The role of pyrazine-N,Nø-dioxide in $[W(CN)_8]^{n-}$ -based hybrid networks: anion-interactions

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Formula ^a	Ligand role	Magnetic features and functionality		
$[{Mn^{II}(pyz)(H_2O)_2}{Mn^{II}(H_2O)_2}{Nb^{IV}(CN)_8}]$ $\cdot 4H_2O$	Bridging, 1D organic connectivity, 3D supramolecular isomerism	3D magnet, pyroelectric ferrimagnet, high MSHG/SHG ratio below $T_c = 48$ K	S1	
$-\{[Mn^{II}(H_2O)(urea)_2]_2[Nb^{IV}(CN)_8]\}_n$	Blocking, high dipolar moment, 3D supramolecular isomerism	3D magnetic chiral polymorh from spontaneous resolution, high MSHG/SHG signal ratio below $T_c = 43$ K, hydration/dehydration tuned $T_c 43$ K 70 K 47 K	S2	
${[Fe((\pm)-4-Brpy)_4]_2[Nb(CN)_8]^2H_2O}_n$	Blocking monodentate	Chiral photomagnets from spontaneous resolution; thermally controlled Fe ^{II} - centred SCO, electronic absorption, space group and SHG (1064 nm 532 nm) intensity; optical control of magnetically ordered phases ($T_c = 15$ K 12 K) and resulting polarisation plane of MSHG signal.	S 3	
$\{[Mn^{II}(pydz)][Mn^{II}][Nb^{IV}(CN)_8]\}_n$	Blocking monodentate, mobile upon structural changes	3D magnet, magnetic sponge with reversible two step tuning of T_c 43 68 100K	S4	
${[Ni(cyclam)]_3[W(CN)_8]_2}_n$	Blocking, cyclic equatorial tetradentate	The honeycomb with reversible guest induced change of magnetic ordering $T_c = 4.9$ K (none), 8.3 K (H ₂ O) and 11.4 K (MeOH)	S5	
${[Mn^{II}_{2}(4,4\phi bpdo)(H_{2}O)_{4}][Nb^{IV}(CN)_{8}]GH_{2}O}_{n}$	Bridging (-4,4,4ø4ø), combination of end-to-end and end-on modes	Pillared spin-flop antiferromagnet below $T_c = 15$ K, magnetic phase diagram determined from monocrystalline magnetic measurements, anisotropy field of 21 kOe originating from symmetry and orientation of $[Nb(CN)_8]^{4-}$	S6	
$ \{ Co^{II}_{9}(MeOH)_{24}[W^{V}(CN)_{8}]_{6} \} \cdot 4, 4 \text{ -bpdo} \cdot MeOH \cdot 2H_{2}O \\ \{ Co^{II}[Co^{II}(4, 4 \text{ -bpdo})_{1.5}(MeOH)]_{8}[W^{V}(CN)_{8}]_{6} \} \cdot 2H_{2}O $	Hydrogen bonded or bridging (-4,4ø), supramolecular isomerism	Change in magnetic relaxation correlated with modification of cluster coordination core	S7	
${Co^{II}_{3}(2,2\phi bpdo)_{4}(H_{2}O)_{4}[W^{V}(CN)_{8}]_{2}BH_{2}O}$	Blocking, 7-membered coordination rings	Layered low-dimensional ferromagnet, $T_c = 5.9$ K, magnetic structure of monolayer simulated from the local anisotropy determined by <i>ab initio</i> calculations for Co(II) moieties	S8	
{ $[Co^{II}((S,S/R,R)-iPr-Pybox)(MeOH)]_3$ $[W^{V}(CN)_8]_2 \cdot 5.5MeOH \cdot 0.5H_2O\}_n$	Blocking, chiral, mer-tridentate	Chiral magnetic chains with slow magnetic relaxation, monocrystalline bulk magnetic anisotropy correlated with local axes of Co(II)	S9	
$[{(H_2O)Fe(L^1)}{Nb(CN)_8}{Fe(L)}]_n$	Blocking, favoring the required 7- coordination bipyramidal Fe ^{II} complex	Slow magnetic relaxation, magnetic hysteresis loop in 1 K, $\hat{e}/k_B = 74$ K $_0 = 4.6 \times 10^{-11}$ s	S10	
$ \{ [Cu_3Tb(L^{Pr})W(CN)_8(DMF)_3(H_2O)_3] \cdot \\ (DMF)_{1.5} \cdot (H_2O)_{0.5} \}_n $	Compartmental, implying the triangular multidirectional {Cu ₃ Tb} array	Coexistence of magnetic ordering, due to bridging of $\{Cu_3Tb\}$ by $[W(CN)_8]^3$, and intrinsic slow magnetic relaxation in $\{Cu_3Tb\}$	S11	
${\hat{e}} - [Mn^{II}(S/R-mpm)_2]_2[Nb^{IV}(CN)_8] {}^{2}H_2O_n$	Chiral, bis-chelating	Ligand directed layered chiral ferrimagnets, $T_c = 23.5$ K, coexistence of natural optical activity (NOA) and magnetic optical activity (MOA)	S12	
${Co^{II}}_{3}Fe^{II}_{6}[W^{V}(CN)_{8}]_{6}(MeOH)_{24}\}\cdot xMeOH$	Blocking	Trimetallic clusters, single crystal to single crystal transformation assisted by charge transfer and spin transition ($T = 192$ K, $T = 205$ K) through two different electron transfer channels W-CN-Co and W-CN-Fe	S13	
{ $[Co^{II}(4-Mepy)(pym)]_2$ [$Co^{II}(H_2O)_2$][$W^V(CN)_8$ }2]·4H ₂ O} _n	Blocking (4-Mepy), Bridging (pym)	3D photomagnet, charge-transfer-induced spin transition ($T = 172$ K, $T = 241$ K), photoswitchable hard magnet ($T_c = 48$, $H_{coer} = 2,7$ T)	S14	
$[CoII(bik)_3]{[W(CN)_8]_3[Co(bik)_2]_3} \cdot 2H_2O \cdot 13CH_3CN$	Blocking, bis-chelating	Mixed valence decorated square, gradual charge-transfer-induced spin transition (300-150 K, $T_c = 215$ K), photoswitchable ground state	S15	

Table 1. Ligand-assisted magnetic functionalities in the most recent [M(CN)8]-based assemblies

Abbreviations: pyr = pyrazine; 4-Brpy = 4-bromopyridine; pydz = pyridazine; cyclam = 1,4,8,11-tetraazacyclotetradecane; 4,4 ϕ bpdo = 4,4 ϕ bipyridyl-N,N ϕ dioxide; 2,2 ϕ bpdo = 2,2 ϕ bipyridyl-1,1 ϕ dioxide; iPr-Pybox = 2,2 -(2,6-pyridinediyl)bis(4-isopropyl-2-oxazoline); L¹ pentadentate macrocycle, N,N ϕ propylenebis(3-methoxysalicylideneiminato); L^{Pr} = multicompartmental ligand; mpm = -methyl-2-pyridine-methanol; 4-Mepy = 4-methylpyridine; pym = pyrimidine; bik = bis(1-methylimidazol-2-yl)ketone.

Table S2. IR spectra of 1-5, $Na_3[W^V(CN)_8]$ $\mathfrak{A} H_2O$, $K_3[W^V(CN)_8] \mathfrak{A} H_2O$ and $K_4[W^{IV}(CN)_8] \mathfrak{A} H_2O$ in the selected regions.

Compound	Stretching C N (2200-2100 cm ⁻¹)	stretching (N-O) (1320-1220 cm ⁻¹), C=C and C=N ring deformations (1500-1430 cm ⁻¹) and C-H ring deformations (1300-1170 cm ⁻¹ , 1100-1000 cm ⁻¹ and 900-800 cm ⁻¹)
1	2148m	1477s, 1461s, 1450s, 1309m, 1292m, 1261vs, 1232s(sh), 1173m, 1080w, 1055s, 946w, 860s, 810vs
2	2139m	1483s, 1465vs, 1444s(sh), 1311w, 1263vs, 1085m, 1051vs, 848s, 813vs
3	2174m, 2150m, 2132w	1477s, 1451s, 1314m, 1251m, 1236m, 1184vw, 1082w, 1053s, 878m, 848m, 811vs
4	2169w(sh), 2148m(sh), 2132s, 2124s	1477m, 1454s, 1311vw, 1294w, 1248m, 1233m, 1186w, 1084w, 1056m, 850m, 807s
5	not essential in this case	1481m, 1456s, 1314vw, 1289w, 1248m, 1233m, 1190w, 1090w, 1056m, 849m, 811s
pzdo	-	1481m, 1445vs, 1385w, 1307w, 1259vs, 1183w, 1031s, 897vw, 870m, 803vs
$K_3[W^V(CN)_8]$ of $k.5H_2O$	2151vs, 2148vs	-
Na ₃ [W ^V (CN) ₈]o#H ₂ O	2160vs, 2154vs, 2144m	-
K ₄ [W ^{IV} (CN) ₈] 2H ₂ O	2130vs, 2125vs	-

1				
Na1		Na2		
Na-O(pzdo)	2.318(3)-2.463(3) av. 2.411	Na-O(pzdo)	2.385(4), 2.554(4)	
Na-N(_{NC})	2.430(4), 2.474(3)	Na-O(water)	2.498(4), 2.509(3)	
Na-N-C	154.7(3) ,165.0(3)	Na-N(_{NC})	2.461(3), 2.585(3)	
Na…W _{cyano}	5.637(2)	Na-N-C	156.8 (3), 162.5(3)	
Na-O-N _{pzdo}	121.5(2)-134.7(2), av. 126.0	Na…W _{cyano}	5.761(2)	
		Na-O-N _{pzdo}	133.3(2), 141.5(2)	
Na3		W1		
Na-O(_{pzdo})	2.282(3), 2.314(3), 2.344(4)	W-C	2.152(3)-2.175(3), av. 2.16	
Na-O(_{water})	2.427(5), 2.800(4)	C-N	1.137(5)-1.150(5), av. 1.1	
Na-N(_{NC})	2.368(3)	W-C-N	175.6(3)-178.9(3), av. 177	
Na-N-C	148.67(3)			
Na…W _{cyano}	5.443(2)			
Na-O-N _{pzdo}	115.5(2), 121.7(2), 154.7(2)			
2				
K2		К3		
K-O(water)	2.689(3)-2.718(3) av. 2.704	K-O(pzdo)	2.720(3), 2.770(3)	
K-N(_{NC})	3.076(4), 3.174(3)	K-N(_{NC})	3.024(4), 3.094(3)	
K-N-C	98.0(2), 104.6(3)	K-N-C	145.7(2), 150.8(2), 167.4(
KW _{cvano}	4.846(4)	K…W _{cvano}	6.099(4)	
		K-O-N _{pzdo}	133.6(2), 138.8(2)	
W1		L		
W-C	2.158(3)-2.174(3), av. 2.166			
C-N	1.151(5)-1.153(4), av. 1.152			
W-C-N	175.1(3)-177.6(3), av. 177.5			
3				
Mn1		Mn2		
Mn-O(_{MetOH})	2.155(5), 2.212(8), 2.219(7)	Mn-O(MetOH)	2.210(4)	
Mn-N(_{NC})	2.178(5), 2.209(5), 2.213(5)	Mn-O(pzdo)	2.144(3), 2.157(4)	
Mn-N-C	164.3(5), 166.8(5), 174.7(5)	Mn-N(_{NC})	2.163(6), 2.193(5), 2.208(5	
Mn…W _{cyano}	5.459(2), 5.459(2), 5.472(2)	Mn-N-C	165.7(5), 171.1(5), 176.4(5	
-		Mn…W _{cvano}	5.436(1), 5.469(1), 5.476(2)	
		Mn-O-N _{pzdo}	123.9(3), 128.5(3)	
Mn3		Mn4		
Mn-O(MetOH)	2.232(3)	Mn-O(MetOH)	2.183(6), 2.189,(6) 2.201(5	
Mn-O(pzdo)	2.122(4), 2.171(4)	Mn-N(_{NC})	2.212(5), 2.216(5), 2.225(
Mn-N(_{NC})	2.142(6), 2.180(5), 2.227(5)	Mn-N-C	168.0(5), 173.1(5), 175.5(
Mn-N-C	166.4(5), 170.6(5), 176.1(5)	MnW _{cvano}	5.487(2), 5.492(2), 5.522(2)	
Mn…Weyano	5.411(1), 5.481(1), 5.487(2)	eyuno		
Mn-O-N	124.9(3), 129.4(3)			
C I vpzdo	12117(3), 127.7(3)			

Table S3. The selected bond distances [Å] and angles [deg] in 1-4.

Mn5		Mn6			
Mn-O(MetOH)	2.234(4)	Mn-O(MetOH)	2.212(4)		
Mn-O(pzdo)	2.170(4), 2.195(4)	Mn-O(pzdo)	2.150(4), 2.182(4)		
Mn-N(_{NC})	2.182(5), 2.225(6), 2.232(5)	Mn-N(_{NC})	2.195(4), 2.196(5), 2.233(5)		
Mn-N-C	158.9(5), 171.6(5), 177.7(5)	Mn-N-C	148.2(5), 159.2(5), 169.4(5)		
$Mn{\cdots}W_{cyano}$	5.451(2), 5.470(1), 5.524(1)	$Mn \cdots W_{cyano}$	5.467(2), 5.472(1), 5.494(1)		
Mn-O-N _{pzdo}	129.0(3), 129.2(3)	Mn-O-N _{pzdo}	130.2(3), 131.1(4)		
W1		W2			
W-C	2.165(5)-2.204(6), av. 2.177	W-C	2.136(5)-2.164(6), av. 2.172		
C-N	1.108(8)-1.144(9), av. 1.129	C-N	1.137(7)-1.157(8), av. 1.145		
W-C-N	177.5(5)-178.8(6), av. 177.9	W-C-N	174.8(5)-179.0(5), av. 178.8		
W3		W4			
W-C	2.152(5)-2.174(5), av. 2.165	W-C	2.152(5)-2.174(5), av. 2.159		
C-N	1.119(8)-1.152(9), av. 1.138	C-N	1.131(8)-1.153(7), av. 1.144		
W-C-N	175.1(5)-179.4(5), av. 177.9	W-C-N	175.7(5)-179.2(5), av. 178.1		
4					
Mn		W			
Mn-O(water)	2.208(2), 2.184(2)	W-C	2.155(3)-2.172(3), av. 2.162		
Mn-O(pzdo)	2.252(2)	C-N	1.148(5)-1.155(3), av. 1.152		
Mn-N(_{NC})	2.204(2), 2.216(2), 2.196(2),	W-C-N	178.1(4)-179.9(2),av.178.77		
Mn-N-C	171.1(2), 171.5(2), 176.0(2)				
Mn…W _{cyano}	5.518(3)				
Mn-O-N _{pzdo}	117.2(2)				



Figure S1. The illustration of the crystal structure of 1 with the atom numbering scheme (a,b). Hydrogen bonding between $\{Na_2O_3\}$ and $\{N_2O_2\}$ nodes (c).

SHAPE calculations

Shape measures analysis suggest strongly that the coordination sphere of W in 1, 2 and 4 is very close to SAPR-8 due to low values of S_{SAPR} in comparison to S_{DD} and S_{JBTP} . In 3, two of tungsten atoms have coordination sphere of slightly-distorted square antiprismatic geometry (W2 and W3) and other two have the shape of slightly-distorted triangular dodecahedron (W1 and W4). All manganese coordination spheres (both in 3 and 4) possess a slightly distorted octahedral geometry, with S_{OC} values smaller than 1 and significantly smaller than S_{TP} values. Results of calculations are presented in Table S4 for tungsten atoms and S5 for manganese atoms.

Table S4. Continuous Shape Measure (CShM) Analysis^a for the coordination spheres of W in1-4

	W (1)	W (2)	W1 (3)	W2 (3)	W3 (3)	W4 (3)	W (4)
S _{SAPR}	0.344	0.473	0.344	1.662	1.905	0.279	0.511
$S_{\rm DD}$	1.625	1.438	1.625	0.322	0.272	1.790	1.880
S _{JBTP}	2.310	2.336	2.310	2.605	2.743	2.366	2.078

* square antiprism, ** triangular dodecahedron, *** biaugmented trigonal prism

^{*a*} S_{SAPR} , S_{DD} , S_{JBTP} ó continuous shape measures related to the SAPR-8, DD-8, JBTP-8 geometry, respectively (equal to 0 if the real geometry coincides with the idealized one)

 Table S5. Continuous Shape Measure (CShM) Analysis^a for the coordination spheres of Mn^{II}

 in 3 and 4

	Mn1 (3)	Mn2 (3)	Mn3 (3)	Mn4 (3)	Mn5 (3)	Mn6 (3)	Mn (4)
S _{OC}	0.433	0.443	0.652	0.179	0.877	0.907	0.181
S_{TP}	13.767	13.465	12.738	15.387	12.449	12.445	15.098

* octahedron, ** trigonal prism

^{*a*} S_{OC} , S_{TP} ó continuous shape measure relatied to the OC-6 and TP-6 geometry, respectively (equal to 0 if the real geometry coincides with the idealized one);

Magnetic properties.

Compounds **1** and **2** in the 50 6 300 K temperature range have constant $T = 0.37 \text{ cm}^3 \text{dKomol}^{-1}$ ¹ per tungsten(V) center, which is very close to the expected spin-only value of 0.375 cm³ dKomol⁻¹ for $S = \frac{1}{2}$ and assuming isotropic g = 2.0 (Figure S2). Below T = 50 K the T(T) dependence starts to decrease reaching at 2 K the values of 0.34 (1) and 0.28 (2) cm³ dKomol⁻¹. Such behavior might indicate a weak antiferromagnetic interactions or significant anisotropy of $[W^V(CN)_8]^{3-}$.

Fitting the T(T) dependence using the mean-field approximation

$$\chi = \chi_0 / (1 - \frac{2zJ'}{Ng^2\beta^2}\chi_0)$$

where $_0$ denotes susceptibility of a separated S = 1/2 spin and zJ' describes an antiferromagnetic interactions between W^V ions, we obtained $g_w = 1.98$ and zJ' = -0.196 cm⁻¹ for **1** and $g_W = 1.98$ and zJ' = -0.455 cm⁻¹ for **2**.

For both compounds the M(H) curves are close to the Brillouin functions for S = 1/2 and g = 1.98 (Figure S3), which is in line with the aforementioned fitting results.

The compound **4** behave as a paramagnet due to the presence of very weakly coupled paramagnetic Mn^{II} centers. The measured high temperature T limit of 8.7 cm³ dK cmol⁻¹ (Figure S7) is in agreement with 8.75 cm³ dK cmol⁻¹ expected for two isolated Mn^{II} ions (S = 5/2, g = 2.0). With the decreasing temperature the signal is almost constant down to ~100 K. Below this point it starts to decrease very slowly. The decrease of the signal becomes pronounced below 25 K. At T = 2 K the T product is 3 cm³ dK cmol⁻¹. Using the approximation similar as in case of **1** and **2**, the best-fit parameters: $g_{Mn} = 2.04$ and zJ' = -0.091 cm⁻¹ were obtained for **4**.

The *M* is a linear function of *H* up to 20 kOe and begins to saturate very slowly above this point to reach a value of 8.2 N at H = 50 kOe which is much below the expected 10 N (for two Mn^{II} centers assuming S = 5/2 and g = 2.0). The M(H) runs much lower than the sum of 2 Brillouin functions for S = 5/2 and g = 2.04 (Figure S8). The Mn^{II} distances in the Mn^{II}-NC-W^{IV}-CN-Mn^{II} linkage are within the range 6.9-10.7 Å, the lowest limit being also the Mn^{II} distance within Mn^{II}-pzdo-Mn^{II} linkage. The magnetic interactions Mn-Mn could operate through the diamagnetic [W(CN)₈]⁴⁻ bridges or through the pzdo bridges.



Figure S2. Magnetic properties of **1** (red) and **2** (black). T(T) at H = 1 kOe. Solid lines represent the best fit to the experimental data (see text above for details).



Figure S3. M(H) curves for **1** (red) and **2** (black) at T = 2 K and T = 5 K. The blue solid lines show the Brillouin functions for spin S = 1/2 and g = 1.98.



Figure S4. Magnetic susceptibility temperature product for **3** from measurements made at 1 kOe (black points) and at 15 Oe (red points). In the inset: enlarged high temperature part.



Figure S5. Magnetic properties of **3**: ac magnetic susceptibility '(T) and ''(T) curves measured using different ac frequencies. The " data are multiplied 10 times to be visible. No shift in the position of the peak is detected.



Figure S6. Magnetic properties of **3**: the complete set of M(H) dependencies (a) and the relevant dM/dH(H) dependencies (b) at *T* range 2 ó 18 K, according to the vertical coloration scale). The maxima of dM/dH(H) were used for magnetic phase diagram determination.



Figure S7. Temperature dependence T(T) at H = 1 kOe calculated for Mn₂W unit for 4. Red solid line is the best fit to the experimental data.



Figure S8. Field dependent magnetization M(H) at T = 2 K for 4. The red solid line shows the Brillouin function for two uncoupled spins S = 5/2 and g = 2.04.

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