Patterns of hydrogen bonding in organometallic crystals

- Supplementary Material -

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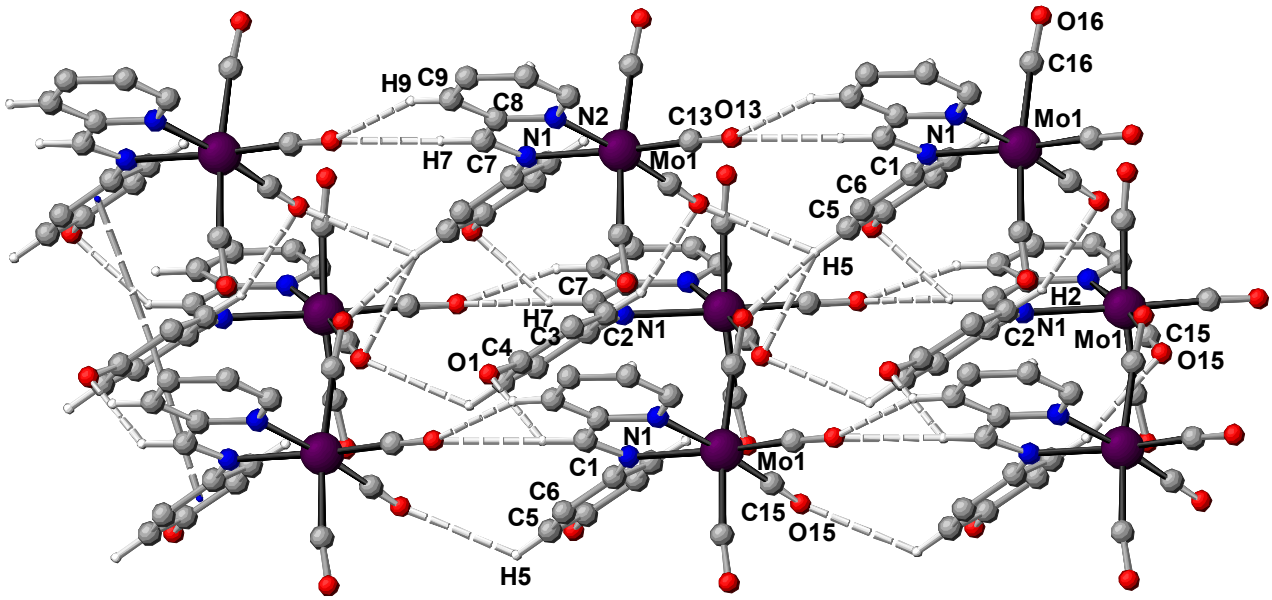
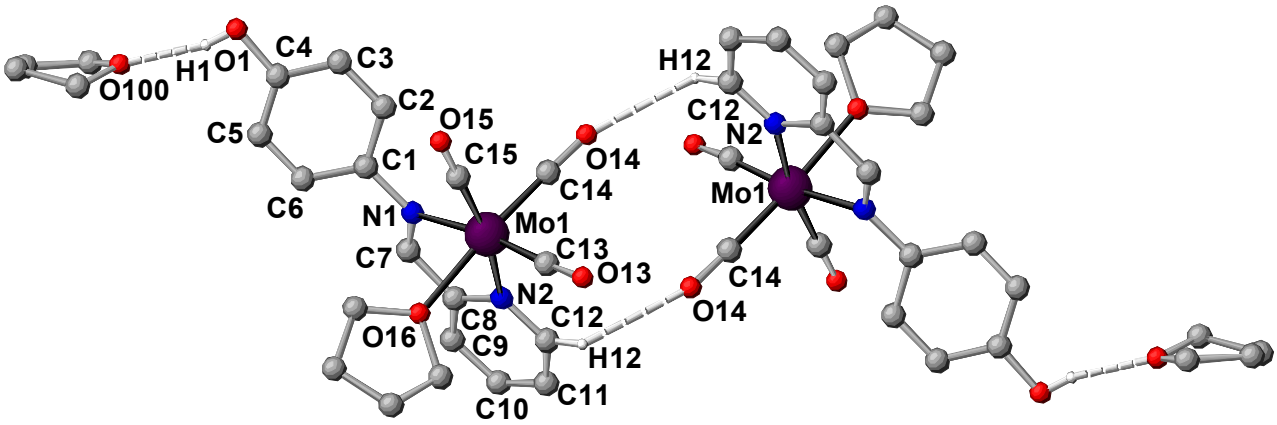
Supplementary material

Figure S1. Packing of **1** in the ac-plane [a]



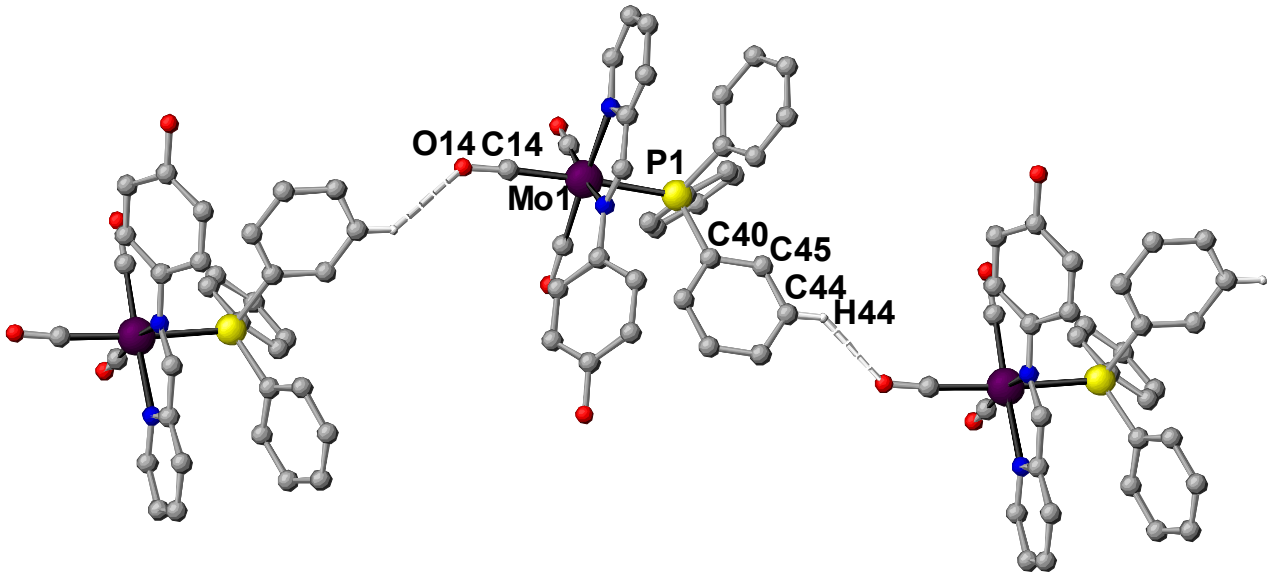
[a] Hydrogen bonds indicated by light dashed lines; π-π interactions by dark dashed lines.

Figure S2. Molecular structure of **2** showing the D and $R^2_2(12)$ motifs [a]



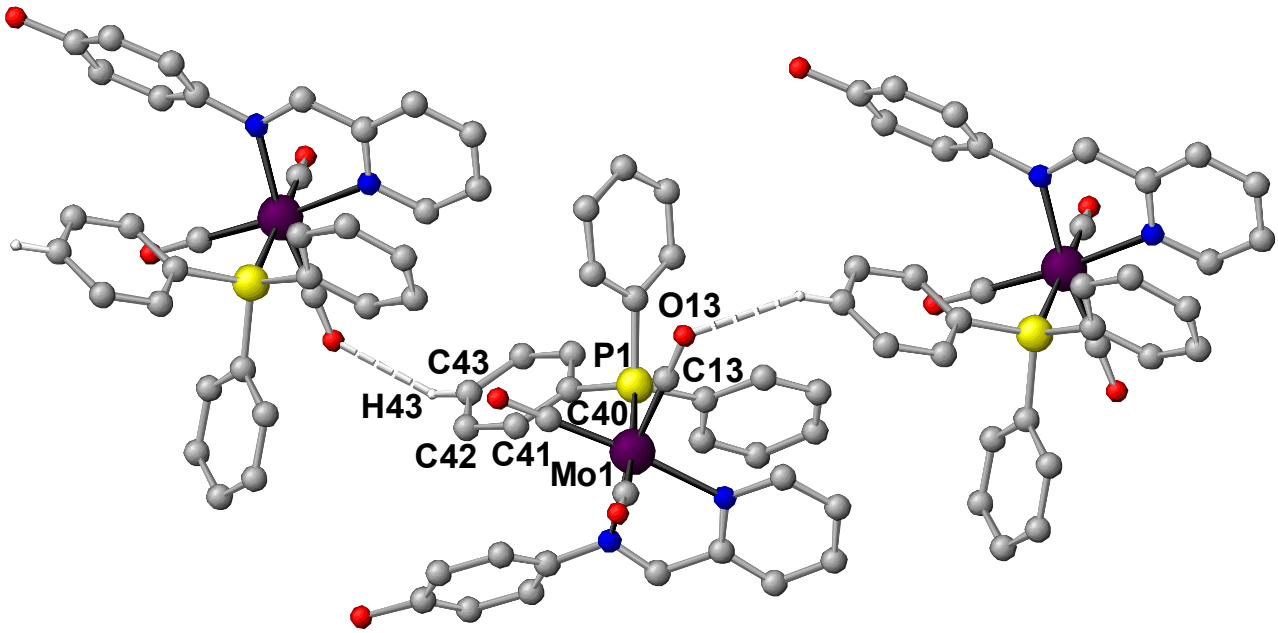
[a] Hydrogen bonds indicated by dashed lines.

Figure S3. Molecular structure of **3a** showing the C(8) motif [a]



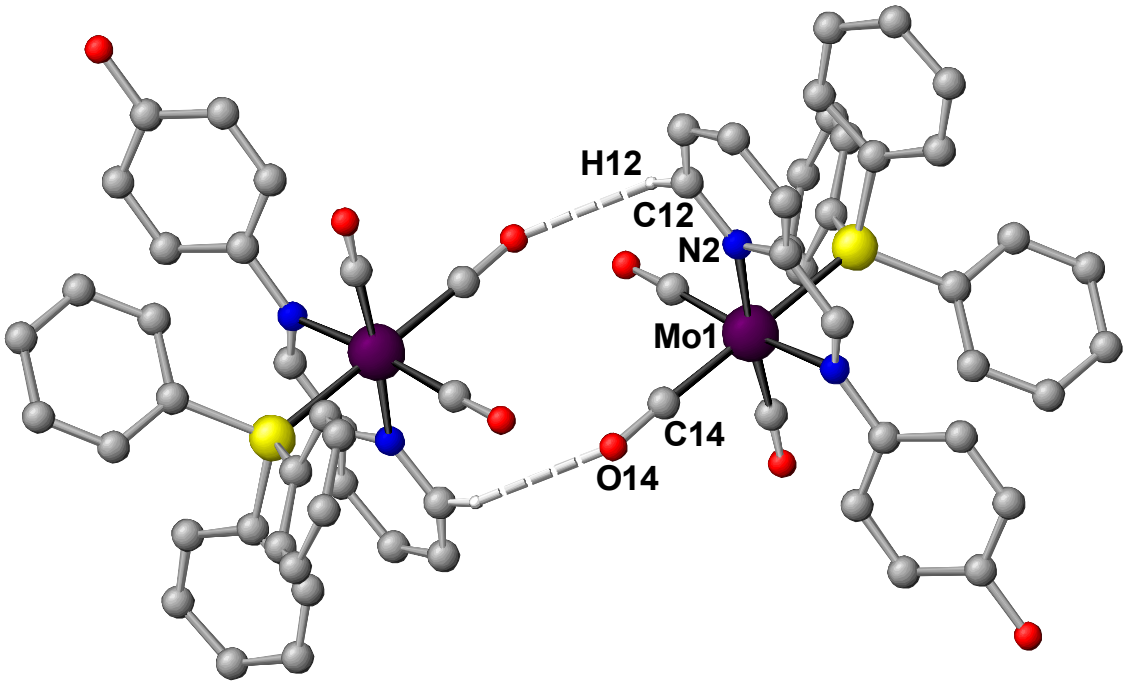
[a] Solvent molecules (Et_2O) omitted. Hydrogen bonds indicated by dashed lines.

Figure S4. Molecular structure of **3a** showing the C(9) motif [a]



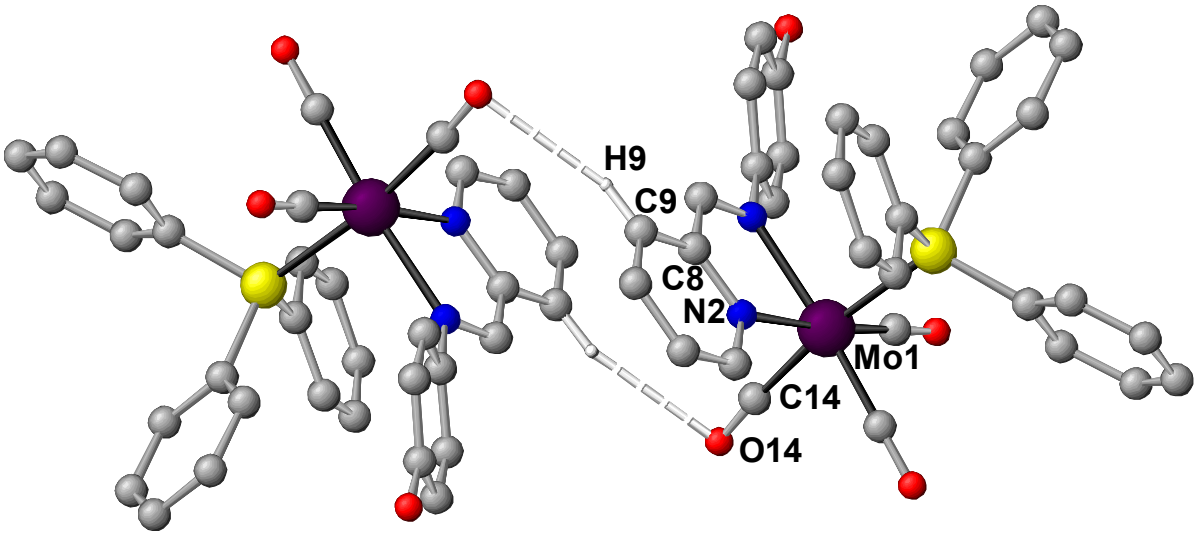
[a] Solvent molecules (Et_2O) omitted. Hydrogen bonds indicated by dashed lines.

Figure S5. Molecular structure of **3a** showing the $R^2_2(12)$ motif [a]



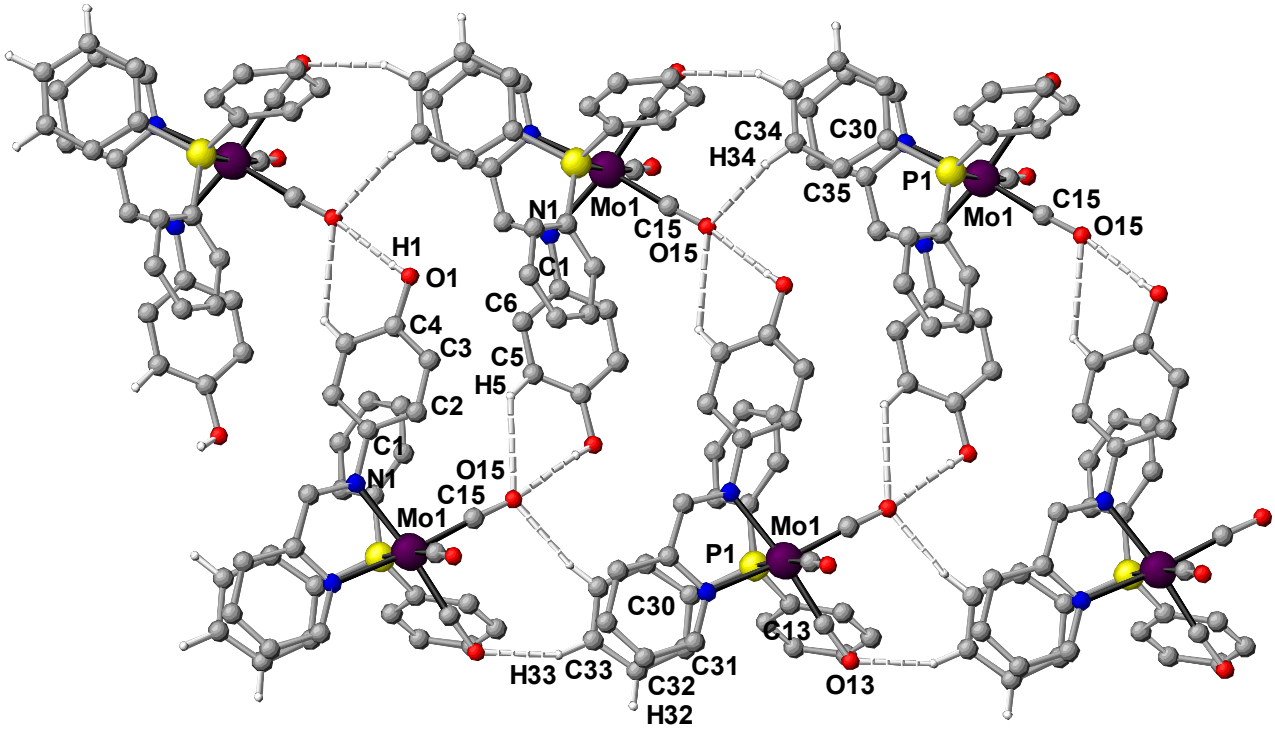
[a] Solvent molecules (Et_2O) omitted. Hydrogen bonds indicated by dashed lines.

Figure S6. Molecular structure of **3a** showing the $R^2_2(14)$ motif [a]



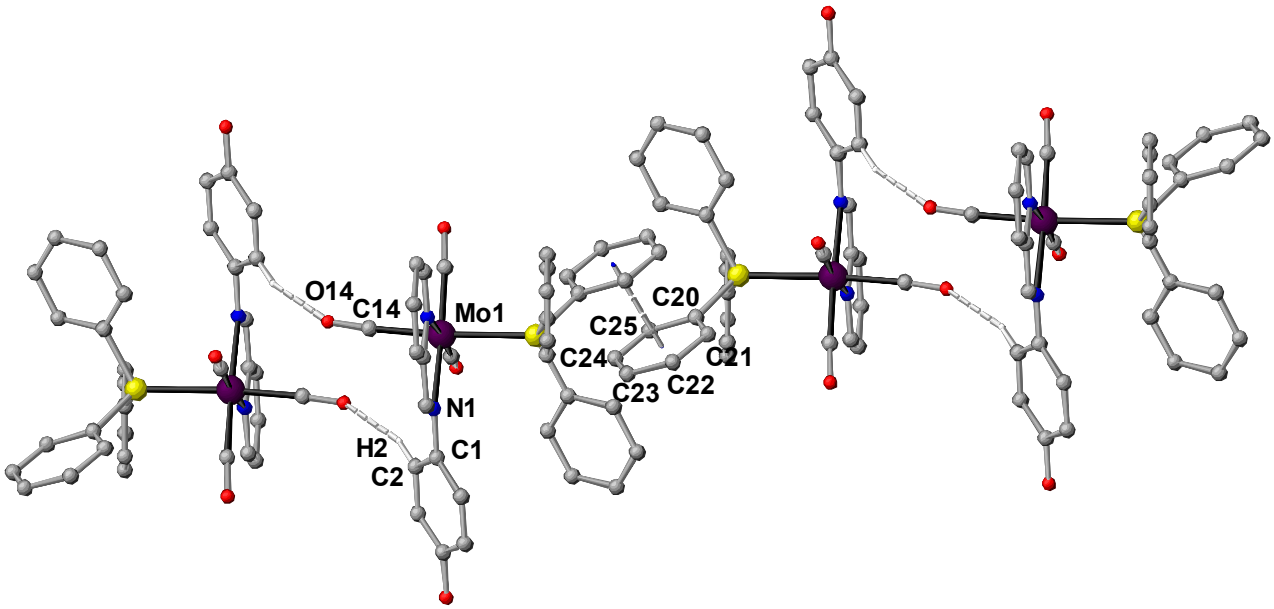
[a] Solvent molecules (Et_2O) omitted. Hydrogen bonds indicated by dashed lines.

Figure S7. Molecular structure of **3b** showing the two C(8), C(9) and C(10) motifs [a]



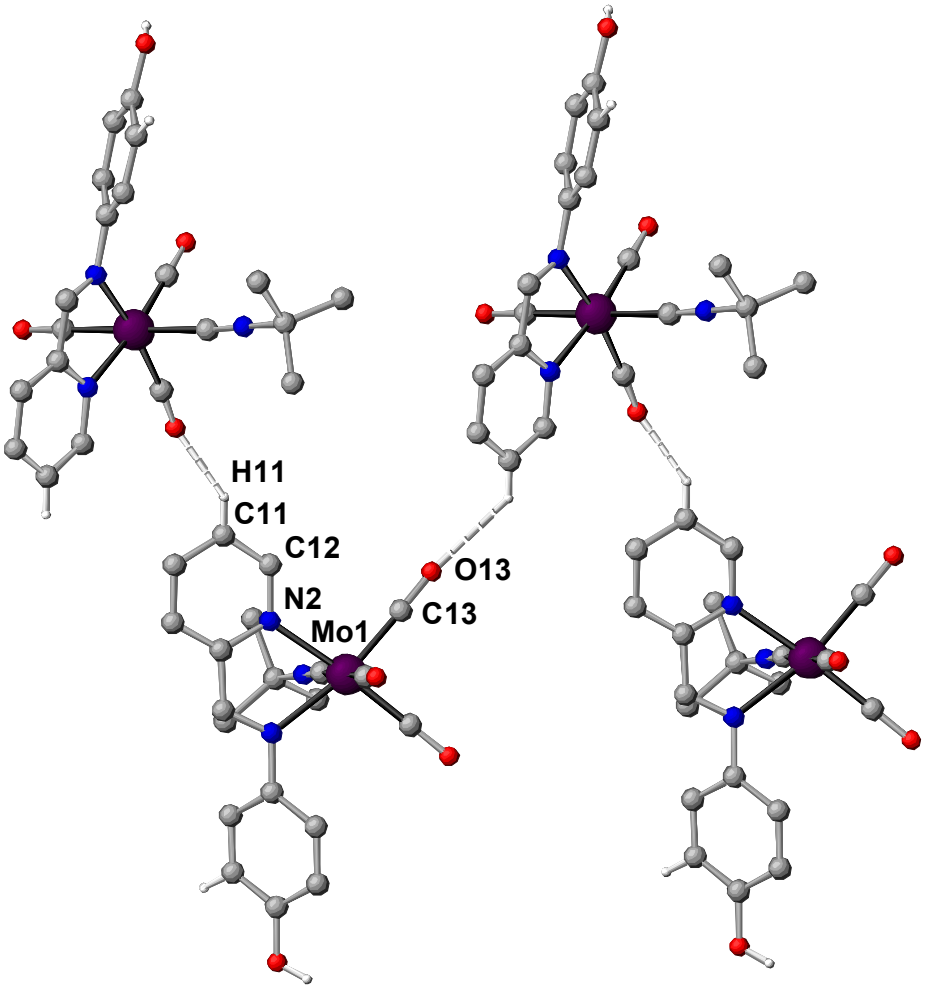
[a] Hydrogen bonds indicated by dashed lines.

Figure S8. Molecular structure of **3b** showing the $R^2_2(14)$ motif and π-π interaction [a]



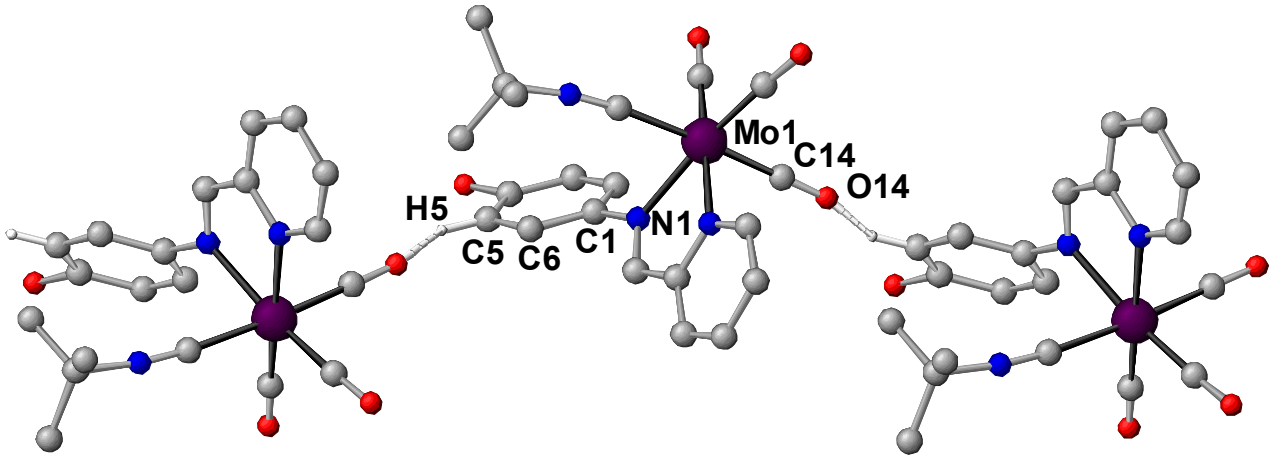
[a] Hydrogen bonds indicated by dashed lines.

Figure S9. Molecular structure of **4** showing the C(7) motif [a]



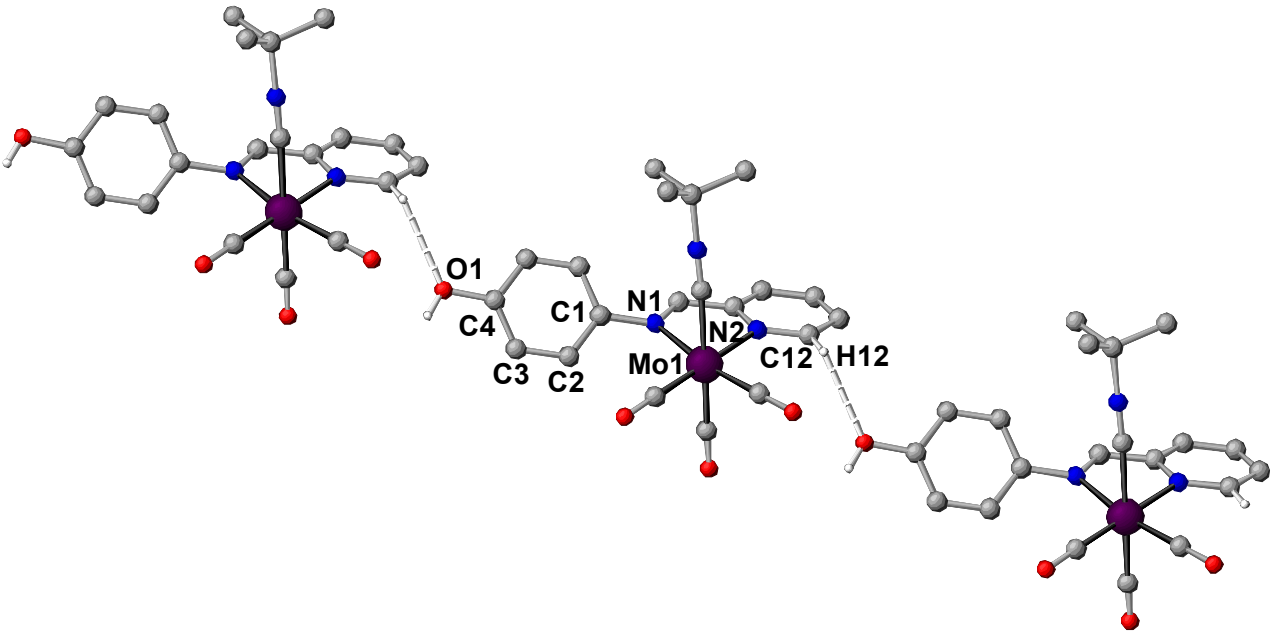
[a] Hydrogen bonds indicated by dashed lines.

Figure S10. Molecular structure of **4** showing the C(8) motif [a]



[a] Hydrogen bonds indicated by dashed lines.

Figure S11. Molecular structure of **4** showing the C(10) motif [a]



[a] Hydrogen bonds indicated by dashed lines.

Figure S12. Superimposed structures of **1** and **D-1**.

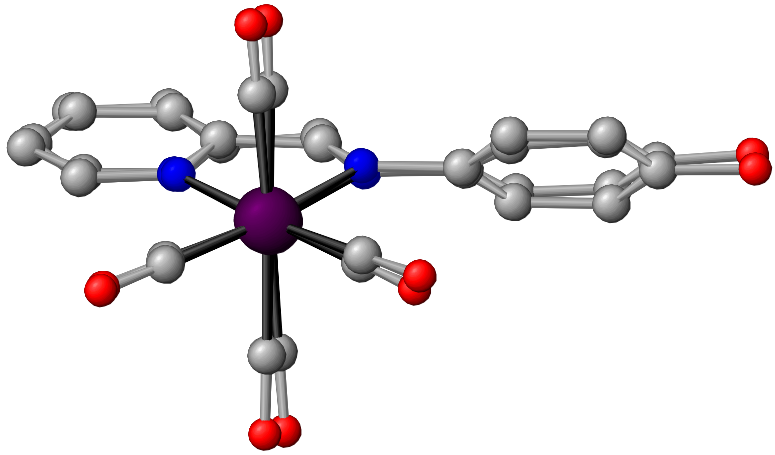


Figure S13. Superimposed structures of **2** and **D-2**.

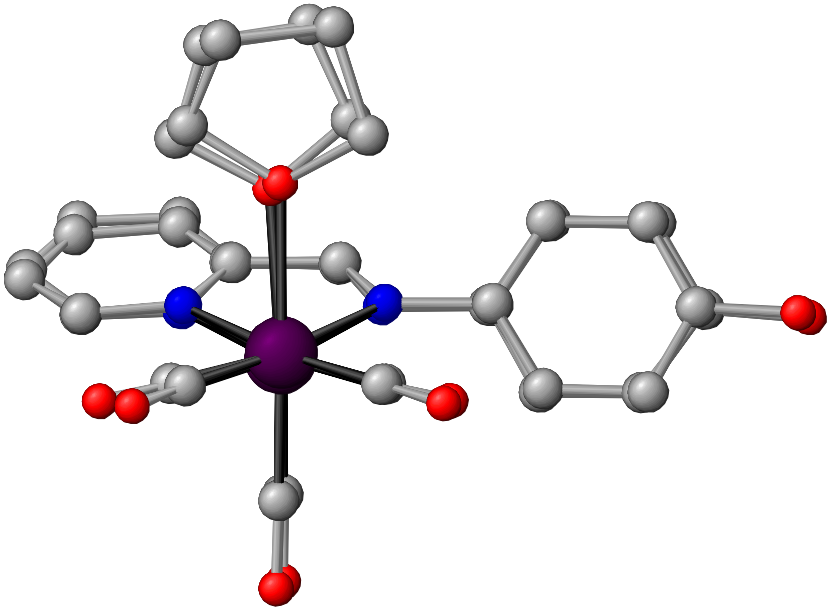


Figure S14. Superimposed structures of **3a** and **D-3**.

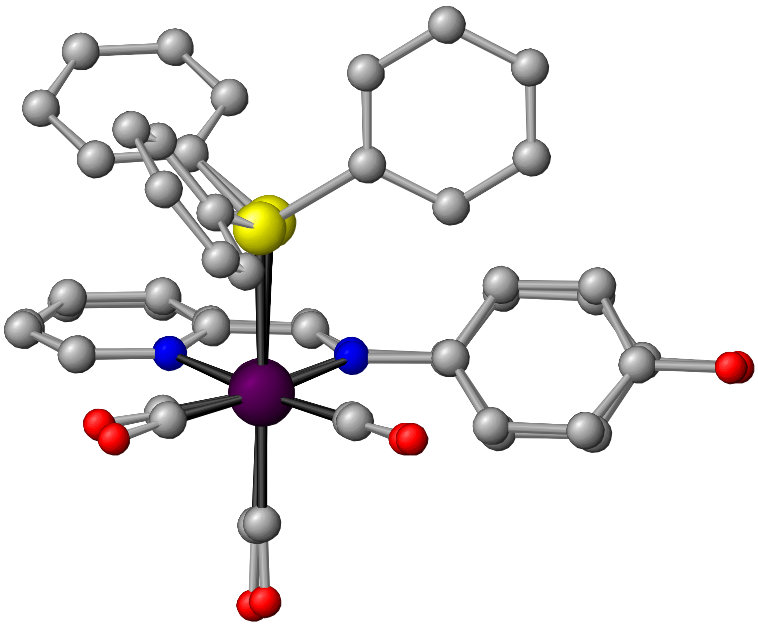


Figure S15. Superimposed structures of **3b** and **D-3**.

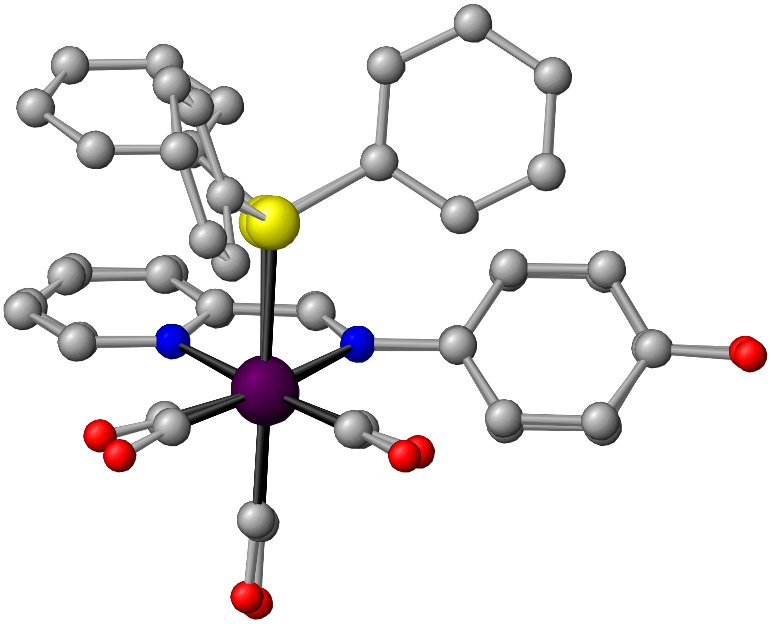


Figure S16. Superimposed structures of **4** and **D-4**.

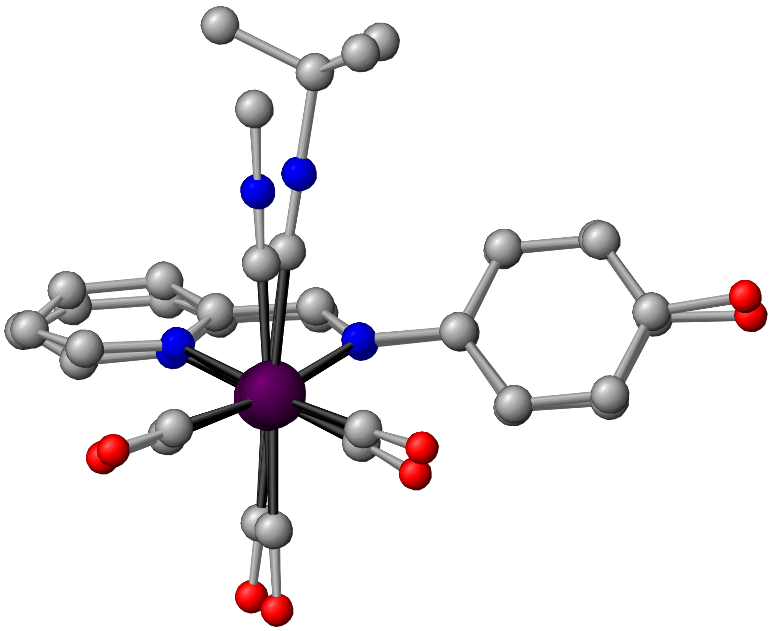


Figure S17. Superimposed structures of **5** and **D-4**.

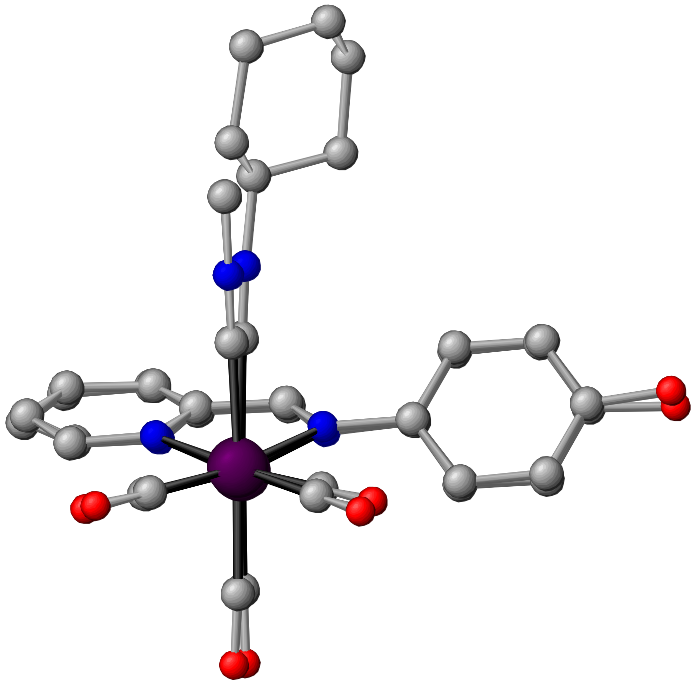


Figure S18. Optimised geometry structure of **D-1·H$_2$O**.

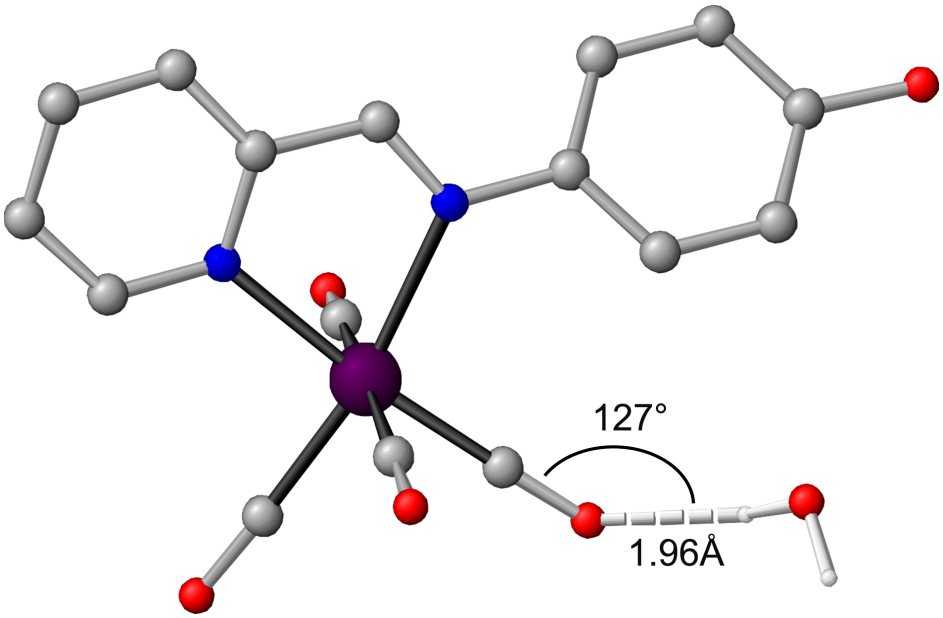


Table S1. DFT Optimised coordinates of **D-1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-.685515	.983444	3.296653
2	1	0	4.571012	-2.240624	1.382316
3	1	0	6.533062	-1.161277	.503026
4	6	0	-.765251	.964973	2.115537
5	6	0	4.020572	-1.564047	.730772
6	8	0	6.095485	-.531523	-.105682
7	1	0	2.091458	-2.301253	1.352196
8	6	0	2.617767	-1.605763	.703325
9	6	0	4.704189	-.630556	-.073762
10	8	0	1.291521	3.359937	.209605
11	6	0	.465004	2.503599	.161199
12	6	0	1.890710	-.710402	-.112282
13	6	0	3.986750	.268363	-.888124
14	1	0	4.535166	.984872	-1.490410
15	6	0	2.588946	.236377	-.894790
16	7	0	.451653	-.739827	-.145421
17	42	0	-.898407	1.062345	.075952
18	6	0	-2.364214	2.368615	.316108
19	8	0	-3.291233	3.106663	.460275
20	6	0	-.153332	-1.907302	-.204498
21	1	0	.404827	-2.838367	-.301460
22	1	0	2.032288	.930959	-1.513911
23	6	0	-1.602890	-1.956204	-.172990
24	7	0	-2.237615	-.738587	-.047411
25	1	0	-1.784782	-4.103397	-.370316
26	6	0	-2.323753	-3.165670	-.269161
27	6	0	-3.598854	-.720964	-.013792
28	1	0	-4.064903	.251753	.087198
29	6	0	-3.724345	-3.135706	-.234381
30	6	0	-4.370598	-1.888420	-.103120
31	1	0	-4.300096	-4.053474	-.307209
32	1	0	-5.452756	-1.815702	-.070540
33	6	0	-1.027304	1.418917	-1.932061
34	8	0	-1.103535	1.702446	-3.079886

Table S2. DFT Optimised coordinates of **D-2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.186455	1.547028	2.600750
2	6	0	-2.231717	1.069609	2.049758
3	42	0	-.739690	.214728	1.094685
4	6	0	.559531	1.427659	1.949776
5	8	0	-.981474	1.628917	-.747030
6	6	0	-.537393	-.970125	2.636779
7	7	0	-2.017345	-1.190021	-.067550
8	7	0	.646945	-.922662	-.246238
9	8	0	1.362702	2.155028	2.462526
10	6	0	-2.294932	2.114649	-1.254646
11	6	0	.089807	2.582028	-1.141158
12	8	0	-.414377	-1.689584	3.586923
13	6	0	-3.358949	-1.383700	.094231
14	6	0	2.077110	-.772723	-.305360
15	6	0	-1.369621	-1.910119	-1.054914
16	6	0	.062359	-1.727359	-1.119414
17	6	0	-1.999637	3.458878	-1.951182
18	6	0	-.500341	3.347954	-2.332556
19	6	0	2.818518	-.695282	.896261
20	6	0	2.760355	-.692077	-1.540287
21	6	0	-4.098264	-2.265983	-.702979
22	6	0	-2.064079	-2.811137	-1.894857
23	1	0	-2.971753	2.206915	-.401175
24	1	0	-2.673529	1.355374	-1.948372
25	1	0	.298838	3.238779	-.288202
26	1	0	.977536	1.988773	-1.372771
27	1	0	-3.830959	-.814689	.886724
28	1	0	.637296	-2.318918	-1.831486
29	6	0	4.210918	-.569281	.866060
30	6	0	4.157286	-.546579	-1.577006
31	6	0	-3.441362	-2.991588	-1.724119
32	1	0	-2.151883	4.293221	-1.256427
33	1	0	-2.643875	3.618169	-2.821912
34	1	0	-.028825	4.327221	-2.465573
35	1	0	-.378044	2.775547	-3.260459
36	1	0	2.294772	-.747632	1.844004
37	1	0	2.203178	-.710213	-2.473850
38	1	0	-5.162479	-2.382831	-.525141
39	1	0	-1.516903	-3.359748	-2.656699
40	6	0	4.882221	-.494649	-.370387
41	1	0	4.788858	-.518120	1.782822
42	1	0	4.670730	-.468021	-2.534253
43	1	0	-3.992978	-3.681183	-2.356362
44	8	0	6.272650	-.358012	-.325270
45	1	0	6.673240	-.308129	-1.217124

Table S3. DFT Optimised coordinates of **D-3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.999854	-1.595412	.689171
2	6	0	2.595615	-1.627248	.691320
3	6	0	4.671149	-.613637	-.065989
4	1	0	4.560810	-2.320365	1.276989
5	8	0	6.063730	-.520307	-.122403
6	6	0	1.854185	-.676065	-.045218
7	6	0	3.941093	.340958	-.801639
8	1	0	2.080894	-2.369550	1.296290
9	6	0	2.543194	.315846	-.779799
10	7	0	.413439	-.692410	-.050903
11	1	0	6.508398	-1.203552	.419681
12	1	0	4.479786	1.092740	-1.368753
13	42	0	-.913679	1.102758	.205231
14	6	0	-.197895	-1.862037	-.145247
15	1	0	1.974729	1.050797	-1.338017
16	6	0	.449683	2.517939	.402498
17	6	0	-2.365040	2.402403	.490323
18	6	0	-1.642349	-1.898042	-.121481
19	7	0	-2.262964	-.670760	.028348
20	6	0	-.996440	1.537976	-1.719047
21	15	0	-.807938	.753369	2.818767
22	1	0	.355226	-2.789562	-.289196
23	8	0	1.283931	3.367732	.522710
24	8	0	-3.296461	3.139511	.656243
25	6	0	-2.380818	-3.094515	-.267091
26	6	0	-3.628316	-.638786	.028039
27	8	0	-1.045578	1.833033	-2.874839
28	1	0	.150327	-.138267	3.419458
29	1	0	-1.960173	.276853	3.537172
30	1	0	-.536793	1.895716	3.640045
31	6	0	-3.779484	-3.046155	-.262880
32	6	0	-4.411915	-1.790702	-.112776
33	1	0	-1.851872	-4.035927	-.387793
34	1	0	-4.083348	.338537	.137127
35	1	0	-4.366570	-3.952529	-.377167
36	1	0	-5.493614	-1.703052	-.109814

Table S4. DFT Optimised coordinates of **D-4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	.837336	-1.659045	2.801680
2	6	0	.848949	-1.336683	1.654353
3	6	0	.817354	-2.130649	4.148160
4	42	0	.870084	-.925497	-.436553
5	1	0	.348197	-1.389891	4.806616
6	1	0	1.838353	-2.317335	4.502181
7	1	0	.248857	-3.066222	4.213331
8	6	0	-.475786	-2.365233	-.625213
9	7	0	-.494457	.837814	-.130912
10	6	0	2.352254	-2.218515	-.589045
11	7	0	2.183667	.862566	-.149358
12	6	0	.896009	-.784361	-2.448661
13	8	0	-1.298748	-3.225910	-.728398
14	6	0	-1.932210	.780964	-.077185
15	8	0	3.296188	-2.952065	-.662890
16	6	0	.094998	1.997510	.098864
17	6	0	1.539086	2.061872	.085940
18	6	0	3.547397	.864938	-.194711
19	8	0	.913412	-.764676	-3.638995
20	6	0	-2.652100	1.439254	.944509
21	6	0	-2.639437	.046961	-1.055958
22	6	0	2.252548	3.266809	.278173
23	6	0	4.308129	2.026223	-.011076
24	1	0	-.476758	2.911795	.255860
25	1	0	4.020747	-.090641	-.385759
26	6	0	-4.054691	1.374551	.984878
27	6	0	-4.036815	-.005500	-1.032476
28	6	0	3.651227	3.254271	.230952
29	1	0	-2.118578	1.967464	1.730763
30	1	0	-2.086690	-.465989	-1.834758
31	1	0	1.704764	4.188349	.455161
32	1	0	5.390721	1.967806	-.060262
33	6	0	-4.745748	.657553	-.011517
34	1	0	-4.598836	1.867994	1.788858
35	1	0	-4.590237	-.559467	-1.783409
36	1	0	4.219704	4.168586	.373378
37	8	0	-6.139284	.552534	-.042238
38	1	0	-6.566774	1.026297	.700153

Table S5. DFT Optimised coordinates of **D-1·H_2O**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-.822566	.490869	3.431475
2	6	0	-.881891	.634074	2.258491
3	42	0	-.965209	1.000499	.245427
4	6	0	.546348	2.238535	.479290
5	7	0	.152970	-.936367	-.176783
6	6	0	-2.253791	2.452317	.631298
7	7	0	-2.527081	-.585955	-.115103
8	6	0	-1.019658	1.574866	-1.716912
9	8	0	1.480746	2.982808	.587131
10	6	0	1.578472	-1.112595	-.087538
11	8	0	-3.072679	3.289850	.857926
12	6	0	-.603195	-1.988138	-.404798
13	6	0	-2.048348	-1.844919	-.404397
14	6	0	-3.874050	-.394158	-.092679
15	8	0	-1.046387	1.977891	-2.829626
16	6	0	2.131385	-2.231935	.577266
17	6	0	2.444206	-.144712	-.645167
18	6	0	-2.914945	-2.923841	-.680325
19	6	0	-4.786835	-1.426626	-.355208
20	1	0	3.143145	2.970013	-.458494
21	1	0	-.174228	-2.967720	-.614482
22	1	0	-4.214477	.607549	.140846
23	6	0	3.522593	-2.383925	.672840
24	6	0	3.832124	-.292382	-.561105
25	6	0	-4.300965	-2.715731	-.657179
26	8	0	3.749295	2.792933	-1.210577
27	1	0	1.482491	-2.954877	1.065335
28	1	0	2.043567	.718051	-1.162999
29	1	0	-2.497942	-3.900591	-.908112
30	1	0	-5.851275	-1.218867	-.322941
31	6	0	4.371744	-1.415386	.096603
32	1	0	3.939080	-3.235642	1.208446
33	1	0	4.477438	.474070	-.976257
34	1	0	-4.986560	-3.531180	-.867208
35	1	0	3.833449	3.586337	-1.771852
36	8	0	5.762814	-1.504045	.158688
37	1	0	6.068053	-2.292991	.651917

Table S6. Main geometrical parameters for H···O contacts and π-π interactions in complexes **1**, **2**, **3a**, **3b**, **4** and **5** [a)]

	D	A	D-H	H···A	D-H-A	D···A	motif	atoms	symmetry
1	C7-H7	O1	1.00	2.61	128.7	3.33	C(8)	O1-C4-C3-C2-C1-N1-C7-H7	glide plane (c)
	C7-H7	O13	1.00	2.52	148.2	3.41	C(6)	O13-C13-Mo1-N1-C7-H7	translation (a)
	C9-H9	O13	0.93	2.50	149.8	3.34	C(7)	O13-C13-Mo1-N2-C8-C9-H9	translation (a)
	C2-H2	O15	0.93	2.68	146.6	3.50	C(7)	O15-C15-Mo1-N1-C1-C2-H2	glide plane (c)
	C5-H5	O15	0.93	2.79	121.6	3.37	C(8)	O15-C15-Mo1-N1-C1-C6-C5-H5	translation (a)
	C5-H5	O16	0.93	2.79	131.6	3.48	C(8)	O16-C16-Mo1-N1-C1-C6-C5-H5	glide plane (c)
	C1-6	C1-6	-	-	1	3.60		[b)]	glide plane (c)
2	O1-H1	O100(THF)	0.76	1.94	165.0	2.67	D	O100-H1-O1	-
	C7-H7	O13	0.89	2.97	105.5	3.32	C(6)	O13-C13-Mo1-N1-C7-H7	translation (b)
	C9-H9	O13	1.10	2.85	104.9	3.31	C(7)	O13-C13-Mo1-N2-C8-C9-H9	translation (b)
	C12-H12	O14	1.00	2.75	116.1	3.31	$R^2_2(12)$	O14-C14-Mo1-N2-C12-H12	inversion
	C5-H5	O15	0.96	2.49	134.6	3.23	C(8)	O15-C15-Mo1-N1-C1-C6-C5-H5	translation (b)
3a	O1-H1	O1	0.67	2.11	159.8	2.75	D	O1-H1-O1	inversion
	O1-H1	O100(Et_2O)	1.16	1.46	159.1	2.57	D	O100-H1-O1	-
	C7-H7	O13	1.00	2.65	122.8	3.30	C(6)	O13-C13-Mo1-N1-C7-H7	translation (a)
	C9-H9	O13	0.98	2.72	121.4	3.33	C(7)	O13-C13-Mo1-N2-C8-C9-H9	translation (a)
	C43-H43	O13	1.02	2.64	150.7	3.57	C(9)	O13-C13-Mo1-P1-C40-C41-C42-C43-H43	2_1 (b)
	C44-H44	O14	1.00	2.60	142.7	3.45	C(8)	O14-C14-Mo1-P1-C40-C45-C44-H44	glide plane (n)
	C9-H9	O14	0.98	2.67	156.5	3.59	$R^2_2(14)$	O14-C14-Mo1-N2-C8-C9-H9	inversion
	C12-H12	O14	0.92	2.51	132.2	3.20	$R^2_2(12)$	O14-C14-Mo1-N2-C12-H12	inversion
	C5-H5	O15	0.87	2.56	139.9	3.27	C(8)	O15-C15-Mo1-N1-C1-C6-C5-H5	translation (a)
	C30-35	N2-C8-12	-	-	1	3.72		[b)] (intramolecular)	-
3b	C32-H32	O13	0.91	2.53	139.8	3.28	C(8)	O13-C13-Mo1-P1-C30-C31-C32-H32	2_1 (b)
	C33-H33	O13	0.99	2.77	139.5	3.58	C(9)	O13-C13-Mo1-P1-C30-C31-C32-C33-H33	translation (b)
	C2-H2	O14	0.94	2.61	156.1	3.48	$R^2_2(14)$	O14-C14-Mo1-N1-C1-C2-H2	inversion
	O1-H1	O15	0.69	2.14	162.1	2.80	C(10)	O15-C15-Mo1-N1-C1-C2-C3-C4-O1-H1	2_1 (b)
	C5-H5	O15	0.95	2.73	132.1	3.44	C(8)	O15-C15-Mo1-N1-C1-C6-C5-H5	2_1 (b)
	C34-H34	O15	0.95	2.58	150.5	3.44	C(8)	O15-C15-Mo1-P1-C30-C35-C34-H34	translation (b)
	C30-35	N2-C8-12	-	-	7.5	3.40		[b)] (intramolecular)	-
	C20-25	C20-25	-	-	0	3.92		[b)]	inversion
4	C12-H12	O1	0.94	2.58	123.9	3.20	C(10)	O1-C4-C3-C2-C1-N1-Mo1-N2-C12-H12	translation (a)
	C11-H11	O13	0.90	2.53	133.7	3.21	C(7)	O13-C13-Mo1-N2-C12-C11-H11	2_1 (b)
	C5-H5	O14	0.99	2.72	120.4	3.33	C(8)	O14-C14-Mo1-N1-C1-C6-C5-H5	glide plane (n)
	C3-H3	O15	0.88	2.76	132.3	3.43	$R^2_2(16)$	O15-C15-Mo1-N1-C1-C2-C3-H3	inversion
	O1-H1	O15	0.84	1.98	178.0	2.81	$R^2_2(20)$	O15-C15-Mo1-N1-C1-C2-C3-C4-O1-H1	inversion
5	C12-H12	O1	0.92	2.61	138.6	3.36	C(10)	O1-C4-C3-C2-C1-N1-Mo1-N2-C12-H12	translation (a)
	C11-H11	O13	0.92	2.52	132.1	3.21	C(7)	O13-C13-Mo1-N2-C12-C11-H11	2_1 (b)
	C5-H5	O14	0.92	2.94	121.6	3.51	C(8)	O14-C14-Mo1-N1-C1-C6-C5-H5	glide plane (n)
	C3-H3	O15	0.89	2.69	131.8	3.35	$R^2_2(16)$	O15-C15-Mo1-N1-C1-C2-C3-H3	inversion
	O1-H1	O15	0.72	2.15	167.3	2.85	$R^2_2(20)$	O15-C15-Mo1-N1-C1-C2-C3-C4-O1-H1	inversion

[a)] The C-H distances are directly extracted from the crystal structure determinations and are not normalised. All D···A distances < 3.6 A and D-H···A angles > 120° (except for complex 2) are reported. The full report of all contacts is for completeness only, with the aim of extracting common features. Not all contacts are necessarily considered attractive in nature, which might be especially true for the CH···O contacts.

[b)] π-π interaction. Here the D···A distance corresponds to the distance between the ring centres and the D-H···A angle to the angle between the ring planes.