

## Electronic Supplementary Information

# Linking magnetic $M^{II}$ - $[M^V(CN)_8]$ chains into 2D inorganic–organic hybrid materials

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**Table S1.** Results of continuous shape measures analysis for  $M^V$  centers.

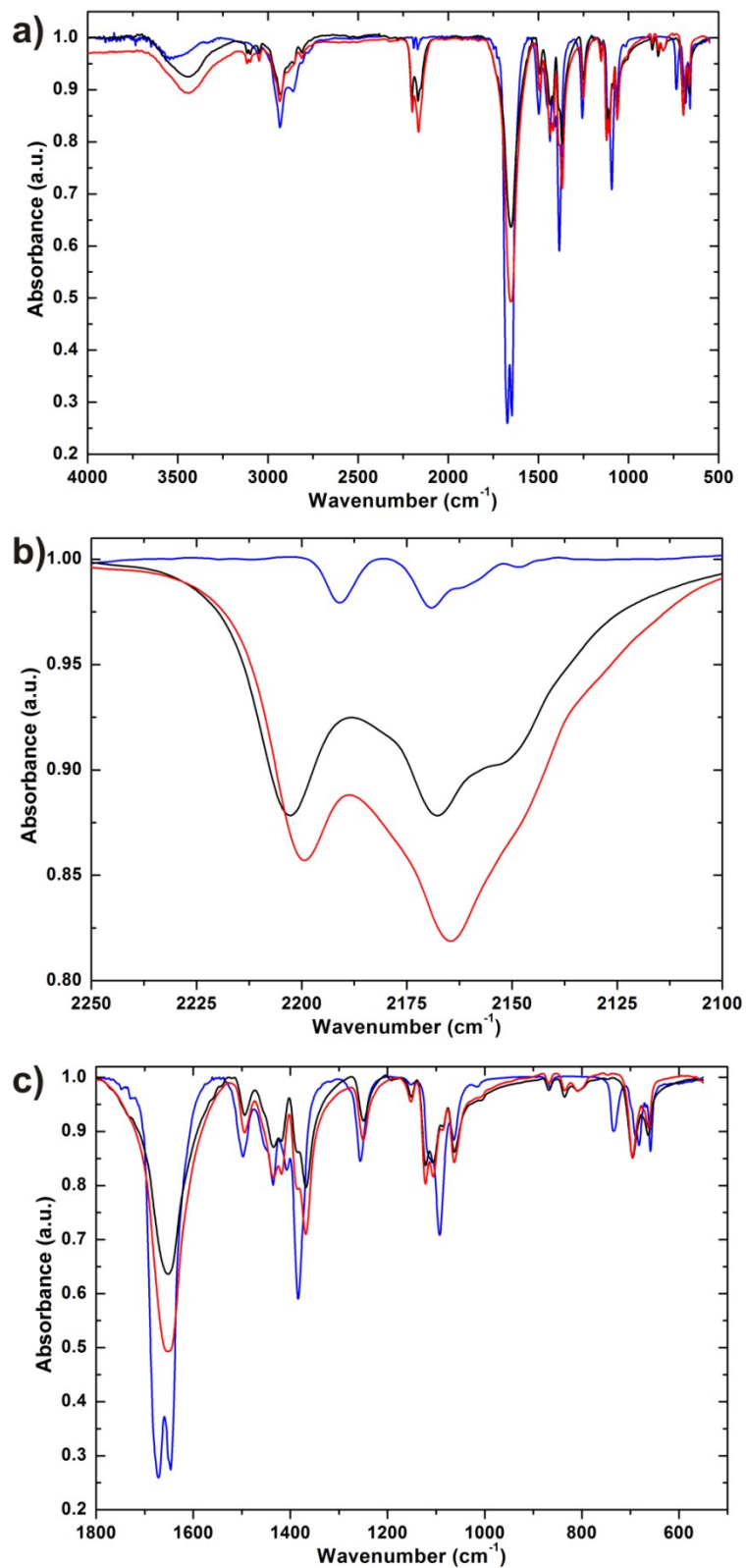
Compound	Geometry	$S_{BTP}$	$S_{SAPR}$	$S_{TDD}$
	ideal BTP-8	0.000	2.262	2.709
	ideal SAPR-8	2.262	0.000	2.848
	ideal TDD-8	2.709	2.848	0.000
1	$[W^I(CN)_8]$	2.064	2.275	0.345
2	$[W^I(CN)_8]$	1.954	1.774	0.393
3	$[Mo^I(CN)_8]$	1.966	1.674	0.497

$S_{BTP}$  – the shape measure relative to the bicapped trigonal prism;  $S_{SAPR}$  – the shape measure relative to the square antiprism;  $S_{TDD}$  – the shape measure relative to the triangular dodecahedron; smaller  $S$ -value reflect a better match with the ideal geometry ( $S = 0$ ).

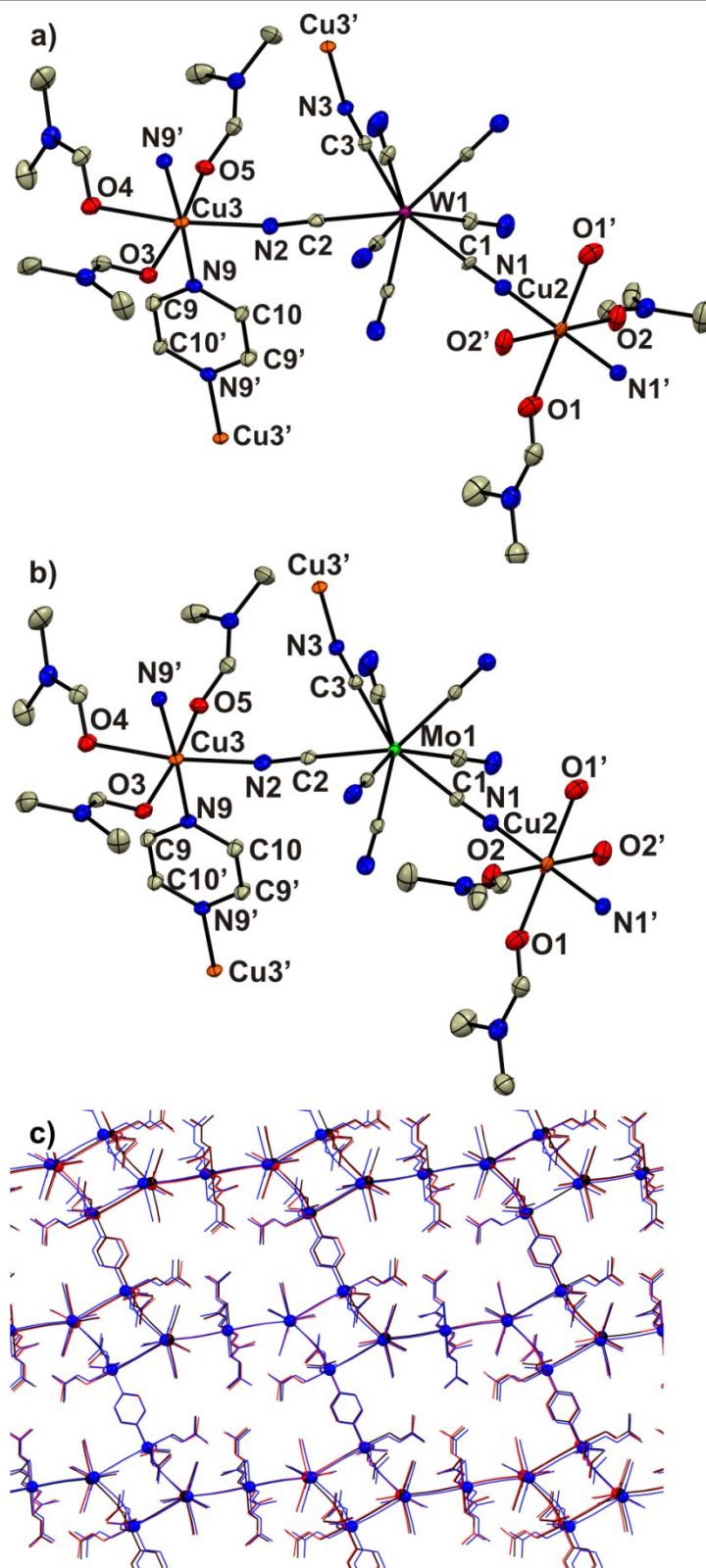
**Table S2.** Results of continuous shape measures analysis for  $M^{II}$  centers.

Compound	Geometry	$S_{OC}$
	OC-6	0.000
1	$[Co^2(NC)_2(DMF)_4]$	0.040
1	$[Co^3(NC)_2(pyZ)(DMF)_3]$	0.345
2	$[Cu^2(NC)_2(DMF)_4]$	0.185
2	$[Cu^3(NC)_2(pyZ)(DMF)_3]$	0.831
3	$[Cu^2(NC)_2(DMF)_4]$	0.426
3	$[Cu^3(NC)_2(pyZ)(DMF)_3]$	0.843

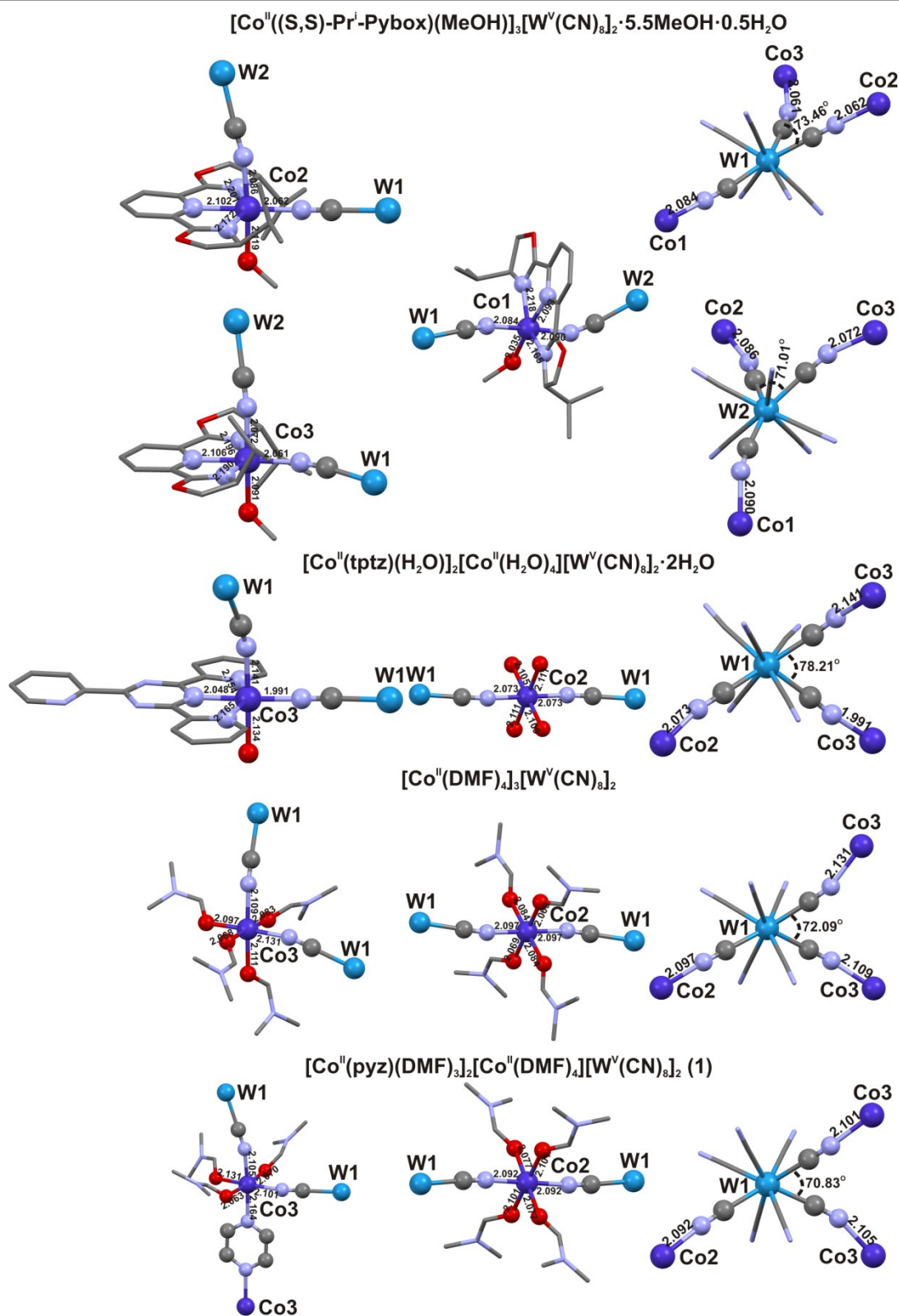
$S_{OC}$  – the shape measure relative to the octahedron; smaller  $S$ -value reflect a better match with the ideal geometry ( $S = 0$ ).



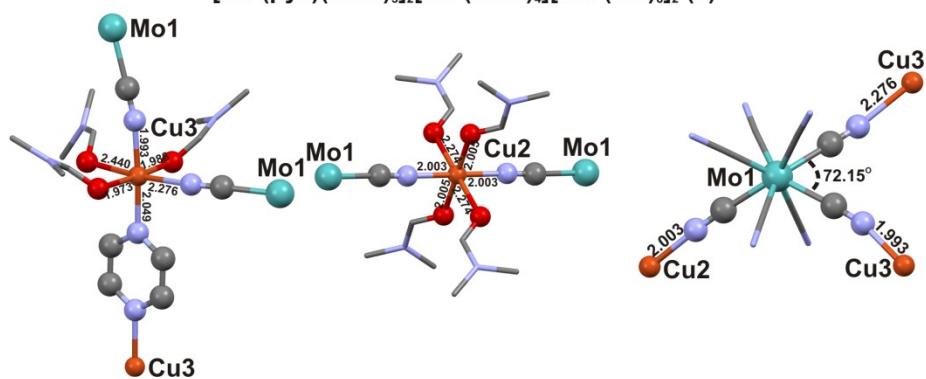
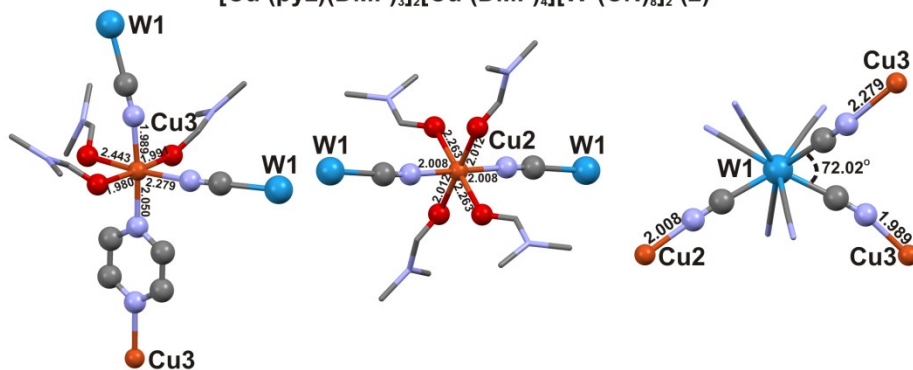
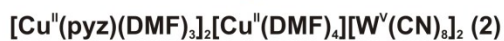
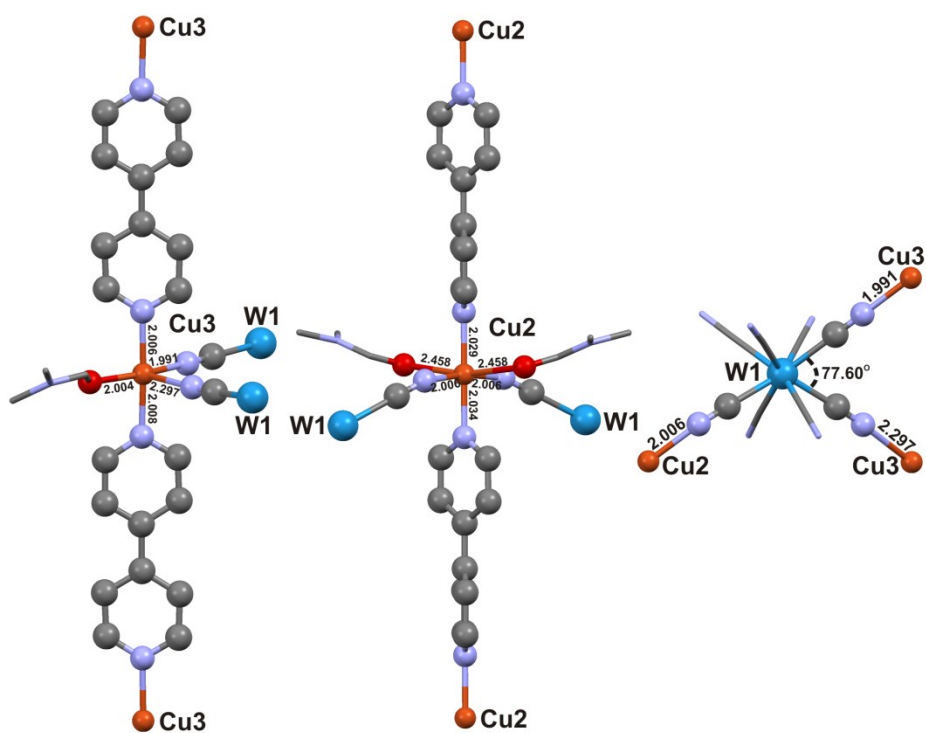
**Figure S1.** IR spectra in full range (4000 - 550 cm<sup>-1</sup>) (a), in the v(C≡N) region (2250 - 2000 cm<sup>-1</sup>) (b) and in the fingerprint region (1800 - 550 cm<sup>-1</sup>) (c) for **1** (blue), **2** (black) and **3** (red).



**Figure S2.** ORTEP diagrams of asymmetric units of **2** (a) and **3** (b) with selected atoms labeling. Colors used: C – gray, Co – yellow, Cu – orange, N – blue, Mo – green, O – red, W – purple. Thermal ellipsoids of 50% probability are shown. c) Superimposed structural diagrams for **1** (blue), **2** (black) and **3** (red).

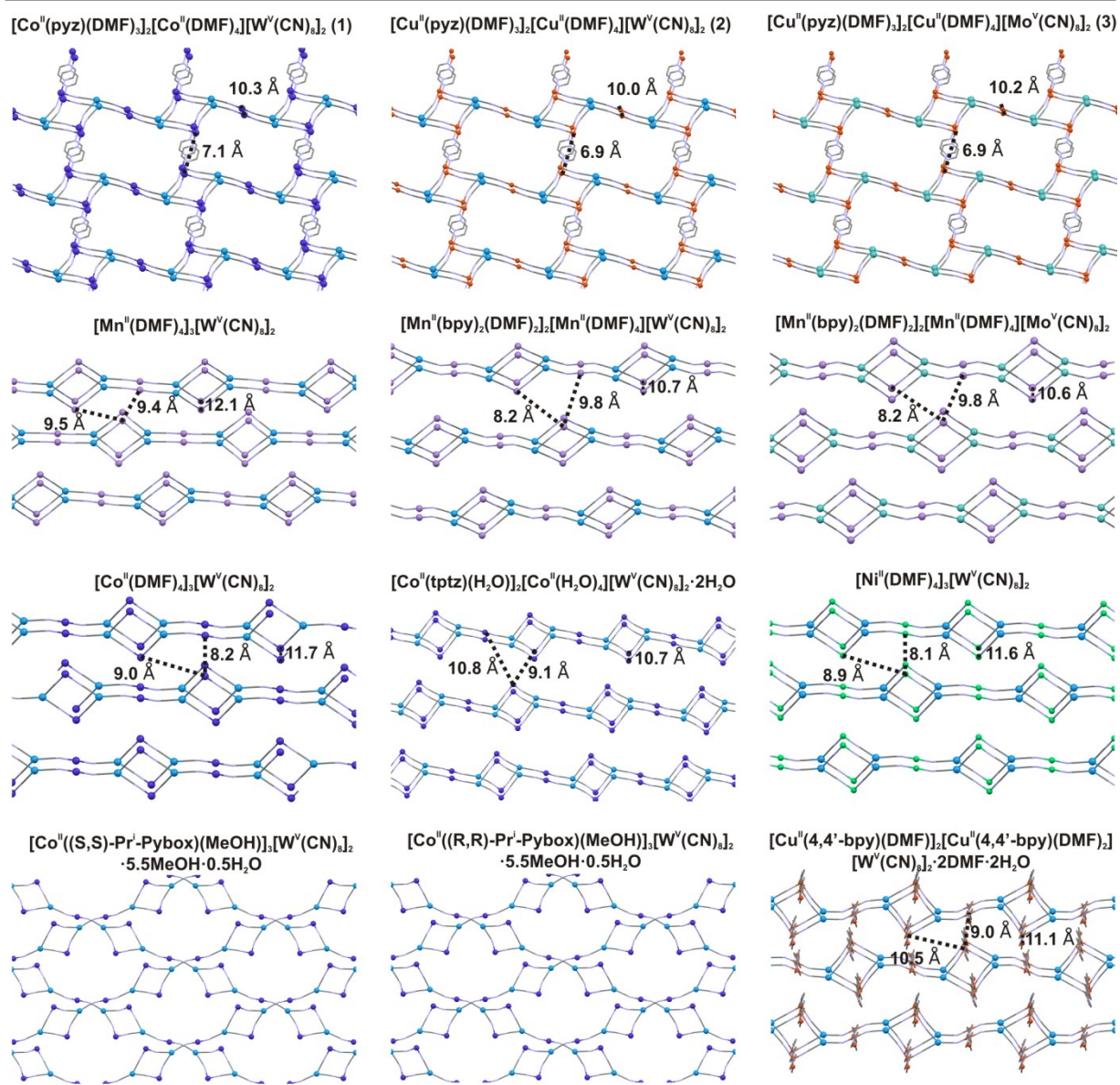


**Figure S3.** Local environments of the metal centers of **1** and other  $\text{Co}^{\text{II}}\text{-W}^{\text{V}}$  systems.

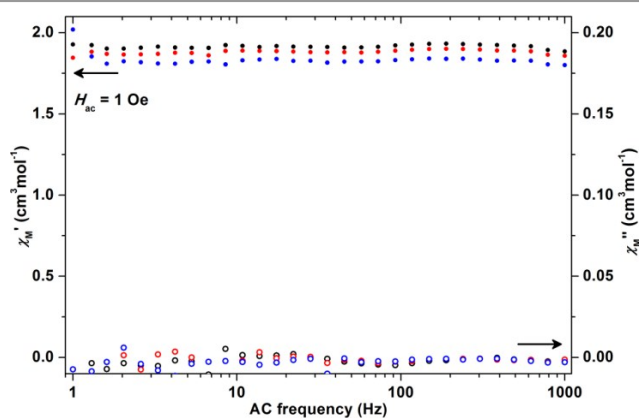


**Figure S4.** Local environments of the metal centers of **2**, **3** and another  $\text{Cu}^{\text{II}}\text{-M}^{\text{V}}$  system.

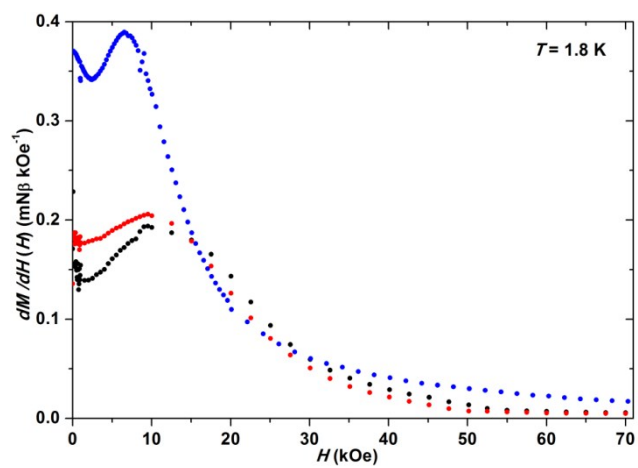




**Figure S5.** Crystal packing for **1** – **3** and other systems containing 3,2–chain entities.



**Figure S6.** The  $\chi_M'(f)$  (full symbols) and  $\chi_M''(f)$  curves (open symbols) for **1** as a function of the AC frequency measured in  $H_{dc} = 0$  (black), 0.5 (red) and 1 kOe (blue) ( $H_{ac} = 1$  Oe) at  $T = 1.8$  K.



**Figure S7.** The first derivative of magnetization vs. magnetic field plots for **1** (blue), **2** (black) and **3** (red).