Supporting Information

Dioxomolybdenum(VI) and Dioxotungsten(VI) complexes Chelated with ONO Tridentate Hydrazone Ligand: Synthesis, Structure and Catalytic Epoxidation Activity

Višnja Vrdoljak,* Jana Pisk, Dominique Agustin,*

Predrag Novak, Jelena Parlov Vuković, Dubravka Matković-Čalogović

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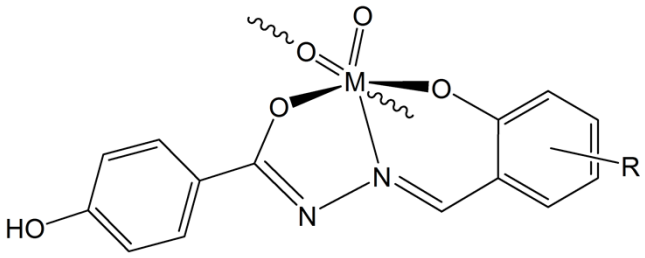
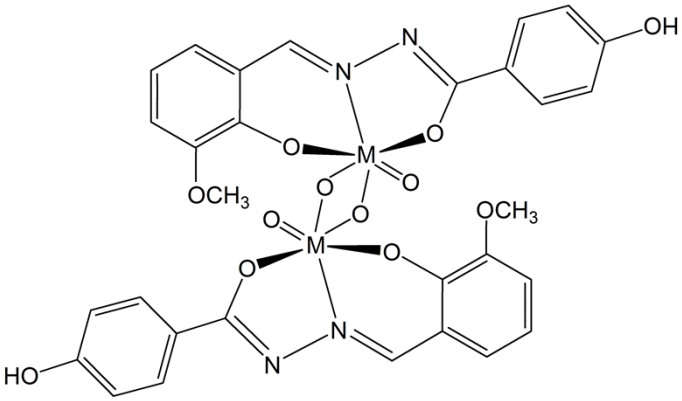
Schemes of polynuclear and dinuclear complexes



M = Mo; R = 3-OCH_3 (**1a**); 4-OCH_3 (**2a**); H (**3a**)

M = W; R = 3-OCH_3 (**4a**); 4-OCH_3 (**5a**); H (**6a**)



Scheme S1 The polynuclear $[MO_2(L^R)]_n$ (**1a-6a**), where M = Mo or W, and dinuclear $[MoO_2(L^R)]_2$ (**1b**) complex.

NMR spectroscopy

Table S1 ^{1}H and ^{13}C chemical shifts (ppm) of compounds $\mathbf{H_2L^{3OMe}}$, **1** and **4**.

Atom	$\mathbf{H_2L^{3OMe}}$		**1**		**4**	
	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
α	8.64	147.59	8.83	154.46	8.84	155.89
1	–	118.88	–	120.67	–	121.05
2	–	147.18	–	149.03	–	147.61
3	–	147.90	–	148.43	–	149.21
4	7.12	121.02	7.27	125.02	7.32	125.12
5	6.87	118.92	7.00	121.59	7.06	121.54
6	7.02	113.72	7.21	116.70	7.31	117.24
1'	11.92	–	–	–	–	–
2'	–	162.46	–	168.94	–	168.59
3'	–	123.23	–	120.37	–	119.96
4', 8'	7.87	129.69	7.85	130.06	7.90	130.21
5', 7'	6.92	115.11	6.87	115.54	6.91	115.69
6'		160.89	–	161.00	–	161.22
OH-2	11.20	–	–	–	–	–
OH-6'	10.19	–	10.19	–	10.27	–
OMe	3.83	55.78	3.81	55.83	3.86	55.87

***** Signals belonging to EtOH were also detected in ^{1}H NMR spectra in dmso solutions of the mononuclear complexes **1** and **4**.

Table S2. ^{1}H and ^{13}C chemical shifts (ppm) of compounds $\mathbf{H_2L^{4OMe}}$, **2** and **5**.

Atom	$\mathbf{H_2L^{4OMe}}$		**2***		**5***	
	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)	δ / ppm (^{1}H)	δ / ppm (^{13}C)
α	8.55	148.21	8.75	154.22	8.73	155.57
1	–	111.81	–	113.72	–	114.16
2	–	159.41	–	161.06	–	159.95
3	6.52	106.29	6.54	103.00	6.62	103.95
4	–	161.88	–	164.88	–	165.31
5	6.53	106.29	6.63	109.14	6.70	109.40
6	7.39	131.17	7.61	135.02	7.63	135.22
1'	11.81	–	–	–	–	–
2'	–	162.31	–	167.74	–	167.35
3'	–	123.33	–	120.49	–	120.12
4', 8'	7.87	129.61	7.82	129.83	7.86	129.95
5', 7'	6.92	115.09	6.87	115.48	6.88	115.62
6'	–	160.81	–	160.73	–	160.93
OH-2	11.83	–	–	–	–	–
OH-6'	10.16	–	10.13	–	10.19	–
OMe	3.79	55.21	3.82	56.73	3.84	55.81

***** Signals belonging to EtOH were also detected in ^{1}H NMR spectra in dmso solutions of the mononuclear complexes **2** and **5**.

Table S3 ^{1}H and ^{13}C chemical shifts (ppm) of compounds $\mathbf{H_2L^H}$, **3** and **6a**.

Atom	$\mathbf{H_2L^H}$		**3***		**6a**	
	δ/ppm (^{1}H)	δ/ppm (^{13}C)	δ/ppm (^{1}H)	δ/ppm (^{13}C)	δ/ppm (^{1}H)	δ/ppm (^{13}C)
α	8.63	147.72	8.58	154.47	8.83	155.89
1	–	118.66	–	120.41	–	120.80
2	–	157.45	–	159.19	–	157.93
3	6.91	119.23	6.94	118.45	7.00	119.37
4	7.30	131.08	7.50	133.93	7.55	135.01
5	6.94	116.37	7.06	121.43	7.07	121.73
6		131.08	7.71	134.46	7.71	134.12
1'	11.94	–	–	–	–	–
2'	–	162.48	–	168.90	–	168.57
3'	–	123.21	–	120.33	–	119.94
4', 8'	7.87	129.70	7.85	130.07	7.88	130.22
5', 7'	6.91	115.11	6.87	115.54	6.88	115.71
6'	10.18	160.91	10.19	161.01	10.25	161.22
OH-2	11.47	–	–	–	–	–
OH-6'	7.51	–	–	–	–	–

* Signals belonging to EtOH were also detected in ^{1}H NMR spectrum in dmso solution of the mononuclear complex **3.**

IR spectroscopy

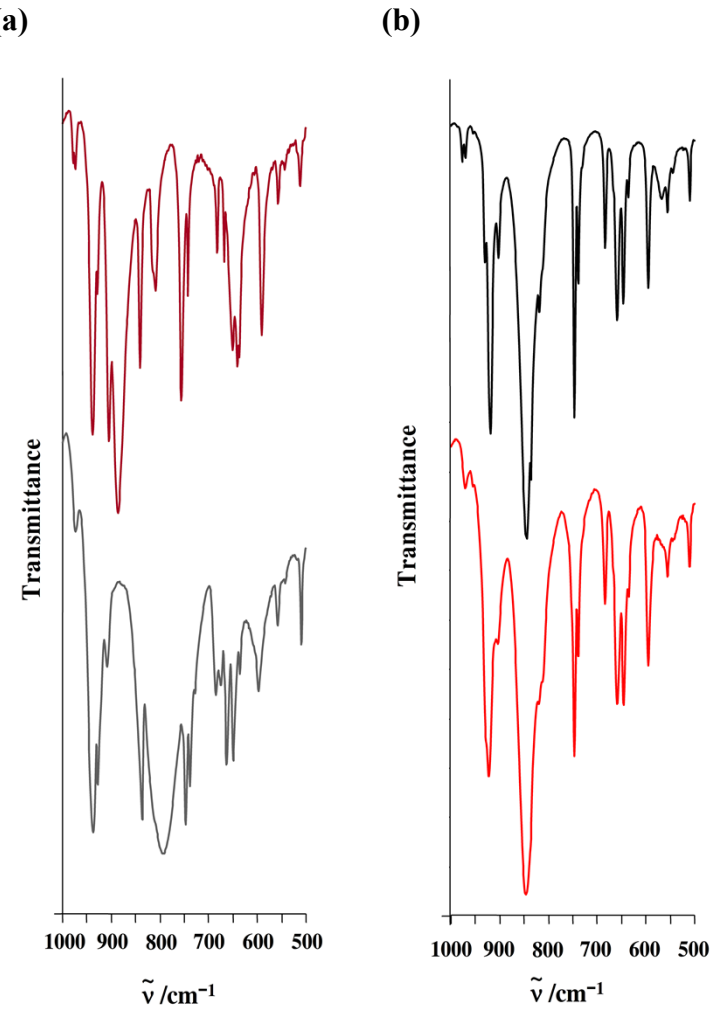


Fig. S1 Comparison of FT-IR spectra of the complexes (a) **3** (dark red) and **6a** (gray) obtained upon reaction of $[MO_2(acac)_2]$ with H_2L^H in C_2H_5OH; (b) **3a** obtained upon conversion of **3** in acetonitrile (black) or upon heating of **3** for 1 hour at 200 °C (red).

Powder X-ray diffraction patterns

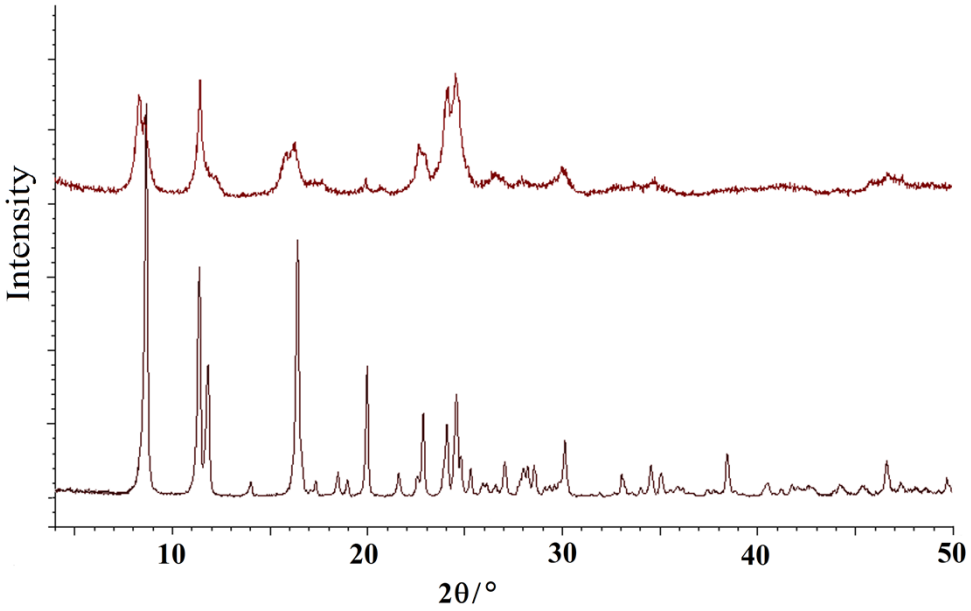


Fig S2 Powder X-ray diffraction patterns of usolvated compoud obtained upon thermally induced reaction and sample **3a** (top); obtained by conversion of **3** in presence of acetonitrile (bottom)

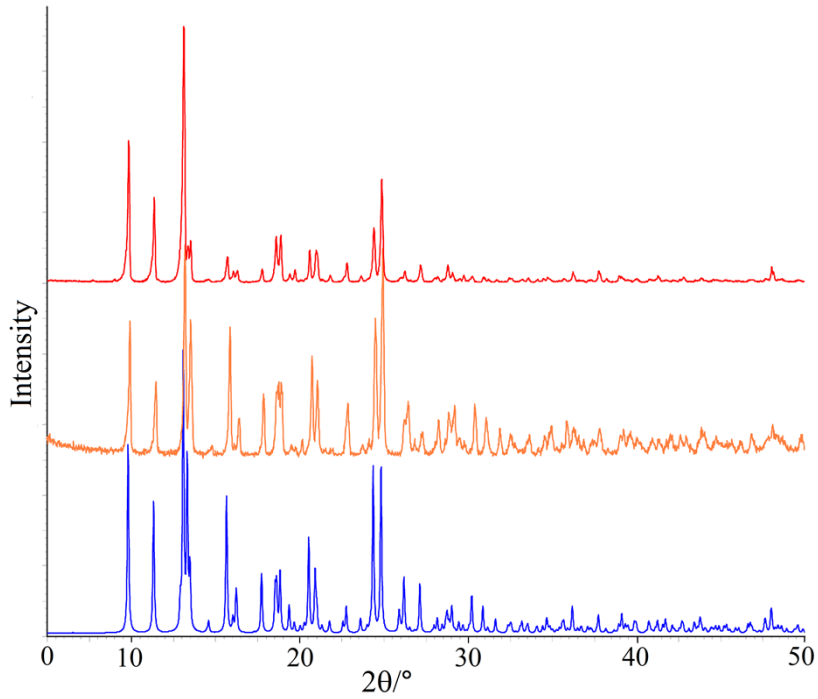


Fig. S3 Powered X-ray diffraction pattern of **1** obtained upon reaction in ethanol (top); of **4** obtained upon reaction in ethanol (middle) and of **1** calculated from the X-ray single-crystal structure (blue).

Crystal and molecular structures

Table S4 Selected bond lengths (Å) and angles (°) for **1**, **2**, **3** **1a·MeCN** and **1b.**

	1	**2**	**3**	**1a·MeCN**	**1b**
Mo–O1	1.6831(17)	1.679(4)	1.6931(13)	1.717(4), 2.273(3)^{i}	1.6855(15)
Mo–O2	1.7166(14)	1.735(4)	1.7275(11)	1.713(4)	1.7608(13), 2.4231(14)^{iii}
Mo–O3	1.9200(16)	1.920(3)	1.9137(12)	1.907(4)	1.8995(13)
Mo–O4	1.9891(14)	1.971(3)	1.9857(12)	1.956(4)	1.9703(13)
Mo–O5	2.3449(17)	2.319(4)	2.3309(12)	-	-
Mo–N1	2.2205(17)	2.211(5)	2.2329(13)	2.236(5)	2.1957(15)
O4–C8	1.334(2)	1.347(6)	1.3354(18)	1.337(8)	1.336(2)
N1–N2	1.398(2)	1.407(5)	1.3991(18)	1.386(7)	1.393(2)
N2–C8	1.285(3)	1.287(7)	1.295(2)	1.314(8)	1.294(3)
N1–C7	1.288(3)	1.294(7)	1.286(2)	1.290(8)	1.292(2)
Mo–O1–Mo	-	-	-	171.5(5)^{ii}	-
Mo–O2–Mo	-	-	-	-	105.53(6)^{iii}
O3–Mo–O4	149.71(6)	148.70(17)	149.88(5)	149.48(19)	151.09(6)
O4–Mo–O1	96.80(7)	98.60(16)	97.07(6)	98.60(18)^{i}, 98.19(16)	96.90(6)
O2–Mo–O4	96.44(6)	98.24(15)	96.73(5)	98.2(2)	95.61(6)
O4–Mo–O5	79.52(6)	79.92(15)	79.12(5)	-	-
N1–Mo–O1	95.23(7)	92.35(17)	95.05(5)	97.9(3)^{i}, 73.6(3)	101.06(6)
O3–Mo–O1	99.70(8)	98.97(16)	98.98(6)	98.3(2)^{i}, 81.34(18)	99.31(7)
O2–Mo–O3	103.48(7)	101.70(16)	103.42(5)	101.58(19)	102.41(6)
O3–Mo–O5	80.67(7)	78.42(15)	81.70(5)	-	-
O3–Mo–N1	81.38(6)	81.39(15)	81.59(5)	80.74(18)	81.43(6)
O1–Mo–O2	105.06(8)	105.59(18)	105.10(6)	105.2(3)^{i}, 83.2(3)	106.64(7), 177.62(6)^{iii}
O1–Mo–O1	-	-	-	171.5(5)^{i}	-
O1–Mo–O5	171.89(7)	170.29(17)	172.28(5)	-	-
O2–Mo–O5	82.63(7)	84.11(17)	82.12(5)	-	-
N1–Mo–O2	157.82(7)	160.93(17)	158.01(6)	156.14(19)	150.90(6), 77.65(6)^{iii}
N1–Mo–O5	76.78(6)	78.04(16)	77.40(5)	-	-

N1–Mo–O4	71.94(6)	72.19(15)	71.72(5)	71.9(2)	72.04(6)

* Symmetry code is for the last atom in the bond or angle (except for O1^{i}-Mo-O2 in **1a·MeCN**): (i) x+1, y, z; (ii) x-1, y, z; (iii) -x, 1-y, 1-z

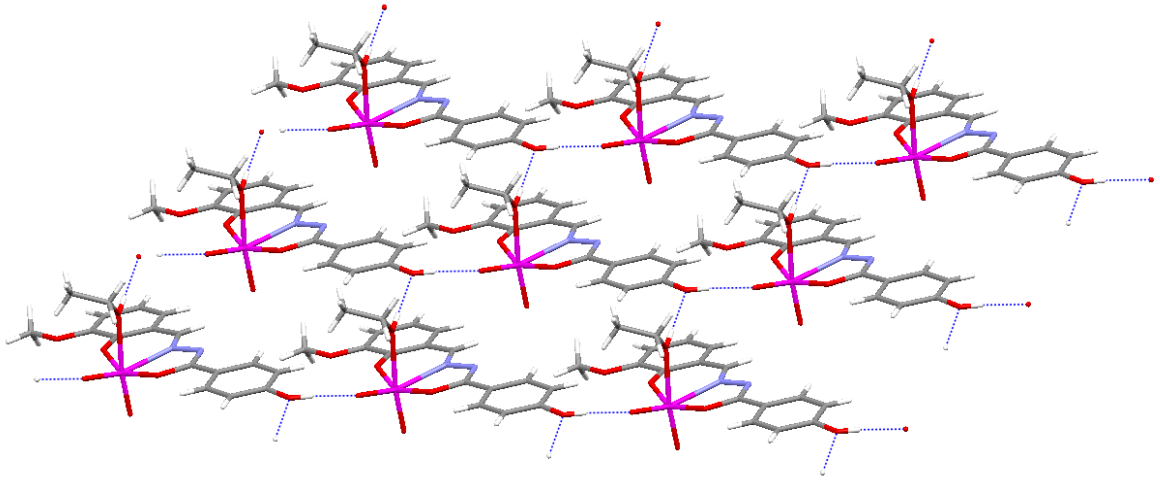
Table S5 Geometry of intra- and intermolecular hydrogen bonds (Å,°) for **1**, **2**, **3**, **1a·MeCN** and **1b**.

complex	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A(°)
1	O5–H5A···O6^{i}	0.80(2)	1.94(2)	2.734(2)	176(3)
	O6–H6A···O2^{ii}	0.82	1.88	2.702(2)	176
	C10–H10···O4	0.93	2.45	2.768(2)	100
2	O5–H5A···O6^{iii}	0.81(5)	1.91(5)	2.725(6)	176(7)
	O6–H6A···O2^{iv}	0.84	1.89	2.705(6)	163
	C5–H5···O1^{v}	0.95	2.57	3.417(7)	148
	C7–H7···O1^{vi}	0.95	2.34	3.216(7)	153
	C10–H10···O4	0.95	2.46	2.788(7)	100
	C11–H11···O3^{iv}	0.95	2.59	3.518(7)	164
3	O6–H6A···O2^{vii}	0.84	1.88	2.7142(16)	171
	O5–H51···O6^{v}	0.806(13)	1.888(13)	2.6817(18)	169(2)
	C5– H5···O1^{viii}	0.94(2)	2.58(2)	3.347(2)	138.9(18)
	C7–H7···O1^{vi}	0.92(2)	2.53(2)	3.3949(19)	156.8(14)
	C14–H14···N2	0.86(2)	2.57(2)	2.856(2)	100.9(16)
1a·MeCN	O6– H6A···O2^{ix}	0.84	2.02	2.853(6)	172
	C13–H13···O4^{ix}	0.95	2.57	3.482(8)	162
	C17–H17B···O2	0.98	2.43	3.377(11)	162
	C17–H17A···O7^{x}	0.98	2.44	3.362(11)	156
1b	O6–H6A···O2^{xi}	0.84	1.97	2.799(3)	167
	C4–H4···O6^{xii}	0.87(2)	2.55(2)	3.397(3)	165(3)
	C7–H7···O1^{xiii}	0.97(3)	2.46(3)	3.195(3)	133(2)
	C14–H14···N2	0.90(3)	2.47(3)	2.828(3)	104(2)

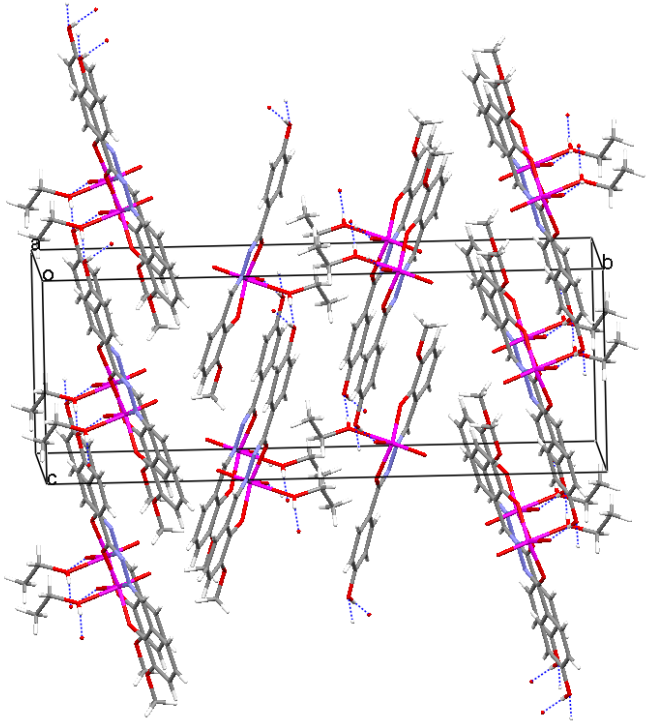
^{i} x, y, 1+z, ^{ii} -1+x, y, -1+z, ^{iii} -x, -1/2+y,1/2-z, ^{iv} 1-x, ½+y, ½-z, ^{v} -x,-y,-z ^{vi} -1+x, y, z, ^{vii} 1-x, -y, -z, ^{viii} -x, -y, 1-z, ^{ix} 1-x, ½+y, -z, ^{x} 1+x, y, z, ^{xi} 1-x, 1-y, 1-z, ^{xii} x, -1+y, 1+z, ^{xiii} 1+x, 1+y, -2+z

Table S6 $\pi\cdots\pi$ interactions (Å) in **1**, **2**, **3** and **1b**. Cg1 is the 6-membered ring C1−C6 and Cg2 is the 6-membered ring C9−C14.

complex	Cg···Cg	d (Å)	Cg···Cg(symmetry code)
1	Cg1···Cg2	3.6022(13)	x,y,1+z
2	Cg1···Cg1	3.524(3)	-x,-y,-z
	Cg1···Cg2	3.558(3)	-x,-1/2+y,1/2-z
3	Cg1···Cg1	3.6729(9)	-x,1-y,1-z
	Cg2···Cg2	3.9628(9)	-x,-y,-z
1b	Cg1···Cg1	3.5390(16)	1-x,1-y,-z
	Cg1···Cg2	4.0253(15)	1-x,1-y,1-z

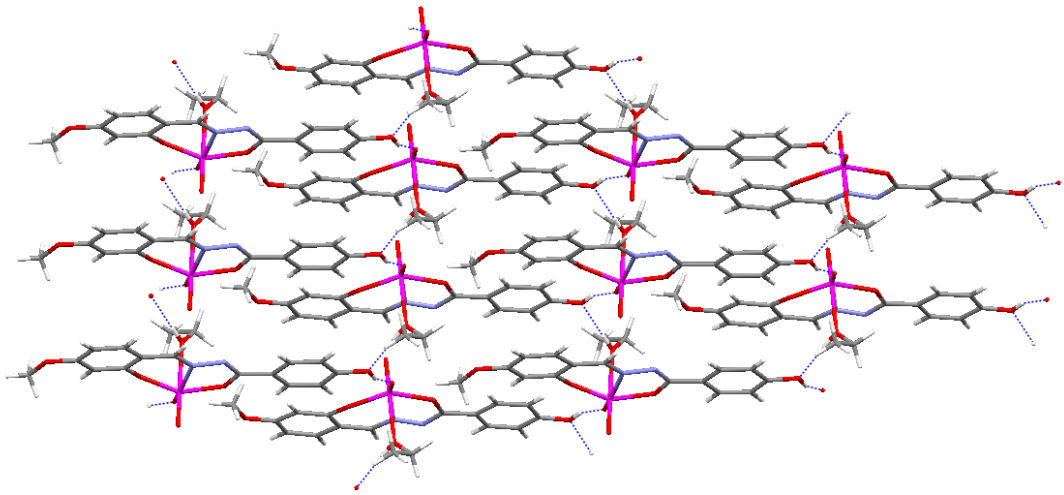


(a)

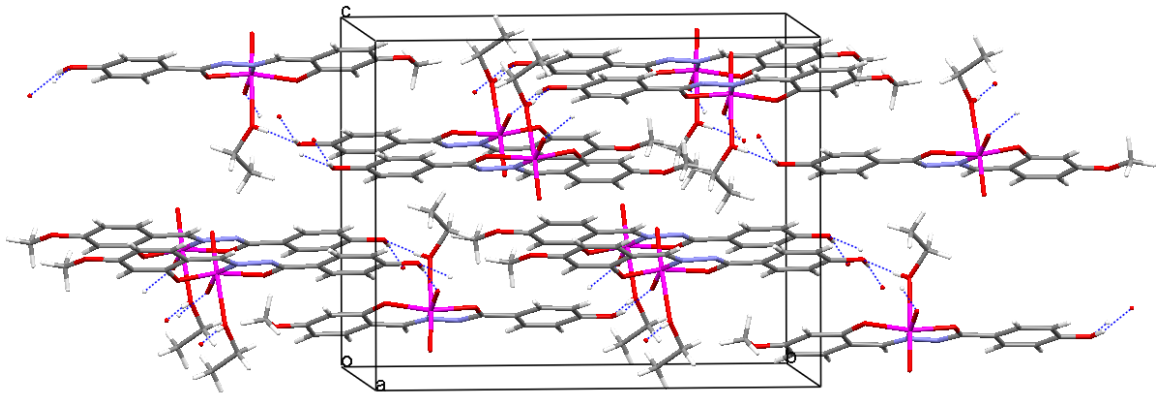


(b)

Fig. S4. (a) Layer of the complex molecules of **1** interconnected by hydrogen bonds; (b) Packing of molecules of **1** in the unit cell. Hydrogen bonds are presented by blue dotted lines.

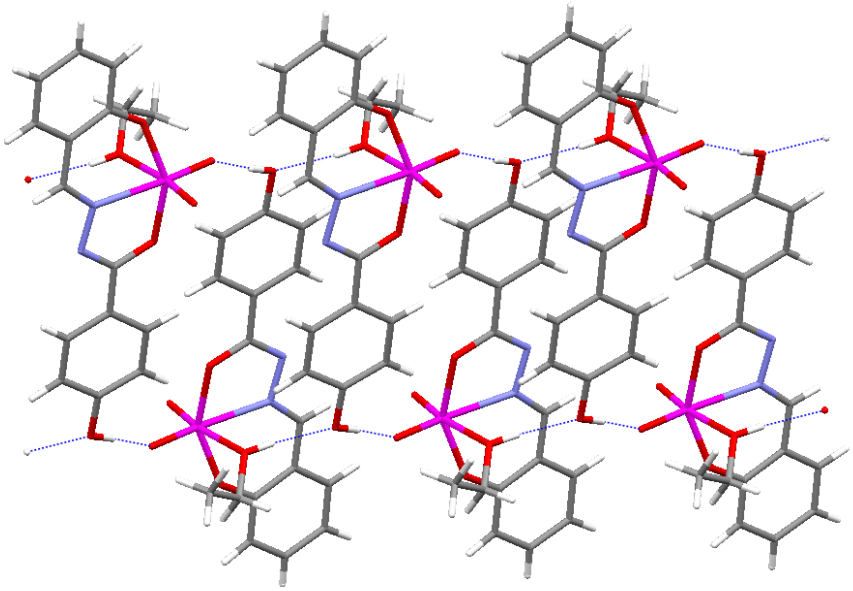


(a)

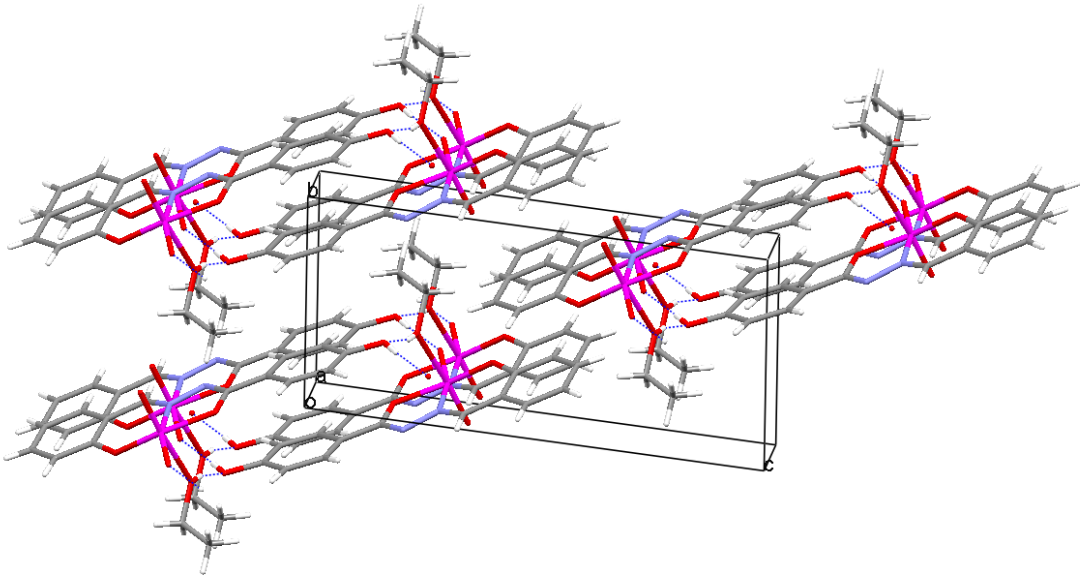


(b)

Fig. S5. (a) Layer of the complex molecules of **2** interconnected by hydrogen bonds; (b) Packing of molecules of **2** in the unit cell. Hydrogen bonds are presented by blue dotted lines.



(a)



(b)

Fig. S6. (a) Double-chain of the complex molecules of **3** interconnected by hydrogen bonds; (b) Packing of molecules of **3** in the unit cell. Hydrogen bonds are presented by blue dotted lines.

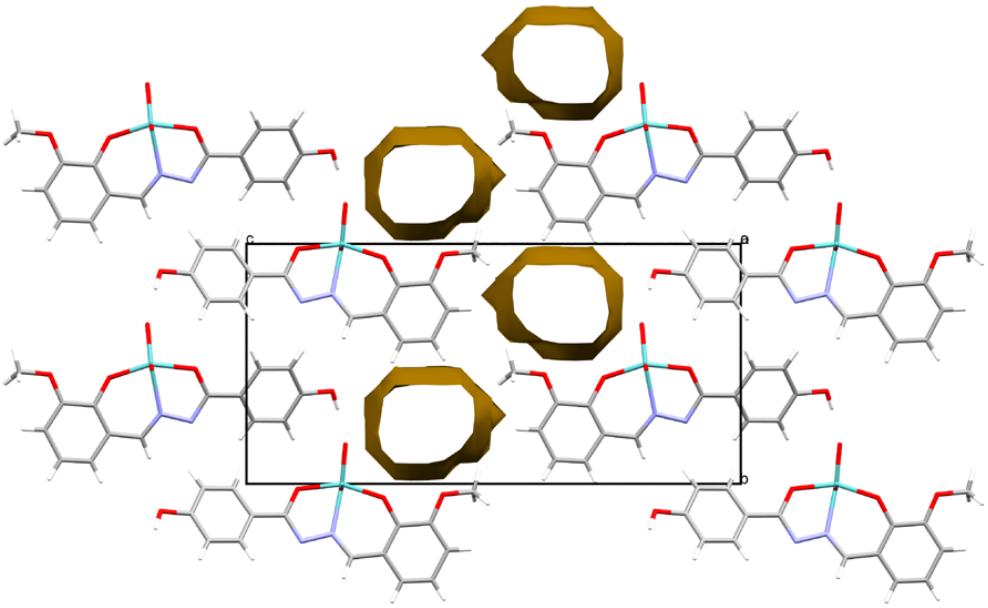
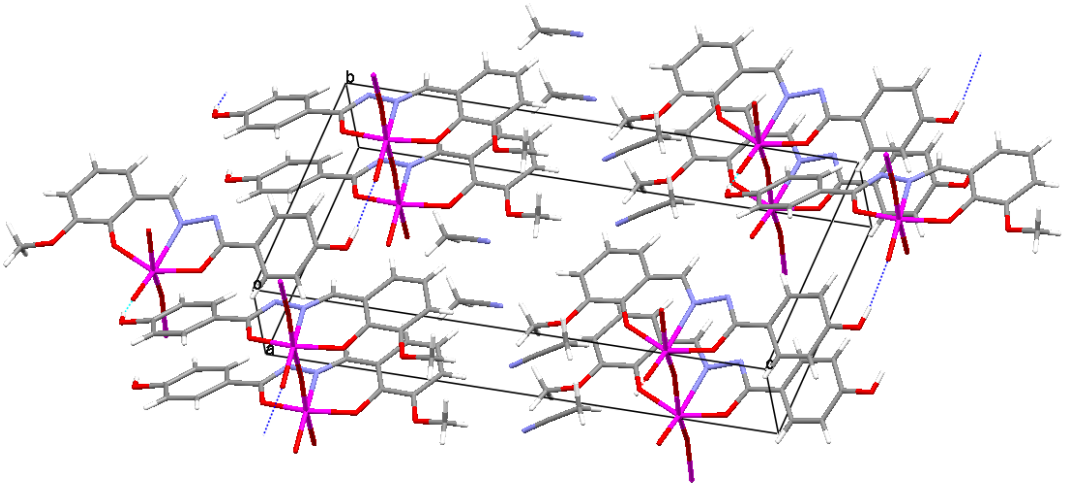
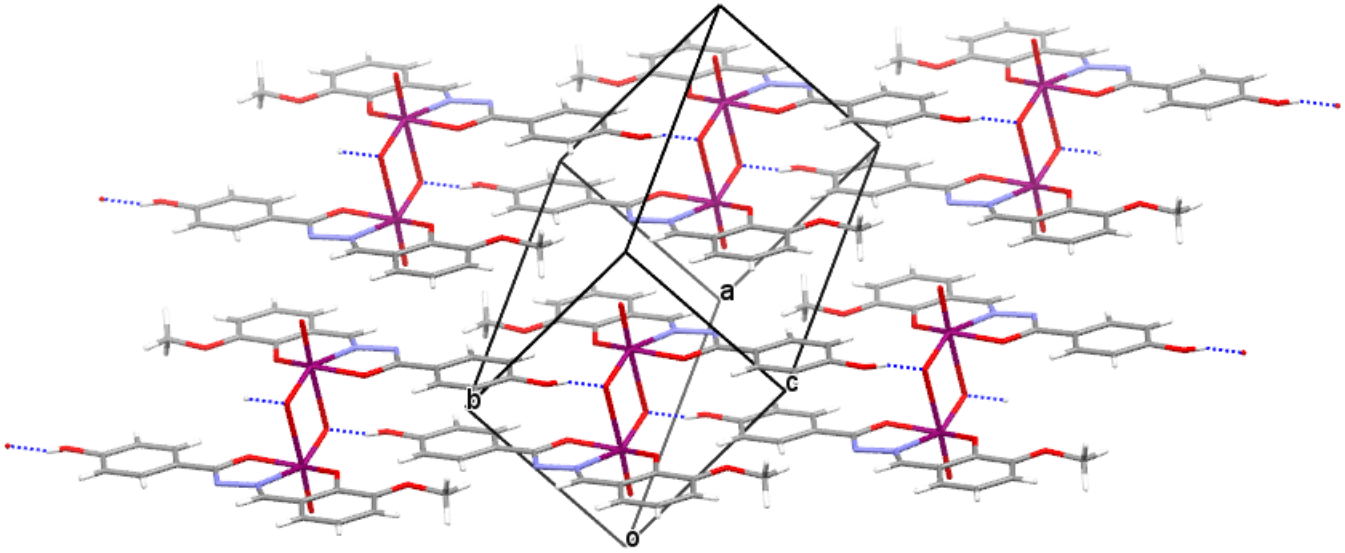


Fig. S7. The crystal packing of the **1a·MeCN.** The solvent acetonitrile molecules are omitted and the void channels are shown in yellow.



(a)



(b)

Fig S8. (a) Packing of complex molecules of **1a·MeCN** in the unit cell; b) packing of complex molecules of **1b** in the unit cell. Hydrogen bonds are presented by blue dotted lines.