Synthesis and structure of malato molybdenum(VI) complexes: Δ-[Co(en)$_3$][MoO$_3$(L-mal)]·H$_2$O and Δ-[Co(en)$_3$]$_n$[Mo$_4$O$_{11}$(L-mal)$_2$ (H$_2$O)$_2$Na]$_n$·4nH$_2$O

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TABLE OF CONTENT:

Synthesis of Δ-$[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl\cdot9H_2O$

Solution-based methods: a) at room temperature, b) under reflux and c) hydrothermal synthesis at 110 °C

Equal amounts of $Na_2MoO_4\cdot2H_2O$ (0.50 mmol) and adipic, fumaric or maleic acid (0.50 mmol), respectively, were dissolved in water (10 mL). The addition of the aqueous solution (10 mL) containing equal amount of Δ-$[Co(en)_3]Cl_3\cdot1.5H_2O$ (0.50 mmol) to the solution of sodium molybdate and corresponding acid resulted in instantaneous precipitation of an orange yellow voluminous product and the pH value of the reaction mixture was between 3 and 5.

a) The resulting reaction mixture was allowed to stand at room temperature. After two weeks the orange yellow voluminous product was completely transformed into orange plate-like crystals of **3.** The product was filtered off, washed with a small amount of cold water, and dried to constant weight in a desiccator (adipic acid: 78.4 mg; fumaric acid: 68.1 mg, maleic acid: 55.4 mg). The crystals of **3** were suitable for single-crystal diffraction experiments.

b) The final mixture was heated under reflux for 1 h. During the heating of the reaction mixture, the orange yellow voluminous product was obtained. The reaction mixture was then left to stand at room temperature. After about two weeks, the orange yellow voluminous product was transformed to the orange plate-like crystals of **3**. The crystals of **3** were filtered off (adipic acid: 78.5 mg, fumaric acid: 65 mg, maleic acid: 61.2 mg), washed with a small amount of cold water, and dried in a desiccator to a constant mass. The crystals were suitable for single-crystal diffraction experiments.

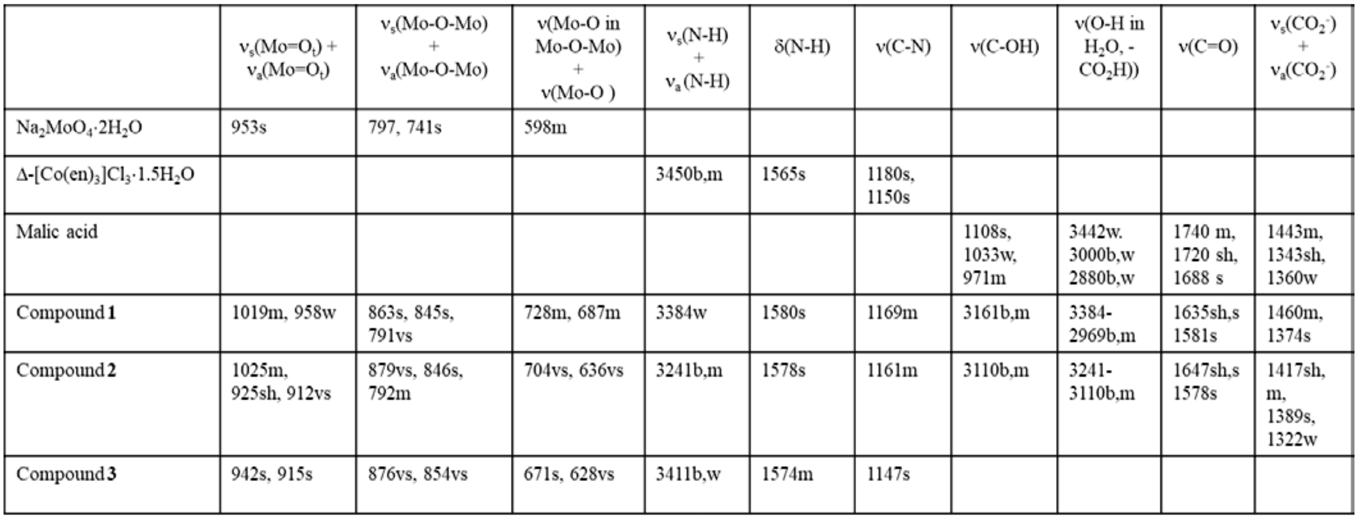
c) The final reaction mixture was heated at 110 °C for 7 h in a 30 mL Teflon-lined reactor. By cooling the orange plate-like crystals of **3** were obtained. The orange crystals of **3** were filtered off, washed with a small amount of cold water, and dried in a desiccator to a constant mass (adipic acid: 89 mg, fumaric acid: 90.1 mg, maleic acid: 59.8 mg). The isolated crystals of **3** were suitable for single-crystal diffraction experiments.

Hand grinding or liquid-assisted ball milling followed by vapor-assisted aging.

d) $Na_2MoO_4\cdot2H_2O$ (0.125 mmol), adipic, fumaric or maleic acid (0.125 mmol), respectively, and Δ-$[Co(en)_3]Cl_3\cdot1.5H_2O$ (0.125 mmol) were ground together in an agate mortar for 10 min, affording a homogeneous mixture, or were placed in a 5 mL stainless steel jar with an addition of acetone (25 μL) and reactants were milled for 1 h at a frequency of 25 Hz. The resulting orange homogeneous powder solid mixture obtained in all reactions, respectively, was exposed to 100% humidity at room temperature. After one day the mixture of orange polycrystalline product and orange powder was observed. After one month the orange balls and orange powder were completely transformed into the orange plate-like crystals of **3**. The product was washed with a small amount of cold water and dried to constant weight in a desiccator (adipic acid: 15.7 mg, fumaric acid: 22.5 mg maleic acid acid: 31.5 mg). The isolated crystals of **3** were suitable for single-crystal diffraction experiments.

Δ-$[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl\cdot 9H_2O$. Selected IR data (cm^{-1}) = 3411 (w, b), 3199 (m, b), 3120 (m), 1574 (m), 1147 (s), 1053 (s), 942 (s), 915 (s), 876 (s, sh), 854 (vs), 671 (vs, sh), 628 (vs); elemental analysis calcd (%) for $C_{12}H_{69}ClCo_2Mo_7N_{12}O_{34}$: C 8.23, H 3.97, Co 6.73, Mo 38.37, N 9.60; found: C 8.18, H 3.80, Co 6.61, Mo 38.48, N 9.50.

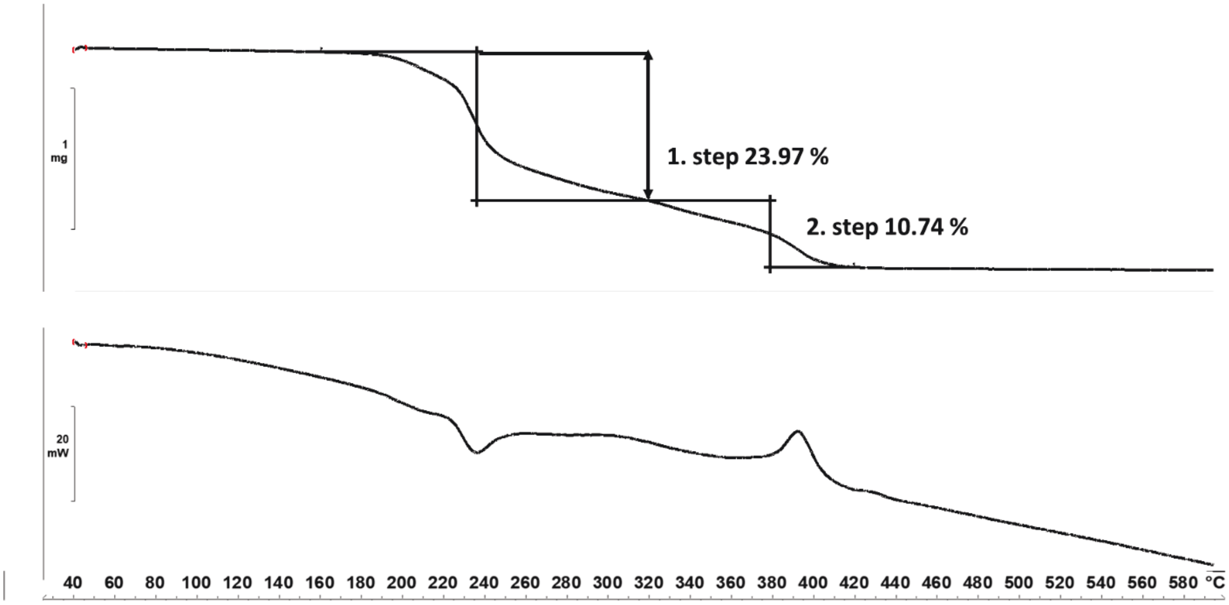
Table S1. Selected bands from the IR spectra of the prepared compounds (**1**-**3**) Δ-$[Co(en)_3][MoO_3(L\text{-}mal)]\cdot H_2O$ (**1**), Δ-$[Co(en)_3]_n[Mo_4O_{11}(L\text{-}mal)_2(H_2O)_2Na]_n\cdot 4nH_2O$ (**2**), Δ-$[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl\cdot 9H_2O$ (**3**) and precursors



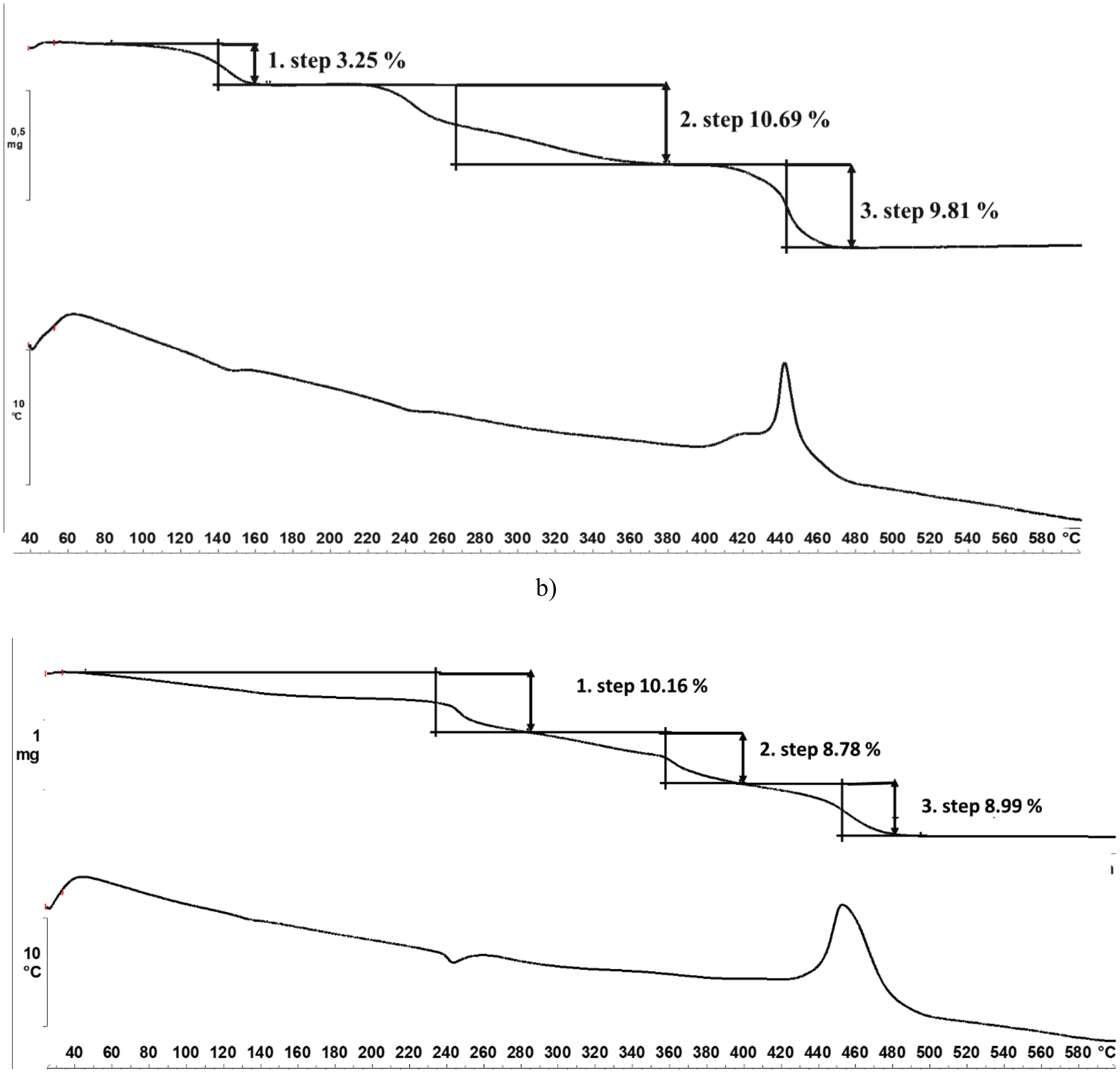
	$\nu_s(Mo=O_t) + \nu_a(Mo=O_t)$	$\nu_s(Mo\text{-}O\text{-}Mo) + \nu_a(Mo\text{-}O\text{-}Mo)$	ν(Mo-O in Mo-O-Mo) + ν(Mo-O)	$\nu_s(N\text{-}H) + \nu_a(N\text{-}H)$	δ(N-H)	ν(C-N)	ν(C-OH)	ν(O-H in H_2O, -CO_2H))	ν(C=O)	$\nu_s(CO_2^-) + \nu_a(CO_2^-)$
$Na_2MoO_4\cdot 2H_2O$	953s	797, 741s	598m							
Δ-$[Co(en)_3]Cl_3\cdot 1.5H_2O$				3450b,m	1565s	1180s, 1150s				
Malic acid							1108s, 1033w, 971m	3442w. 3000b,w 2880b,w	1740 m, 1720 sh, 1688 s	1443m, 1343sh, 1360w
Compound **1**	1019m, 958w	863s, 845s, 791vs	728m, 687m	3384w	1580s	1169m	3161b,m	3384-2969b,m	1635sh,s 1581s	1460m, 1374s
Compound **2**	1025m, 925sh, 912vs	879vs, 846s, 792m	704vs, 636vs	3241b,m	1578s	1161m	3110b,m	3241-3110b,m	1647sh,s 1578s	1417sh, m, 1389s, 1322w
Compound **3**	942s, 915s	876vs, 854vs	671s, 628vs	3411b,w	1574m	1147s				

Table S2. Results of thermal analysis of Δ-$[Co(en)_3][MoO_3(\text{L-mal})]\cdot H_2O$ (**1**), Δ-$[Co(en)_3]_n[Mo_4O_{11}(\text{L-mal})_2(H_2O)_2Na]_n\cdot 4nH_2O$ (**2**) and Δ-$[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl\cdot 9H_2O$ (**3**)

	1st	2nd	3rd
1	3.25 %	10.69 %	9.81 %
	74-157°C	157-367 °C	370-468 °C
2	23.97	10.74	
	146-315 °C	315-420 °C	
3	10.16 %	8.78 %	8.99 %
	41-280.5 °C	165-361 °C	403-523 °C



a)



b)

c)

Figure S1. TG/DTA for a) Δ-$[Co(en)_3][MoO_3(L\text{-mal})]\cdot H_2O$ (**1**), b) Δ-$[Co(en)_3]_n[Mo_4O_{11}(L\text{-mal})_2(H_2O)_2Na]_n\cdot 4nH_2O$ (**2**) and c) Δ-$[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl\cdot 9H_2O$ (**3**)

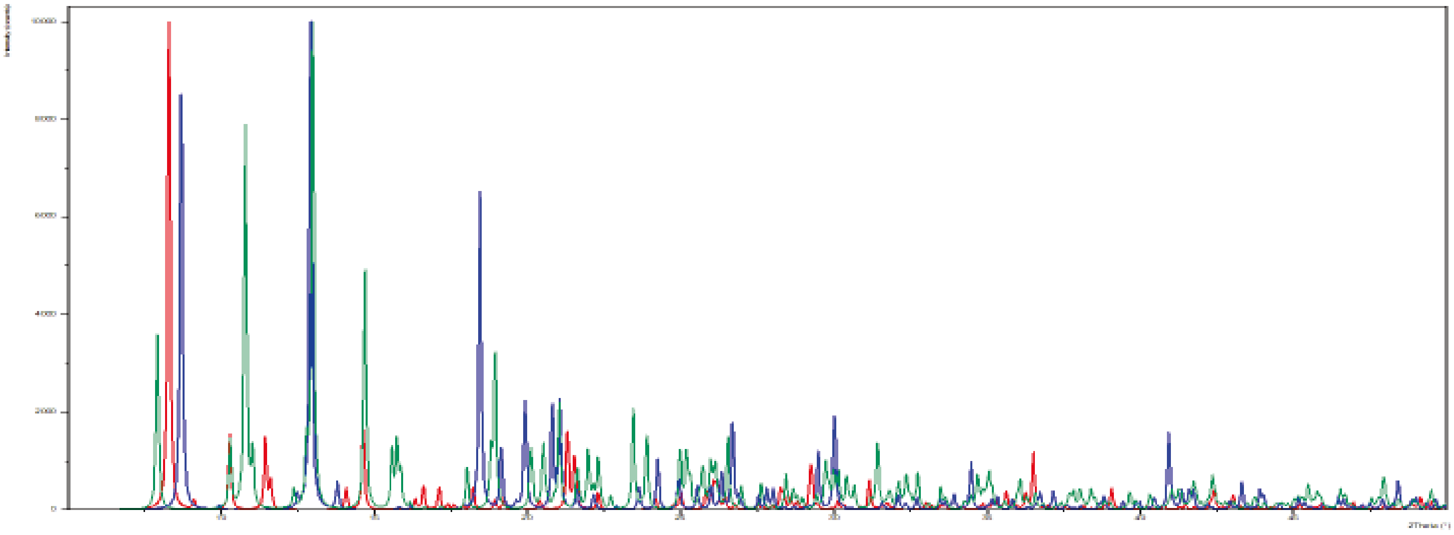


Figure S2. PXRD patterns of a) Δ-$[Co(en)_3][MoO_3(L\text{-}mal)]\cdot H_2O$ (black), b) Δ-$[Co(en)_3]_n[Mo_4O_{11}(L\text{-}mal)_2(H_2O)_2Na]_n\cdot 4nH_2O$ (green) and c) Δ-$[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl\cdot 9H_2O$ (red)

Table S3. Crystallographic data of compounds **1** and **2**

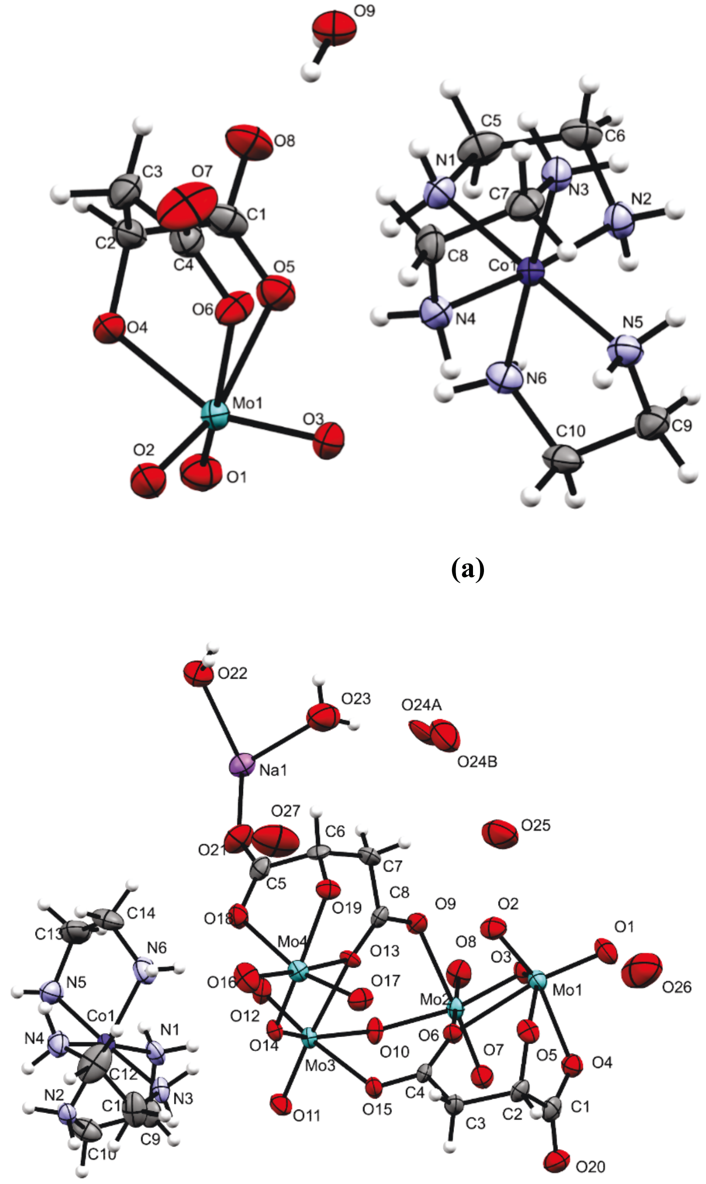
	1	**2**
Formula	$C_{10}H_{29}CoMoN_6O_9$	$C_{14}H_{42}CoMo_4N_6NaO_{27}$
M_r	532.26	1192.21
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	9.2773(2)	8.9088(5)
b (Å)	9.8695(3)	22.3385(9)
c (Å)	20.2566(4)	9.1327(5)
α (°)	90	90
β (°)	90	105.135(6)
γ (°)	90	90
V (Å^3)	1470.20(7)	1754.47(16)
Z	4	2
Reflections unique	8630	20714
Reflections observed [$I > 2\sigma(I)$]	3645	11420
Parameters	247	490
R_1(obs)	0.0444	0.0511
wR_2(obs)	0.1215	0.0580
GooF	1.050	0.971
Flack	-0.006(7)	-0.013(16)

Table S4. Geometry of hydrogen bonds for **1**

D–H···A	D–H	H···A	D···A	∠ D–H···A
N1–H1A···O5	0.91	2.17	3.066(10)	167
N1–H1B···O9	0.91	2.16	3.004(8)	154
N2–H2A···O1	0.91	2.14	2.998(9)	157
N2–H2A···O4	0.91	2.53	3.203(8)	131
N2–H2B···O1	0.91	2.46	3.190(9)	137
N3–H3A···O2	0.91	2.50	3.254(9)	140
N3–H3A···O4	0.91	2.06	2.870(8)	147
N3–H3B···O9	0.91	2.08	2.972(8)	165
N4–H4A···O3	0.91	2.48	3.109(9)	126
N4–H4A···O6	0.91	2.15	3.024(9)	161
N4–H4B···O2	0.91	1.89	2.797(9)	177
N5–H5A···O2	0.91	2.07	2.945(9)	162
N5–H5B···O2	0.91	2.42	3.199(9)	143
N5–H5B···O3	0.91	2.51	3.324(9)	149
N6–H6A···O3	0.91	1.87	2.760(9)	167
N6–H6B···O1	0.91	1.94	2.852(8)	177
O9–H9C···O8	0.87	1.89	2.742(9)	166
O9–H9D···O7	0.87	1.87	2.725(10)	167

Table S5. Geometry of hydrogen bonds for **2**

D–H···A	D–H	H···A	D···A	∠ D–···A
N1–H1A···O27	0.89	2.23	3.056(10)	155
N1–H1B···O12	0.89	2.12	2.946(8)	153
N2–H2A···O4	0.89	2.11	2.866(8)	142
N2–H2B···O8	0.89	2.07	2.944(8)	166
N3–H3C···O26	0.89	2.23	3.033(11)	151
N3–H3D···O14	0.89	2.15	3.032(8)	170
N4–H4A···O1	0.89	2.26	3.042(9)	146
N4–H4A···O24A	0.89	2.35	3.03(10)	132
N4–H4B···O20	0.89	2.19	3.044(8)	161
N5–H5A···O27	0.89	2.23	2.945(10)	137
N5–H5B···O24B	0.89	2.02	2.85(2)	154
N5–H5B···O24A	0.89	2.10	2.90(6)	149
N6–H6A···O18	0.89	2.40	2.850(9)	112
N6–H6B···O12	0.89	2.14	2.997(8)	160
O22–H22A···O20	0.86	2.49	2.994(8)	118
O23–H23A···O24B	0.86	2.10	2.84(3)	143
O23–H23A···O24A	0.86	1.71	2.55(6)	164
O23–H23B···O20	0.86	2.04	2.899(9)	174



(a)

(b)

Figure S3. ORTEP view of the molecular structures of: a) **1** and b) **2**. The displacement ellipsoids are drawn at a 50% probability level. Hydrogen atoms are presented as spheres of arbitrarily small radii.