Electronic Supplementary Information (ESI)

Dioxidomolybdenum(VI) complexes with isoniazid-related hydrazones: solution-based, mechanochemical and UV-light assisted deprotonation

Višnja Vrdoljak, Biserka Prugovečki, Ivana Pulić, Marko Cigler, Dora Sviben, Jelena Parlov Vuković, Predrag Novak, Dubravka Matković-Čalogović and Marina Cindrić*

** Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a,10000 Zagreb, Croatia*

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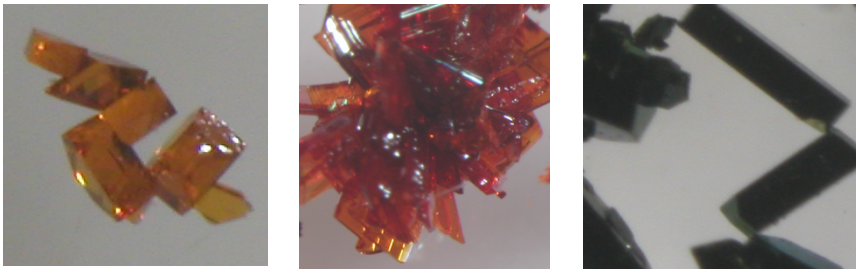


(a) **(b)** **(c)**

Fig. S1 Photos of (a) **1**, (b) **2** and (c) **3**.

Powder X-ray diffraction patterns

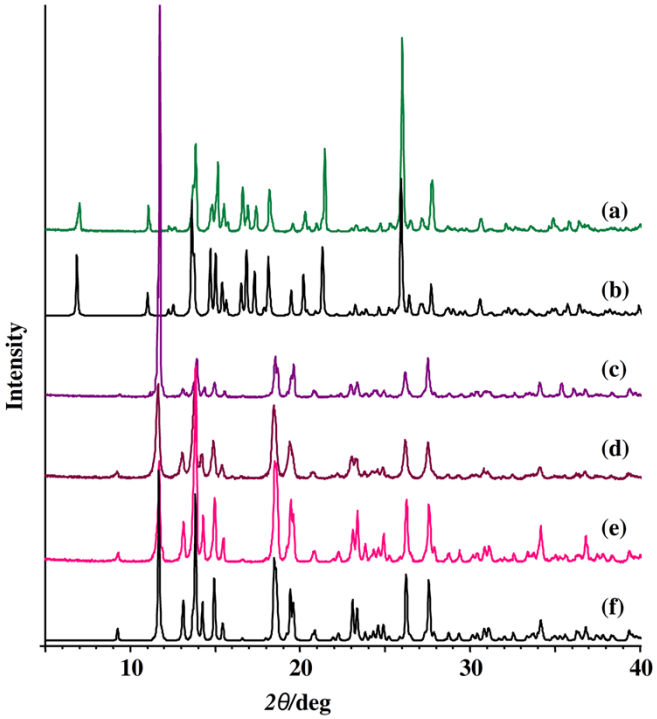


Fig. S2 PXRD patterns of **1** (a and b); **4** (c-f). The colored lines indicate patterns obtained by powder diffraction ((c) sample obtained by method A, (d) sample obtained by method B and (e) sample obtained by method C)), while the black lines indicate patterns calculated from the X-ray single-crystal structures of the corresponding compounds.

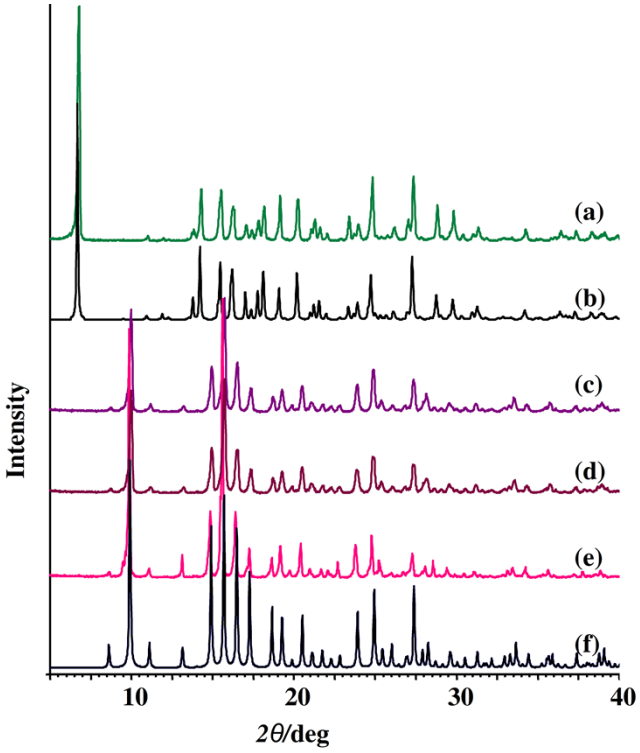


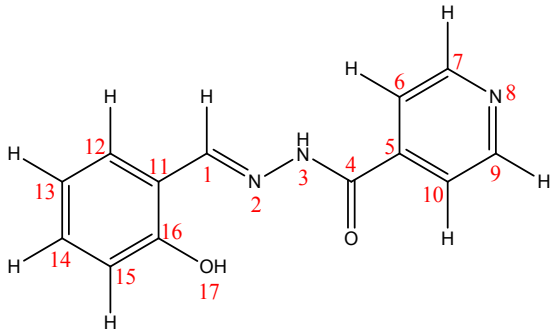
Fig. S3 PXRD patterns of **2** (a and b); **5** (c-f). The colored lines indicate patterns obtained by powder diffraction ((c) sample obtained by *method A*, (d) sample obtained by *method B* and (e) sample obtained by *method C*)), while the black lines indicate patterns calculated from the X-ray single-crystal structures of the corresponding compounds.

NMR spectroscopy

Table S1. ^{1}H and ^{13}C chemical shifts (ppm) of compounds **1** and **4**.

Atom	$[MoO_2(HL^{SIH})(MeOH)]Cl$ (1)		$[MoO_2(L^{SIH})(MeOH)]$ (4)	
	δ / ppm (DMSO)		δ / ppm (DMSO)	
	^{1}H	^{13}C	^{1}H	^{13}C
1	9.07	158.90	9.03	157.67
2	-	-		
3	-	-		
4	-	166.36		167.05
5	-	141.61		137.42
6, 10	8.14	123.57	7.88	121.54
7, 9	8.89	147.56	8.76	150.61
8	3.95	-	-	
11	-	120.46		120.08
12	7.81	135.34	7.78	134.70
13	7.13	122.41	7.13	121.85
14	7.59	136.26	7.57	135.51
15	6.99	116.93	6.98	118.66
16	-	160.05		159.51
17	-	-		

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

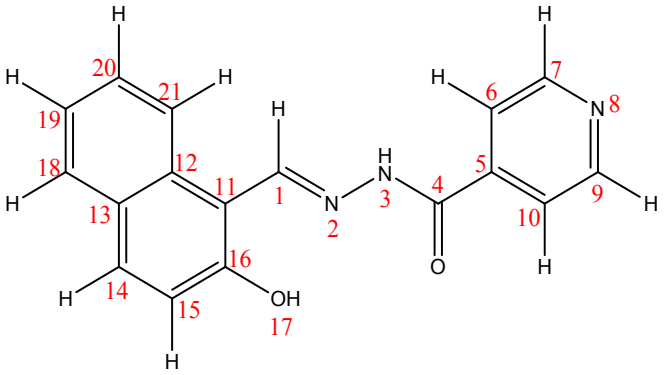


Scheme S1 The structural formula of H_2L^{SIH} with the NMR numbering scheme

Table S2. ^{1}H and ^{13}C chemical shifts (ppm) of compounds **2** and **5**.

Atom	$[MoO_2(HL^{NIH})(MeOH)]Cl$ (2)		$[MoO_2(L^{NIH})(MeOH)]$ (5)	
	δ / ppm		δ / ppm	
	^{1}H	^{13}C	^{1}H	^{13}C
1	9.86	154.94	9.82	154.20
2	-	-		
3	-	-		
4	-	165.89		166.82
5	-	140.33		137.86
6, 10	8.18	123.23	7.93	121.97
7, 9	8.94	148.22	8.79	151.07
8	4.66	-		
11	-	111.95		111.97
12	-	132.94		132.91
13	-	129.35		129.32
14	7.99	137.29	8.17	136.97
15	7.24	120.77	7.23	120.77
16	-	161.48		161.28
17	-	-		
18	8.19	129.54	7.97	129.49
19	7.54	125.47	7.52	125.40
20	7.69	129.25	7.68	129.18
21	8.55	122.19	8.54	122.18

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

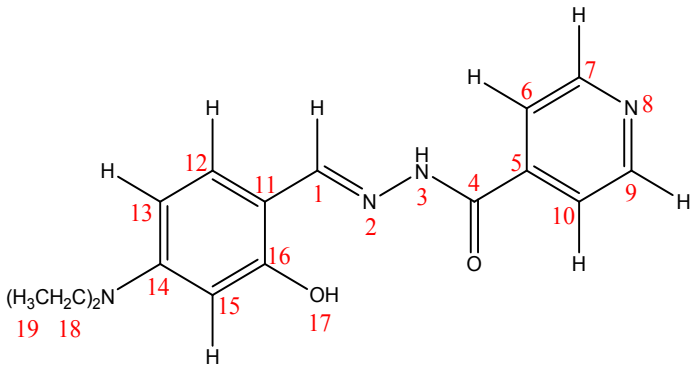


Scheme S2 The structural formula of H_2L^{NIH} with the NMR numbering scheme

Table S3. ^{1}H and ^{13}C chemical shifts (ppm) of compounds **3** and **6**

Atom	$[MoO_2(HL^{Et2NSIH})(MeOH)]Cl$ (3)		$[MoO_2(L^{Et2NSIH})]_n$ (6)	
	δ / ppm		δ / ppm	
	^{1}H	^{13}C	^{1}H	^{13}C
1	8.72	157.57	8.69	156.72
2	-	-		
3	-	-		
4	-	162.54		164.26
5	-	143.73		138.31
6, 10	8.16; 8.19	123.69	7.81	121.90
7, 9	8.88; 8.90	145.73	8.71	150.88
8	3.17	-		
11	-	108.74		108.70
12	7.48; 7.51	136.78	7.45	136.42
13	6.50	107.15	6.46	106.81
14	-	154.47		154.07
15	6.19	99.59	6.16	99.55
16	-	162.24		162.00
17	-	-		
18	3.45	44.74	3.43	44.64
19	1.13	13.01	1.12	13.01

* Signals belonging to MeOH were also detected in ^{1}H NMR spectra in dmso solutions of the mononuclear complexes **3**.



Scheme S3 The structural formula of $H_2L^{Et2NSIH}$ with the NMR numbering scheme

Crystallographic studies

Table S4. Angle between the pyridyl and the phenyl (compound **1**, **3**, **6**, **1a**, **3a·H_2O**) / the naphtyl moieties (compound **2**, **5**, **2a**), φ /° and angle between the five- and six-membered chelate rings, ψ / ° for compounds **1**, **2**, **3**, **5**, **6, 1a**, **2a**, **3a·H_2O**

	φ /°	ψ /°
1	7.85(9)	5.73(6)
2	8.47(9)	8.07(8)
3	4.57(15)	5.20(10)
5	6.92(10)	8.32(9)
6	3.85(12)	5.99(3)
1a	7.91(14)	7.60(9)
2a	5.98(10)	7.27(10)
3a·H_2O	4.20(10)	6.95(7)

Table S5 Geometry of intermolecular hydrogen bonds (Å, °) for **1**, **2, 3, 5, 6, 1a**, **2a** and **3a·H_2O**

	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A(°)
1	O5−H05···Cl	0.72(2)	2.38(2)	3.0936(16)	171(3)
	N3−H3···Cl[a]	0.86	2.16	3.0199(16)	174
	C5−H5···Cl[b]	0.93	2.78	3.566(2)	143
	C6−H6···O3[c]	0.93	2.51	3.057(2)	118
	C7−H7···O1	0.93	2.39	2.716(2)	100
	C7−H7···O4[d]	0.93	2.38	3.036(2)	127
2	N3−H3···Cl[e]	0.80(3)	2.24(3)	3.017(2)	166(2)
	O5−H05···Cl	0.73(3)	2.37(3)	3.0770(19)	165(3)
	C5−H5···Cl[f]	0.93	2.73	3.609(3)	157
	C7−H7···O1	0.91(3)	2.38(3)	2.764(3)	105(2)
	C18−H18C···O3[g]	0.96	2.60	3.014(3)	106
3	N3−H3···Cl	0.83(4)	2.17(4)	2.988(3)	169(4)
	O5−H05···Cl[h]	0.67(4)	2.40(4)	3.057(3)	165(3)
	C1−H1···O3[i]	0.93(4)	2.56(4)	3.269(4)	134(3)
	C4−H4···N2	0.82(4)	2.54(4)	2.834(4)	103(3)
	C5−H5···O4[g]	0.95(4)	2.54(4)	3.131(4)	120(3)
5	O5−H05···N3[j]	0.89(2)	1.84(2)	2.709(3)	164(3)
	C12−H12···O4[i]	0.93	2.52	3.227(3)	133
	C13−H13···O2[i]	0.93	2.54	3.468(3)	173
	C14−H14···O3[h]	0.93	2.58	3.409(3)	149
	C16-H16···O4[k]	0.93	2.49	3.377(3)	159
6	C1−H1···O3[g]	0.93(3)	2.54(3)	3.355(3)	146(2)
	C1−H1···O3[l]	0.93(3)	2.47(3)	3.027(3)	119(2)
	C4−H4···N2[m]	0.90(3)	2.45(3)	2.764(3)	101(2)
	C5−H5···O4	0.89(3)	2.36(3)	2.888(4)	118(3)
1a	O5–H05A···Cl[n]	0.77(3)	2.41(3)	3.172(2)	174(4)
	O5–H05B···Cl[o]	0.83(4)	2.32(4)	3.133(2)	170(4)
	N3–H3···Cl[p]	0.77(4)	2.29(4)	3.053(3)	170(4)
	C1–H1···O4[q]	0.93	2.55	3.469(3)	171
	C5–H5···Cl[o]	0.93	2.60	3.500(3)	163
	C6–H6···Cl[r]	0.93	2.74	3.512(3)	141
	C13–H13···O3[s]	0.93	2.51	3.271(4)	140
2a	O5–H05A···Cl	0.80(4)	2.26(4)	3.044(3)	168(4)
	O5–H05B···Cl[t]	0.79(3)	2.33(4)	3.073(3)	157(3)
	N3–H3···Cl[u]	0.86	2.79	3.394(2)	129
	N3–H3···Cl[v]	0.86	2.48	3.123(2)	132
	C5–H5···Cl[v]	0.93	2.72	3.250(3)	117
	C17–H17···Cl[w]	0.93	2.81	3.582(3)	141
3a·H_2O	O6–H06A···N2[x]	0.77(3)	2.25(3)	3.006(2)	168(3)
	O6–H06B···Cl[t]	0.81(3)	2.37(3)	3.1729(18)	175(3)
	N3–H3···Cl[y]	0.86	2.22	3.0608(16)	165
	O5–H05A···O6	0.84(3)	1.84(3)	2.666(2)	172(3)
	O5–H05B···Cl[z]	0.68(3)	2.42(3)	3.0814(16)	166(2)
	C7–H7···O1	0.93	2.46	2.772(2)	100
	C10–H10···O[a1]	0.93	2.42	3.277(2)	153
	C16–H16B···O3[x]	0.97	2.52	3.159(3)	123

[a]1+x,y,1+z; [b]1–x,1–y,2–z; [c]x,y,1+z; [d]1/2+x,1/2-y,1/2+z; [e]x,y,-1+z; [f]1-x,1-y,-z; [g]-1+x,y,z; [h]1-x,-y,-z; [i]1-x,-y,1-z; [j]3/4-x,3/4+y,3/4+z; [k]-1/4+x,1/4-y,-1/4+z; [l]-x,-y,1-z; [m]-1/2-x,-1/2+y,1/2-z; [n]1-x,1/2+y,3/2-z; [o]-1+x,1+y,z; [p]-1+x,3/2-y,1/2+z; [q]x,3/2-y,1/2+z; [r]1-x,3/2+y,3/2-z; [s]1-x,-1/2+y,3/2-z; [t]1-x,1-y,1-z; [u]3/2-x,1/2+y,3/2-z; [v]-1/2+x,3/2-y,1/2+z; [w]-1/2+x,1/2-y,1/2+z; [x]x,3/2-y,-1/2+z; [y]1+x,1+y,1+z; [z]1+x,3/2-y,1/2+z; [a1]x,3/2-y,1/2+z

Table S6. $\pi\cdots\pi$ interactions in crystal structure of compounds **1**, **2**, **3**, **5** and **2a**

	CgX	CgY	CgX–CgY (Å)
1	Cg3 (N3, C3–C7)	Cg4 (C8–C13)	3.6597(11)[i]
			3.8484(11)[ii]
2	Cg3 (N3, C3–C7)	Cg4 (C8–C13)	3.7770(14)[iii]
	Cg3 (N3, C3–C7)	Cg5 (C10, C11, C14–C17)	3.6530(15)[iii]
3	Cg3 (N3, C3–C7)	Cg4 (C8–C13)	3.7879(19)[iv]
	Cg3 (N3, C3–C7)	Cg3 (N3, C3–C7)	3.8898(18)[v]
5	Cg3 (N3, C3-C7)	Cg4 (C8-C13)	3.9168(14)[vi]
	Cg3 (N3, C3-C7)	Cg5 (C10, C11, C14–C17)	3.7563(15)[vi]
2a	Cg3 (N3, C3-C7)	Cg4 (C8-C13)	3.5855(15)[vii]
	Cg3 (N3, C3-C7)	Cg5 (C10, C11, C14–C17)	3.5529(16)[vii]

[i]x, y, 1+z, [ii]1+x, y, 1+z, [iii]2-x, 1-y, z, [iv]1-x, -y, 1-z, [v]1-x, -y, -z, [vi]1-x, -y, -z, [vii]1-x, 1-y, 2-z

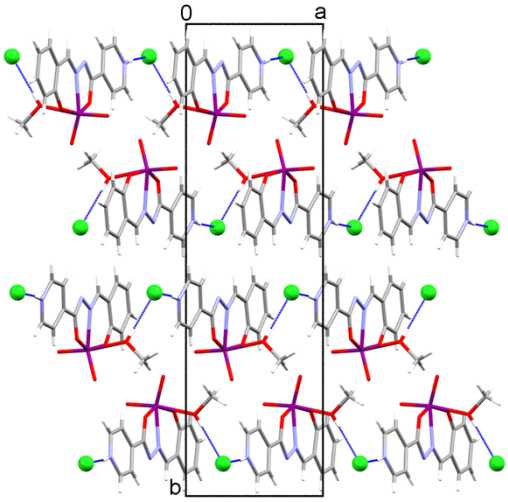


Fig. S4. Packing arrangement of the complex **1** displayed in the unit cell. Hydrogen bonds N3−H3···Cl[1+x,y,1+z] and O5−H05···Cl are shown as blue dashed lines.

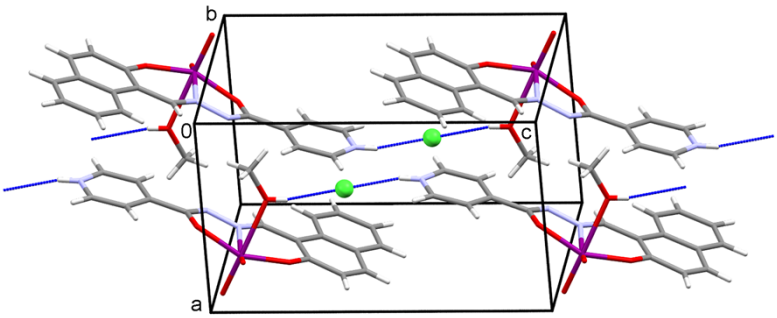


Fig. S5. Packing arrangement of the complex **2** displayed in the unit cell. Hydrogen bonds N3−H3···Cl[x,y,1-z] and O5−H05···Cl are shown as blue dashed lines.

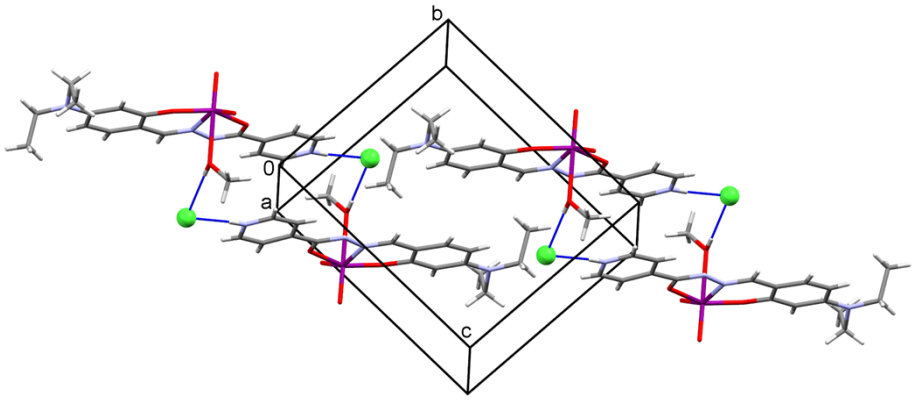


Fig. S6 Packing arrangement of the complex **3** displayed in the unit cell. Hydrogen bonds N3−H3···Cl[x,y,1-z] and O5−H05···Cl are shown as blue dashed lines.

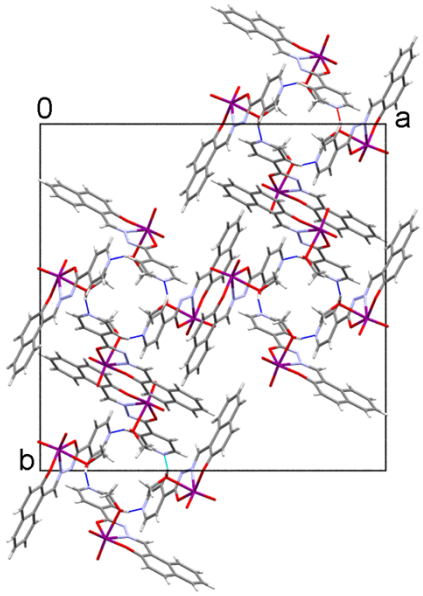


Fig. S7 Packing arrangement of molecules of the complex **5** displayed in the unit cell. Hydrogen bonds O5−H05···N3 [1/4-x,1/4+y,3/4+z] are shown as blue dashed lines.

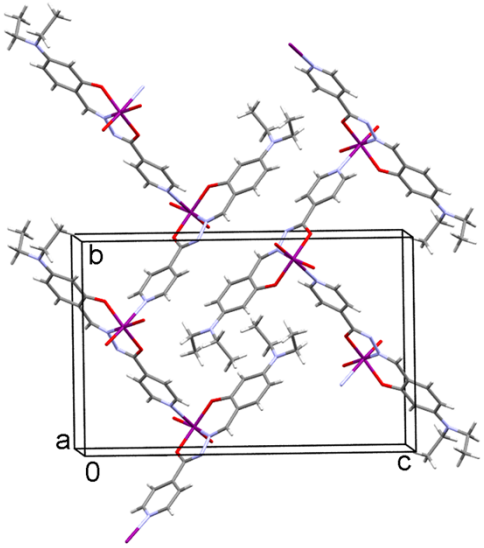


Fig. S8 Packing arrangement of molecules of the complex **6** displayed in the unit cell.

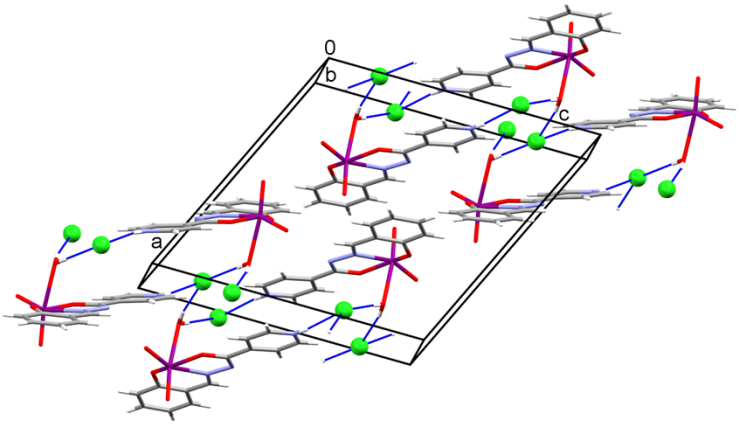


Fig. S9 Packing arrangement of the complex **1a** displayed in the unit cell. Hydrogen bonds O5–H05A···Cl[1-x,1/2+y], N3–H3···Cl[-1+x,3/2-y] and O5–H05B···Cl[-1+x,1+y,z] are shown as blue dashed lines.

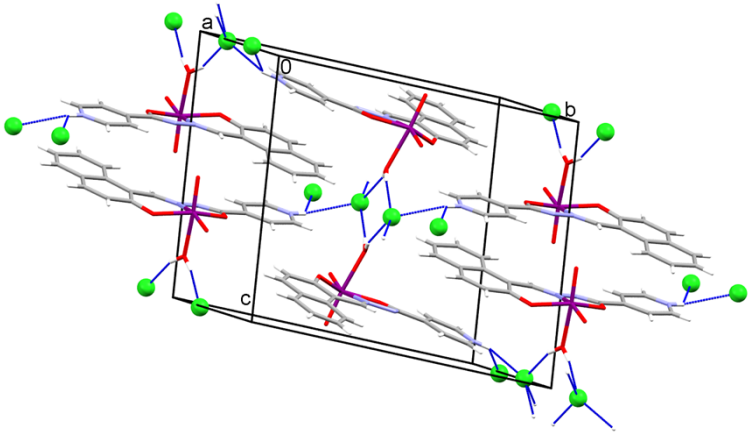


Fig. S10 Packing arrangement of the complex **2a** displayed in the unit cell.
Hydrogen bonds O5–H05A···Cl, O5–H05B···Cl[1-x,1-y,1-z], N3–H3···Cl[3/2-x,1/2+y,3/2-z] and N3–H3···Cl[-1/2+x,3/2-y,1/2+z] are shown as blue dashed lines.

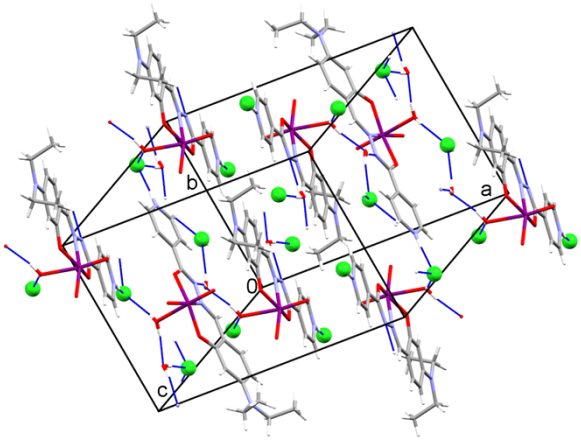


Fig. S11 Packing arrangement of the complex **3a·H_2O** displayed in the unit cell. Hydrogen bonds O6–H06A···N2[x,3/2-y,-1/2+z], O6–H06B···Cl[1-x,1-y,1-z], N3–H3···Cl[1+x,1+y,1+z], O5–H05A···O6 and O5–H05B···Cl[1+x,3/2-y,1/2+z] are shown as blue dashed lines.

Ligands H_2L^R

H_2L^{SIH} ligand. Selected IR data (cm^{-1}): 3180 (N−H), 1685 (C=O), 1624 (C=N)py, 1601 (C=N), 1566 ($C-O_{phenol}$). DSC melting peak: onset 242.0 °C (179.4 J/g).

H_2L^{NIH} ligand. Selected IR data (cm^{-1}): 3216 (N−H), 1679 (C=O), 1623 (C=N)py, 1603 (C=N), 1575 ($C-O_{phenol}$). DSC melting peak: onset 261.0 °C (105.6 J/g).

$H_2L^{Et2NSIH}$ ligand. Selected IR data (cm^{-1}): 3163 (N−H), 1678 (C=O), 1630 (C=N)py, 1597 (C=N), 1556 ($C-O_{phenol}$). DSC melting peak: onset 226.8 °C (123.65 J/g).