Electronic Supplementary Information for Dalton Transactions

Metal oxide-organic frameworks (MOOFs), a new series of coordination hybrids constructed from molybdenum(VI) oxide and bitopic 1,2,4-triazole linkers

Andrey B. Lysenko,[a] Ganna A. Senchyk,[a] Jörg Lincke,[b] Daniel Lässig,[b] Andrey A. Fokin,[c] Ekaterina D. Butova,[c] Peter R. Schreiner,[d] Harald Krautscheid[b] and Konstantin V. Domasevitch*[a]

[a] *Inorganic Chemistry Department, National Taras Shevchenko University of Kyiv, Volodimirska Street 64, Kyiv 01033, Ukraine. E-mail: dk@univ.kiev.ua*

[b] *Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leipzig, Deutschland*

[c] *Department of Organic Chemistry, Kiev Polytechnic Institute, Peremogy Ave 37, Kyiv 03056, Ukraine.*

[d] *Institut für Organische Chemie, Justus-Liebig Universität, Heinrich-Buff-Ring 58, 35392 Giessen, Deutschland*

SUPPORTING INFORMATION –

Details for weak interactions (convenient hydrogen bonding OH---O, NH---N,O; weak hydrogen bonding CH---O) in the structures 1-7

Table S1 Weak interactions in structures $[Mo_4O_{12}(tr_2eth)_2]$ **1,** $[Mo_2O_6(tr_2cy)]$ **3** and $[MoO_3(trtz)]$ **7 (Type A)**

Donor	Hydrogen	Acceptor	D…A/ Å	D-H/ Å	H…A/ Å	∠DH…A/ °
$[Mo_4O_{12}(tr_2eth)_2]$ **(1)**						
C1	H1	O6 (1.5-*x*, 1.5-*y*, -0.5+*z*)	2.972(14)	0.94	2.35	123.2
C2	H2	O4 (1.5-*x*, 1.5-*y*, 0.5+*z*)	3.148(15)	0.94	2.39	137.9
C4	H4	O5	2.961(14)	0.94	2.23	134.3
C5	H5	O3 (1.5-*x*, 1.5-*y*, -0.5+*z*)	3.039(14)	0.94	2.30	135.2
$[Mo_2O_6(tr_2cy)]$ **(3)**						
C1	H1	O3 (0.5+*x*, 0.5-*y*, 1-*z*)	2.949(7)	0.94	2.33	122.7
C2	H2	O1 (-*x*, 0.5-*y*, *z*)	3.079(7)	0.94	2.34	134.7
$[MoO_3(trtz)]$ **(7)**						
Conventional hydrogen bonding: The bifurcated NH···N,O *bond of tetrazole group*						
N7	H1N	N6 (-0.5-*x*, 0.5-*y*, 0.5-*z*)	2.937(3)	0.87	2.42	118.6
N7	H1N	O2 (-0.5+*x*, *y*, 0.5-*z*)	3.004(3)	0.87	2.23	147.9
	Weak hydrogen bonding CH···O					
C1	H1	O3 (0.5-*x*, -*y*, 0.5+*z*)	3.018(3)	0.94	2.29	134.0
C2	H2	O2 (0.25-*y*, *x*-0.25, *z*-0.25)	2.938(2)	0.94	2.30	124.3

Table S2 Weak interactions in structures $[Mo_2O_6(tr_2pr)]$ **2,** $[Mo_2O_6(tr_2ad)]\cdot 6H_2O$ **4** and $[Mo_2O_6(4,9\text{-}tr_2dia)]\cdot 0.5H_2O$ **5 (Type B).**

Donor	Hydrogen	Acceptor	D…A/ Å	D-H/ Å	H…A/ Å	∠DH…A/ °
$[Mo_2O_6(tr_2pr)]$ **(2)**						
C1	H1	O6 (0.5-*x*, 2-*y*, -0.5+*z*)	3.165(5)	0.93	2.32	150.6
C2	H2	O3 (0.5-*x*, 2-*y*, 0.5+*z*)	2.889(5)	0.93	2.39	113.4
C3	H3	O2 (1-*x*, -0.5+*y*, -0.5-*z*)	3.040(5)	0.93	2.29	137.2
C4	H4	O5 (1-*x*, -0.5+*y*, 0.5-*z*)	3.158(5)	0.93	2.50	128.0
$[Mo_2O_6(tr_2ad)]\cdot 6H_2O$ **(4)**						
	Conventional hydrogen bonding OH···O					
O5	H1W	O1 (1+*x*, *y*, *z*)	2.886(3)	0.86	2.03	171.9
O5	H2W	O7	2.703(5)	0.83	1.88	174.5
O6	H3W	O2 (0.5-*x*, *y*-0.5, *z*-0.5)	2.965(3)	0.82	2.16	170.3
O6	H3W	O5 (1-*x*, -0.5+*y*, -*z*)	2.753(3)	0.86	1.89	172.4
O7 [a)]	H5W	O8 (0.5+*x*, *y*, -0.5-*z*)	2.749(3)	0.89	1.87	169.2
O8	H6W	O4 (-*x*, -0.5+*y*, -*z*)	3.085(3)	0.83	2.32	154.2
O8	H7W	O6	2.807(4)	0.89	2.00	151.1
	Weak hydrogen bonding CH···O					
C1	H1	O4 (-*x*, 1-*y*, -*z*)	3.120(3)	0.94	2.35	139.4
C2	H2	O2 (0.5-*x*, 1-*y*, -0.5+*z*)	3.162(3)	0.94	2.40	137.6
[a)] Atom O7 is situated on a mirror plane, only one H atom is unique (H5W).						
$[Mo_2O_6(4,9\text{-}tr_2dia)]\cdot 0.5H_2O$ **(5)**						
C1	H1	O3 (0.5-*x*, 1.5-*y*, 1-*z*)	3.057(3)	0.93	2.23	146.7

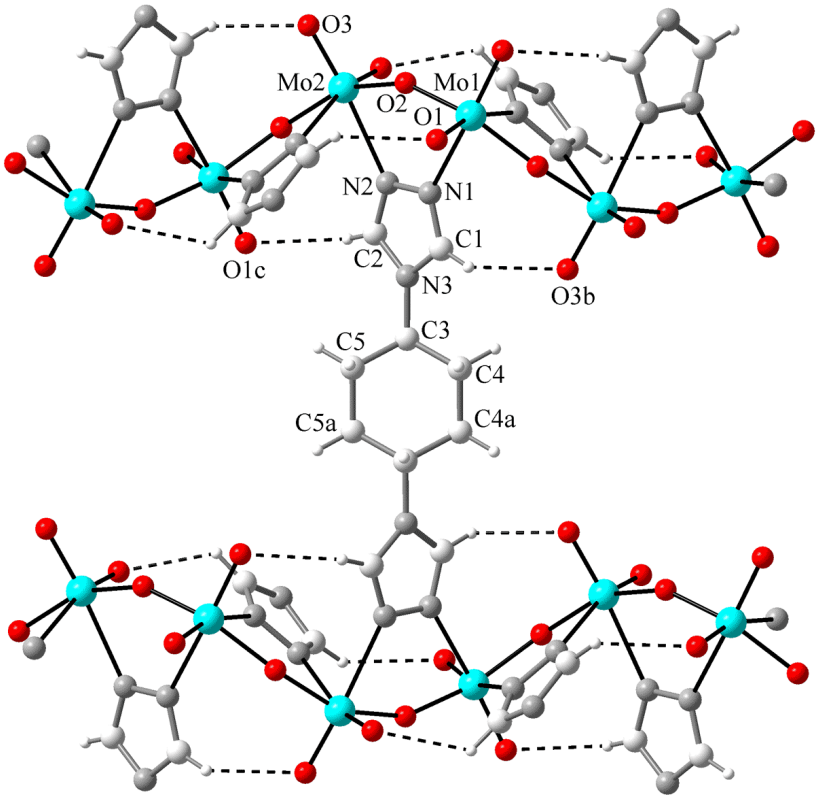

Figure S1. Weak CH···O hydrogen bonding in the structure of [Mo_2O_6(*tr*$_2$*cy*)] **(3).** Symmetry codes: a) *x*, 1-*y*, 0.5-*z*; b) 0.5+*x*, 0.5-*y*, 1-*z*; c) –*x*, 0.5-*y*, *z*.

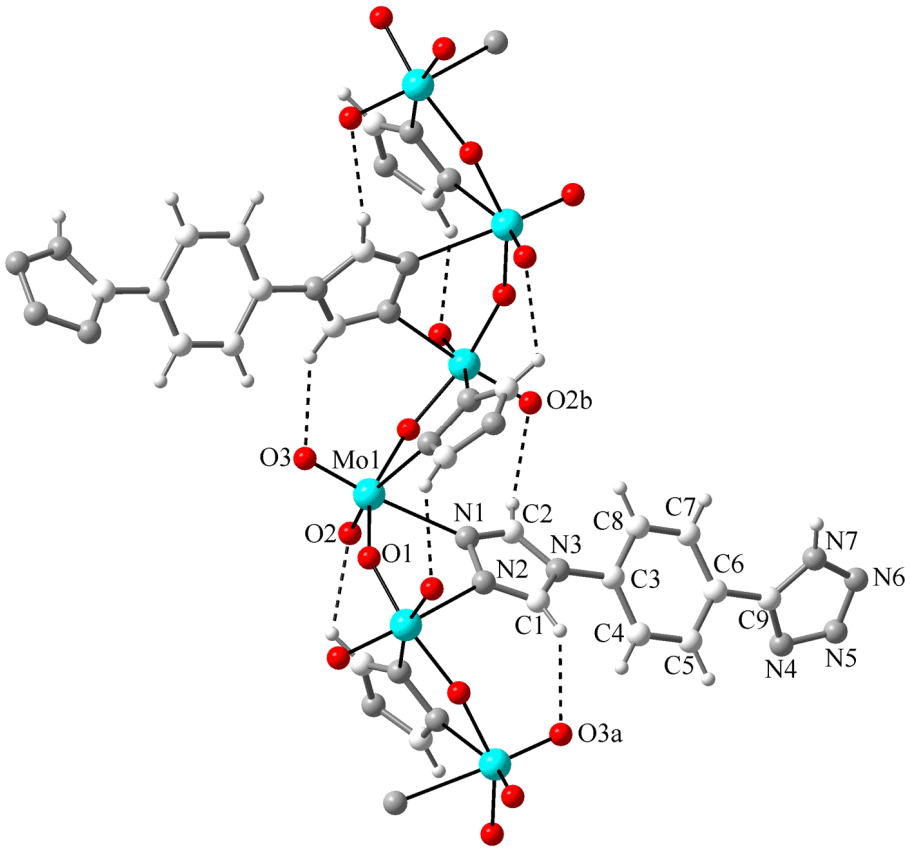

Figure S2. Weak CH···O hydrogen bonding in the structure of [MoO_3(*trtz*)] **(7).** Symmetry codes: a) 0.5-*x*, -*y*, 0.5+*z*; b) 0.25-*y*, 0.25+*x*, -0.25+*z*.

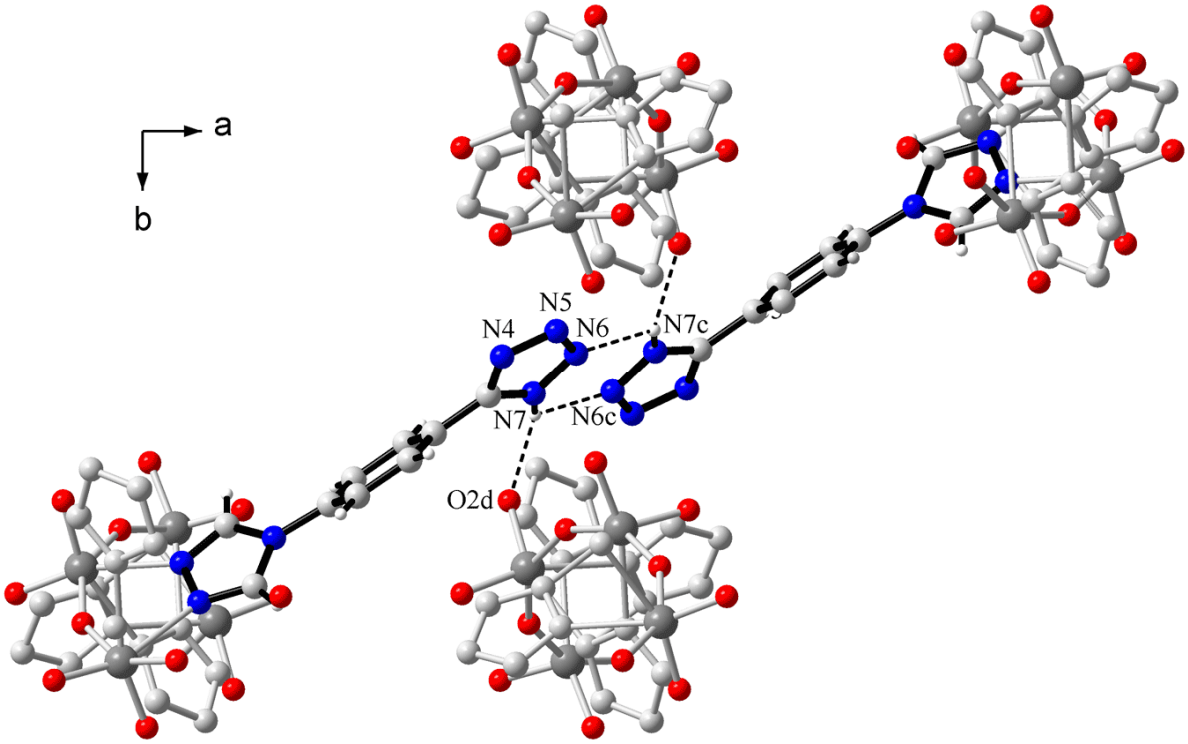

Figure S3. The bifurcated hydrogen bonding of the tetrazole group in the structure of [MoO_3(*trtz*)] **(7),** viewed along the direction of Mo-oxide helices. Symmetry codes: c) -0.5-*x*, 0.5-*y*, 0.5-*z*; d) -0.5+*x*, *y*, 0.5-*z*.

When neglecting N7-H---O2d branch of this bifurcated bond, the hydrogen bonded dimer tetrazole/tetrazole provides simple connection of the ligands into "extended linker" between MoO_3 helices. This convenient scheme was used for the discussion of the resulting 3D structure, as five-fold interpenetrated "**asf**" framework. However, taking into account the additional NH---O interactions (which completely cross all the interpenetrated nets), the interpenetration disappears and a single 3D framework of complex topology is found.

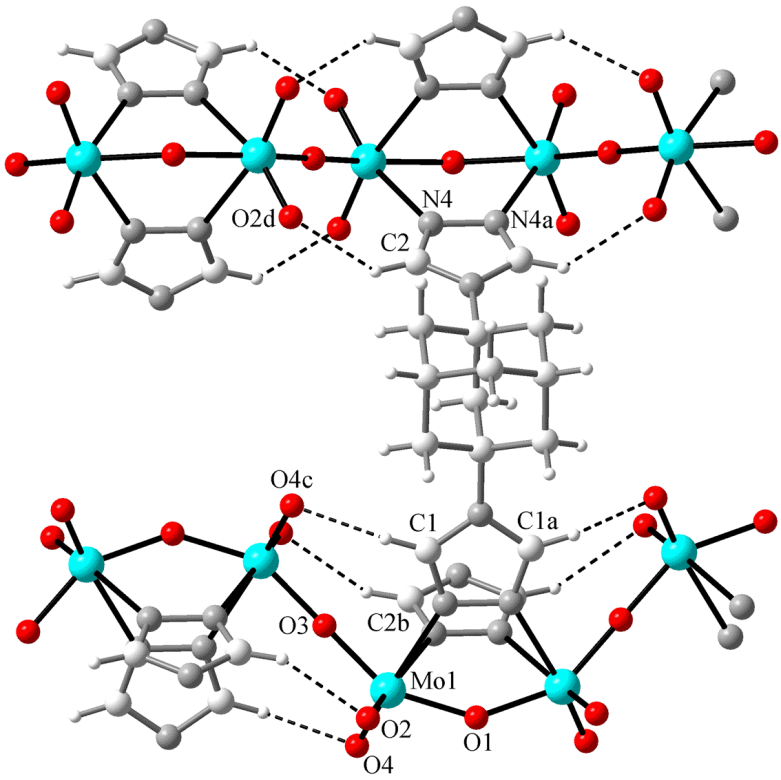

Figure S4. Weak CH···O hydrogen bonding in the structure of $[Mo_2O_6(tr_2ad)]\cdot 6H_2O$ **(4)**
Symmetry codes: a) *x*, 0.5-*y*, *z*; b) -0.5+*x*, *y*, -0.5-*z*; c) –*x*, 1-*y*, -*z*; d) 0.5-*x*, 1-*y*, -0.5+*z*.

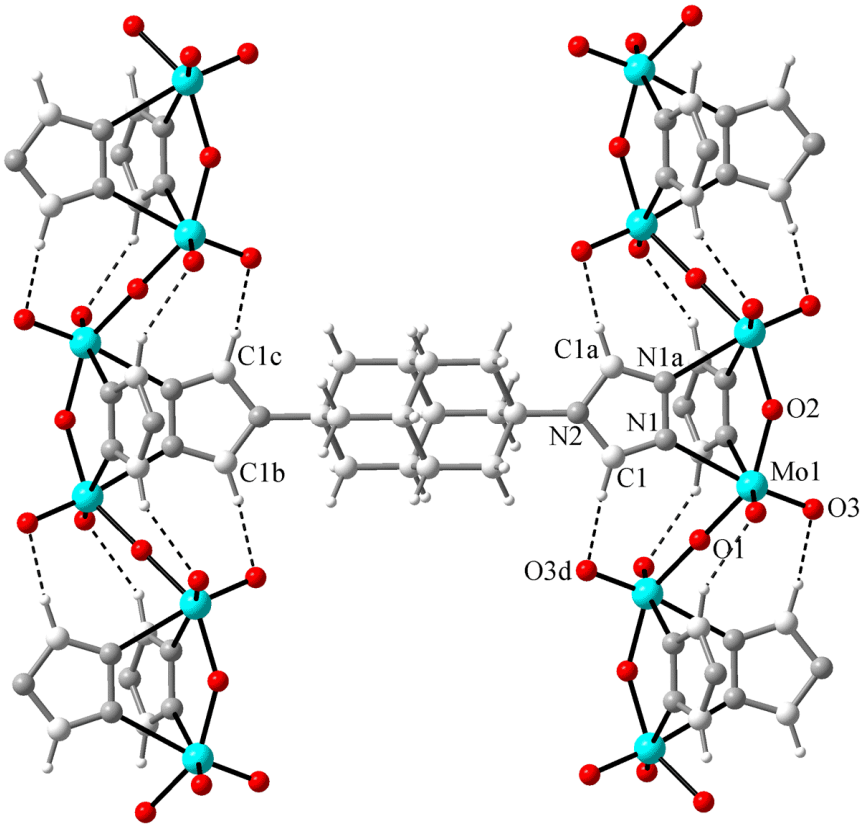

Figure S5. Weak CH···O hydrogen bonding in the structure of $[Mo_2O_6(4,9\text{-}tr_2dia)]\cdot 0.5H_2O$ **(5)** Symmetry codes: a) *–x*, *y*, *z*; b) *x*, 2-*y*, 2-*z*; c) *–x*, 2-*y*, 2-*z*; d) 0.5-*x*, 1.5-*y*, 1-*z*.

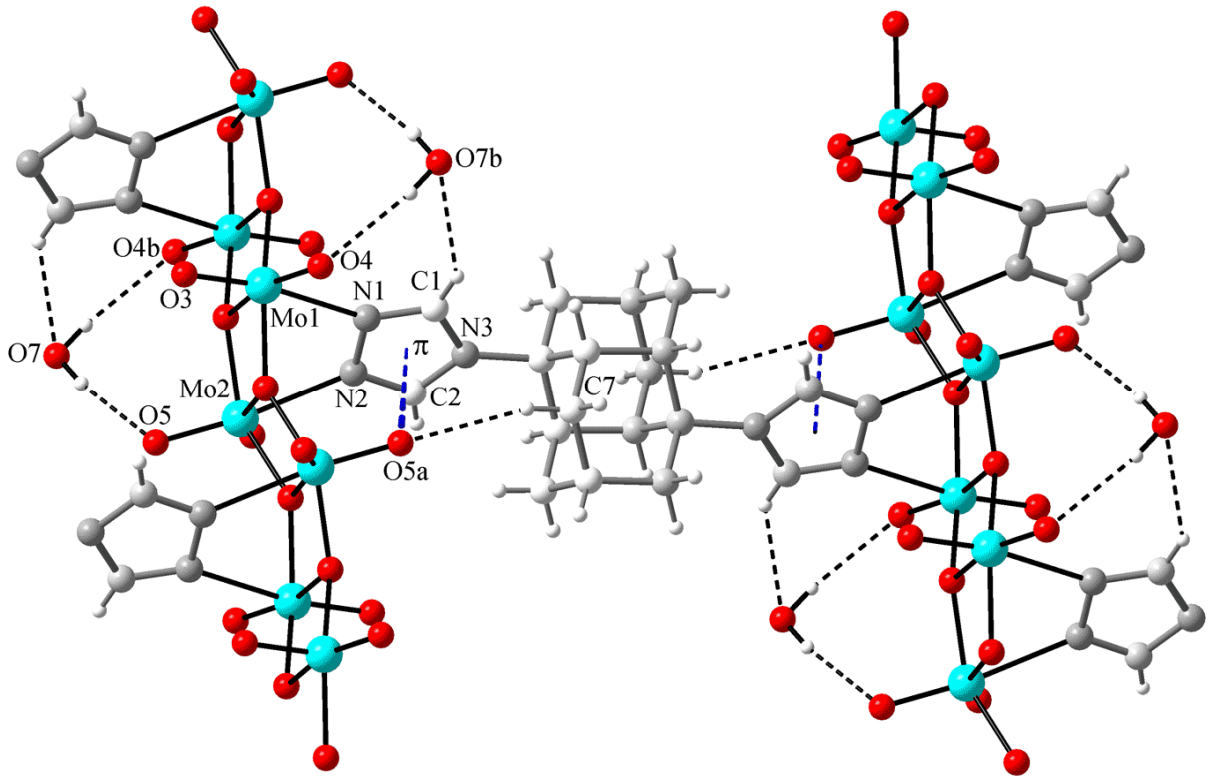

Figure S6. Weak CH···O hydrogen bonding in the structure of $[Mo_4O_{12}(1,6\text{-}tr_2dia)]\cdot 2H_2O$ **(6).**

Note the CH···O bonding with aliphatic diamantane skeleton and the structural role of solvate water molecule.

Also notable feature is a specific O···π interaction with the triazole ring:

O5···C(N) 3.069-3.411 Å; O5···π 3.029 Å.

Table S3 Weak interactions in structure $[Mo_4O_{12}(1,6\text{-}tr_2dia)]\cdot 2H_2O$ **(6).**

Donor	Hydrogen	Acceptor	D…A/ Å	D-H/ Å	H…A/ Å	∠DH…A/ º
O7	H2W	O4 (1-*x*, 1-*y*, 1-*z*)	3.168(5)	0.86	2.31	171.4
O7	H1W	O5	3.000(5)	0.86	2.14	171.3
C1	H1	O7 (1-*x*, 1-*y*, 1-*z*)	3.227(6)	0.94	2.44	141.0
C7	H7B	O5 (-*x*, 1-*y*, 1-*z*)	3.444(4)	0.98	2.50	162.4
C2	H2	O6 (-*x*, -*y*, 1-*z*)	3.215(4)	0.94	2.28	172.1