+1/2,-z+1 (5) x-1/2,+y+1/2,+z (6) -x-1/2,-y+1/2,-z+1 (7) x-1/2,-y+1/2,+z-1/2 (8) -x,+y,-z+1/2 (9) –x,+y,-z+1/2+1

Complex (**VI**)

X-H···Y	**X···Y**	**X···H**	**∠X-H···Y**
Cation···anion			
C11-H11···O13	3.444(9)	2.89	118
C12-H12A···O16	3.205(9)	2.53	125
C15-H15···O25	3.214(9)	2.61	122
C16-H16···O25	3.249(9)	2.65	122
C16-H16···O31	3.429(9)	2.54	155

C16-H16···O32	3.443(9)	2.68	137
C36-H36A···O37	3.562(9)	2.76	138
N3-H3B···O14	2.962(9)	2.06	173
N3-H3B···O16	3.019(9)	2.66	104
N11-H11A···O29	3.291(8)	2.72	122
N11-H11A···O47	2.862(8)	2.10	140
N11-H11B···O27	3.485(8)	2.83	130
N11-H11B···O32	3.154(8)	2.44	136
N11-H11B···O35	2.742(8)	1.93	147
N1-H1C···O20[1]	2.775(9)	1.89	162
C2-H2···O20[1]	3.266(9)	2.52	136
C22-H22···O18[2]	3.560(8)	2.76	142
N5-H5C···O42[2]	2.939(8)	2.04	171
N5-H5C···O44[2]	3.126(8)	2.76	105
C22-H22···O19[2]	3.518(8)	2.64	153
C22-H22···O23[2]	3.418(8)	2.82	121
C23-H23···O23[2]	3.341(9)	2.68	127
C15-H15···O40[2]	3.590(9)	2.99	123
C18-H18B···O44[2]	3.311(9)	2.63	126
N1-H1B···O3[3]	3.475(8)	2.90	123
N1-H1B···O8[3]	2.741(8)	1.92	148
N1-H1B···O21[3]	3.186(8)	2.46	137
C6-H6A···O9[3]	3.592(9)	2.76	141
N1-H1A···O6[3]	2.791(8)	1.98	148
N1-H1A···O18[3]	3.284(8)	2.70	123
C10-H10···O21[4]	3.294(8)	2.51	140
C10-H10···O22[4]	3.628(8)	2.76	152
C10-H10···O23[4]	3.294(8)	2.69	122
C6-H6B···O12[4]	2.923(9)	2.44	109
C11-H11···O23[4]	3.297(9)	2.72	120
C28-H28···O30[5]	3.666(9)	2.78	154

C29-H29···O25[5]	3.507(9)	2.94	119
N3-H3C···O33[5]	3.029(9)	2.38	128
C12-H12B···O32[5]	3.332(8)	2.39	158
C12-H12B···O33[5]	3.185(9)	2.68	112
C8-H8···O35[5]	3.746(9)	2.82	164
C8-H8···O36[5]	3.294(9)	2.60	130
N7-H7B···O49[5]	3.168(8)	2.54	127
C8-H8···O33[5]	3.353(9)	2.67	130
C24-H24A···O29[5]	3.511(8)	2.58	157
C24-H24A···O49[5]	3.285(9)	2.74	115
C20-H20···O44[5]	3.454(9)	2.75	132
C20-H20···O49[5]	3.417(9)	2.72	131
C28-H28···O25[5]	3.439(9)	2.78	127
C28-H28···O29[5]	3.524(9)	2.73	141
C14-H14···O17[6]	3.204(9)	2.52	129
N5-H5B···O17[6]	3.220(8)	2.66	120
C18-H18A···O17[6]	3.136(9)	2.52	120
C18-H18A···O18[6]	3.648(8)	2.68	166
C14-H14···O16[6]	3.346(9)	2.70	125
N11-H11C···O26[6]	2.740(9)	1.86	161
N9-H9B···O24[7]	3.063(8)	2.35	135
C30-H30A···O21[7]	3.270(8)	2.39	147
C30-H30A···O24[7]	3.382(9)	2.94	108
C23-H23···O13[7]	3.389(9)	2.83	118
C24-H24B···O10[7]	3.497(9)	2.75	132
C26-H26···O8[7]	3.711(9)	2.80	160
C26-H26···O10[7]	3.425(9)	2.69	134
C26-H26···O24[7]	3.541(8)	2.83	132
N7-H7C···O9[7]	2.869(8)	1.98	165
N9-H9C···O36[8]	3.234(8)	2.90	103
N9-H9C···O37[8]	2.834(8)	1.94	167

C29-H29···O40[8]	3.217(9)	2.67	117
C30-H30B···O36[8]	3.365(8)	2.65	129
C32-H32···O43[9]	3.443(1)	2.87	119
C32-H32···O41[9]	3.442(1)	2.81	125
C36-H36B···O41[9]	2.945(9)	2.46	109
Cation··· water			
C12-H12A···O7W	3.359(1)	2.52	142
C24-H24A···O21W	3.172(1)	2.74	107
C36-H36B···O22W	3.187(1)	2.62	116
N11-H11A···O22W	3.320(1)	2.71	125
C3-H3···O13W[1]	2.761(8)	1.89	150
C4-H4···O21W[2]	3.376(1)	2.61	138
C6-H6B···O14W[3]	3.263(1)	2.65	120
N1-H1A···O14W[3]	3.330(1)	2.73	124
C18-H18A···O15W[4]	3.167(1)	2.75	106
N3-H3C···O12W[5]	2.899(1)	2.07	152
C35-H35···O7W[6]	2.726(9)	1.84	154
N5-H5B···O9W[6]	2.868(8)	1.99	160
N9-H9B···O10W[7]	3.016(8)	2.40	125
C30-H30B···O13W[8]	3.569(9)	2.68	149
C32-H32···O10W[10]	3.433(1)	2.65	141
C34-H34···O15W[10]	3.355(1)	2.58	139
N7-H7B···O17W[11]	2.884(9)	2.19	133
Cation··cation			
C27-H27···N7	2.895(9)	2.04	149
C17-H17···N3[6]	2.924(9)	1.98	172
Water···anion			
O1W···O23[1]	2.862(9)	*	*
O2W···O24[1]	2.999(8)	*	*
O4W···O32[5]	2.766(8)	*	*

O10W···O43[7]	2.865(8)	*	*
O11W···O37[9]	2.905(9)	*	*
O11W···O40[9]	3.013(9)	*	*
O19W···O13[9]	2.961(9)	*	*
O19W···O14[9]	2.998(9)	*	*
O19W···O9[9]	2.968(9)	*	*
O20W···O29[9]	2.828(9)	*	*
O22W···O41[9]	3.093(1)	*	*
O5W···O21[12]	2.721(8)	*	*
O8W···O4[12]	2.857(8)	*	*
O8W···O22[12]	3.014(8)	*	*
O3W···O48[13]	3.055(7)	*	*
Water··· water			
O4W···O16W[5]	2.875(8)	*	*
O11W···O16W[5]	2.909(1)	*	*
O21W···O22W[5]	3.029(1)	*	*
O16W···O20W[6]	2.937(9)	*	*
O15W···O8W[10]	3.085(1)	*	*
O14W···O15W[12]	2.856(1)	*	*
O3W···O20W[13]	2.818(9)	*	*
O10W···O11W[13]	3.037(9)	*	*
O1W···O5W[14]	2.827(8)	*	*
O1W···O8W[14]	2.938(8)	*	*
O1W···O19W[14]	2.879(1)	*	*
O2W···O8W[14]	2.838(8)	*	*
O2W···O17W[14]	2.857(8)	*	*

(1) x-1,+y,+z (2) x-1/2,-y+1,+z (3) -x+1,-y,+z-1/2 (4) x-1/2,-y,+z

(5) -x+1/2+1,+y,+z+1/2 (6) -x+1/2+1,+y,+z-1/2 (7) x,+y+1,+z

(8) -x+2,-y+1,+z+1/2 (9) -x+2,-y+1,+z-1/2 (10) -x+2,-y,+z-1/2

(11) -x+1/2+1,+y+1,+z+1/2 (12) -x+2,-y,+z+1/2 (13) x,+y-1,+z (14) -x+1,-y,+z+1/2

Table TS2. Showing important IR spectral peaks in complexes (**I-VI**)

Complex	-OH	Mo-O (terminal)	Mo-O (H-bonded)	Mo-O-Mo (corner sharing)	Mo-O-Mo (edge-sharing)	Mo-O (trans to terminal oxygen)
(I)	3477	948	883	846	672	570, 484
(III)	3447, 3138	941, 914	892	848, 819	658	557-525
(IV)	3384	925, 911	897, 883	848, 859	659	571
(V)	3447, 3352	934	887	838	674	565
(VI)	3549	929	882	834	672	585

Table TS3. Showing number of various interactions in complexes (**I-VI**)

Complex (I)			**Complex (II)**		
	Total interactions	**Bond distance range (Å)**		**Total interactions**	**Bond distance range (Å)**
Mo-O···Ow	44	2.641-3.033	Mo-O···Ow	34	2.710-3.005
C-H···O-Mo	25	2.330-2.940	C-H···O-Mo	18	2.460-2.890
C-H···N	3	2.280-2.880	C-H···Ow	3	2.790-2.930
C-H···Ow	1	2.070-2.860	Ow···Ow	13	2.306-3.037
Ow···Ow	11	2.820-3.098			
Complex (III)			**Complex (IV)**		
Mo-O···Ow	5	2.870-2.981	Mo-O···Ow	11	2.653-3.014
C-H···O-Mo	21	2.290-2.990	Mo-O···H-N	14	2.659-3.069
Ow···Ow	0		C-H···O-Mo	27	2.380-2.980
			C-H···Ow	5	2.620-2.830
			N-H···Ow	6	1.940-2.730
			Ow···Ow	01	1.950
Complex (V)			**Complex (VI)**		
Mo-O···Ow	6	2.250-3.005	Mo-O···Ow	15	2.721-3.038
Mo-O···H-N	5	2.130-2.920	C-H···O-Mo	49	2.460-2.940
C-H···O-Mo	12	2.510-2.950	C-H···Ow	11	1.890-2.680
C-H···Ow	6	2.810-2.930	C-H···N	2	2.040
C-H···N	1	2.910	N-H···Ow	6	1.990-2.730
Ow···Ow	12	2.173-2.929	N-H···O-Mo	23	1.920-2.830
			Ow···Ow	13	2.818-3.085