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Low Dimensional Solids based on Mo_6 Cluster Cyanides and Mn^{2+}, Mn^{3+} or Cd^{2+} Metal Ions: Crystal Chemistry, Magnetic and Optical Properties.

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SUPPLEMENTARY

- Atomic coordinates, relevant selected bond lengths and angles
- Asymmetric unit of **1**-**5**. Thermal ellipsoids are represented at the 50% probability level.
- Summary of possible combination of Mn^{2+}, Mn^{3+} in low and high spin configurations with diamagnetic or paramagnetic clusters.
- Compositions, charges, radius and volumes of $[M_6Q_8(CN)_6]^{n-}$ reported in the literature
- Reflectance,
- Projection of the structure of **5** along the *c* axis.

Table S1A Atomic coordinates, site occupancy and equivalent isotropic displacement (Å^2) parameters refined at 150 K for compound **1**.

Atom		Site	*x*	*y*	*z*	Occ.	U(eq)
	1						
Mo1		8*i*	0.20052(6)	1/4	0.63444(9)	1.00	0.0104(3)
Mo2		16*j*	0.30751(5)	0.37651(9)	0.70034(6)	1.00	0.0148(2)
Br1		8*i*	0.31393(8)	1/4	0.53823(11)	1.00	0.0246(5)
Br2		16*j*	0.20186(7)	0.49917(11)	0.63655(9)	1.00	0.0261(3)
Br3		8*i*	0.08827(8)	1/4	0.7337(1)	1.00	0.0233(5)
Mn		4*e*	1/2	3/4	0.6355(3)	1.00	0.0184(9)
C1		8*i*	0.1404(9)	1/4	0.501(1)	1.00	0.020(4)
N1		8*i*	0.105(1)	1/4	0.433(1)	1.00	0.040(6)
C2		16*j*	0.3787(7)	0.526(1)	0.648(1)	1.00	0.044(4)
N2		16*j*	0.420(6)	0.599(1)	0.630(1)	1.00	0.044(4)
O1		4*e*	1/2	1/4	0.4707(15)	1.00	0.058(9)
O2		4*e*	1/2	1/4	0.799(2)	1.00	0.059(9)

Table S1B Selected bond lengths (Å) and angles (°) for compounds **1** and [trans-$Cd(H_2O)_2$][$Mo_6Br_8(CN)_6$][14]

1					
Mo1-Mo2	2.635(1)	Mo2-Br1	2.596(2)	Mo1-C1-N1	176.1(2)
Mo1-Mo2$^{\#1}$	2.635(1)	Mo2-Br2	2.585(2)	Mo2-C2-N2	172.8(1)
Mo1-Mo2$^{\#2,3}$	2.635(1) (×2)	Mo2-Br2$^{\#2}$	2.592(1)	Mn1-N2-C2	165.2(1)
Mo2-Mo2$^{\#1}$	2.634(1)	Mo2-Br3$^{\#2}$	2.593(2)		
Mo2-Mo2$^{\#2}$	2.635(1)	Mo2-C2	2.21(1)		
Mo1-Br1	2.586(2)				
Mo1-Br2	2.594(1)	Mn-N2	2.22(1)		
Mo1-Br2$^{\#1}$	2.594(1)	Mn-N2$^{\#4,5,6}$	2.22(1) (×3)		
Mo1-Br3	2.588(2)	Mn-O1	2.27(2)		
Mo1-C1	2.20(2)	Mn-O2	2.25(3)		

2					
[trans-$Cd(H_2O)_2$][$Mo_6Br_8(CN)_6$]					
Mo-Mo	2.6421(5)	Mo-C	2.226(5)	Mo1-C1-N1	178.4(6)
Mo-Br (min)	2.5929(7)	Cd-N	2.289(5)	Mo2-C2-N2	173.9(4)
Mo-Br (max)	2.6027(5)	Cd-O	2.414(9)	Cd1-N2-C2	164.2(4)

Symmetry transformations used to generate equivalent atoms:

#1: x,-y+1/2,z; #2: -x+1/2,y,-z+3/2; #3: -x+1/2,-y+1/2,-z+3/2; #4: -x+1,-y+3/2,z; #5: -x+1, y, z. #6: x, 3/2-y, z

Table S2A. Atomic coordinates, site occupancy and equivalent isotropic displacement (Å^2) parameters refined at 150K and at room temperature for compounds **2** and **3**, respectively

Atom	Site	x	y	z	Occ.	U(eq)
2						
Mo1	8*i*	0.30244(2)	3/4	0.63651(3)	1.0	0.0102(1)
Mo2	16*j*	0.30696(2)	0.62257(2)	0.80194(2)	1.0	0.0114(1)
Br1	8*i*	0.41123(3)	3/4	0.74095(5)	0.5	0.0159(2)
S1	8*i*	0.41123(3)	3/4	0.74095(5)	0.5	0.0159(2)
Br2	16*j*	0.30045(2)	0.49724(3)	0.63801(3)	0.83	0.0158(1)
S2	16*j*	0.30045(2)	0.49724(3)	0.63801(3)	0.17	0.0158(1)
Br3	8*i*	0.19028(3)	3/4	0.53507(4)	0.83	0.0148(1)
S3	8*i*	0.19028(3)	3/4	0.53507(4)	0.17	0.0148(1)
Mn	4*e*	1/2	1/4	0.87747(7)	1.0	0.0124(2)
C1	8*i*	0.3686(3)	3/4	0.5076(4)	1.0	0.019(1)
N1	8*i*	0.4073(3)	3/4	0.4427(4)	1.0	0.032(1)
C2	16*j*	0.3788(2)	0.4749(4)	0.8554(3)	1.0	0.025(1)
N2	16*j*	0.4206(2)	0.3999(4)	0.8754(3)	1.0	0.032(1)
O1	4*e*	1/2	1/4	0.7151(5)	1.0	0.052(3)
O2	8*h*	1/2	0.287(1)	1.0384(6)	0.50	0.041(4)
Cs1	8*h*	1/2	1.0152(1)	0.4275(1)	0.337	0.0429(4)
3						
Mo1	8*i*	0.30167(3)	3/4	0.63643(5)	1.0	0.0170(2)
Mo2	16*j*	0.30704(2)	0.62183(5)	0.80109(3)	1.0	0.0180(2)
Br1	8*i*	0.41143(3)	3/4	0.73925(6)	0.75	0.0289(3)
Se1	8*i*	0.41143(3)	3/4	0.73925(6)	0.25	0.0289(3)
Br2	16*j*	0.29971(3)	0.49657(6)	0.63816(5)	0.75	0.0288(2)
Se2	16*j*	0.29971(3)	0.49657(6)	0.63816(5)	0.25	0.0288(2)
Br3	8*i*	0.18944(4)	3/4	0.53715(6)	0.75	0.0278(3)
Se3	8*i*	0.18944(4)	3/4	0.53715(6)	0.25	0.0278(3)
Mn	4*e*	1/2	1/4	0.87469(12)	1.0	0.0183(5)
C1	8*i*	0.3676(4)	3/4	0.5089(6)	1.0	0.033(3)
N1	8*i*	0.4070(4)	3/4	0.4459(6)	1.0	0.054(3)
C2	16*j*	0.3785(3)	0.4738(6)	0.8543(5)	1.0	0.036(2)
N2	16*j*	0.4208(2)	0.3998(5)	0.8740(4)	1.0	0.043(2)
O1	4*e*	1/2	1/4	0.7114(6)	1.0	0.062(4)
O2	4*e*	1/2	1/4	1.0349(6)	1.0	0.094(6)
Cs1	8*h*	1/2	1.0104(2)	0.43955(19)	0.408	0.0879(8)

Table S2B Selected bond lengths (Å) and angles (°) for compounds **2** and **3**.

2					
Mo1-Mo2	2.6267(5)	Mo2-L1	2.5657(6)	Mo1-C1-N1	175.8(5)
Mo1-Mo2$^{\#1}$	2.6267(5)	Mo2-L2$^{\#2}$	2.5998(5)	Mo2-C2-N2	173.1(4)
Mo1-Mo2$^{\#2,3}$	2.6485(5) (×2)	Mo2-L2	2.5997(5)	Mn1-N2-C2	166.9(4)
Mo2-Mo2$^{\#1}$	2.6272(3)	Mo2-L3$^{\#2}$	2.5968(6)		
Mo2-Mo2$^{\#2}$	2.6451(5)	Mo2-C2	2.198(4)		
Mo1-L1	2.5656(7)	Mn1-N2	2.191(4)		
Mo1-L2	2.6059(3)	Mn1-N2$^{\#4,5,6}$	2.191(4) (×3)		
Mo1-L2$^{\#1}$	2.6059(3)	Mn1-O1	2.231(7)		
Mo1-L3	2.5981(7)	Mn1-O2	2.244(8)		
Mo1-C1	2.193(6)	Mn1-O2$^{\#6}$	2.244(8)		
3					
Mo1-Mo2	2.6382(8)	Mo2-L1	2.5822(7)	Mo1-C1-N1	174.7(7)
Mo1-Mo2$^{\#1}$	2.6382(8)	Mo2-L2$^{\#2}$	2.5992(8)	Mo2-C2-N2	172.4(5)
Mo1-Mo2$^{\#2,3}$	2.6528(7) (×2)	Mo2-L2	2.6044(8)	Mn1-N2-C2	166.4(6)
Mo2-Mo2$^{\#1}$	2.6380(7)	Mo2-L3$^{\#2}$	2.6023(9)		
Mo2-Mo2$^{\#2}$	2.6484(6)	Mo2-C2	2.198(6)		
Mo1-L1	2.5821(9)	Mn1-N2	2.189(5)		
Mo1-L2	2.6084(6)	Mn1-N2$^{\#4,5,6}$	2.189(5) (×3)		
Mo1-L2$^{\#1}$	2.6084(6)	Mn1-O1	2.263(8)		
Mo1-L3	2.596(1)	Mn1-O2	2.221(8)		
Mo1-C1	2.190(8)				

Symmetry transformations used to generate equivalent atoms:

#1: x, -y+3/2, z; #2: -x+1/2, y, -z+3/2; #3: -x+1/2, -y+3/2, -z+3/2; #4: x, -y+1/2, z; #5: -x+1, y, z; #6: -x+1, -y+1/2, z.

Table S3A. Atomic coordinates, site occupancy and equivalent isotropic displacement (Å^2) parameters refined at 150K for **4** and **5**, respectively.

Atom	Site	*x*	*y*	*z*	Occ.	U(eq)
			4			
Mo1	3*b*	0.4946(2)	0.4946(2)	1/2	1.0	0.0335(7)
Mo2	6*c*	0.3763(2)	0.3321(2)	0.6265(1)	1.0	0.0290(5)
Mo3	3*b*	0.2135(2)	0.2135(2)	1/2	1.0	0.0291(6)
Mo4	6*c*	0.2754(1)	0.4319(2)	0.5358(1)	1.0	0.0244(5)
Br1	6*c*	0.4362(2)	0.5471(2)	0.6594(2)	0.75	0.0404(9)
S1	6*c*	0.4362(2)	0.5471(2)	0.6594(2)	0.25	0.0404(9)
Br2	6*c*	0.1602(2)	0.2703(2)	0.6605(2)	0.75	0.0368(8)
S2	6*c*	0.1602(2)	0.2703(2)	0.6605(2)	0.25	0.0368(8)
Br3	6*c*	0.1158(2)	0.3124(3)	0.4103(2)	0.75	0.0382(9)
S3	6*c*	0.1158(2)	0.3124(3)	0.4103(2)	0.25	0.0382(9)
Br4	6*c*	0.3945(3)	0.5926(2)	0.4109(2)	0.75	0.0438(9)
S4	6*c*	0.3945(3)	0.5926(2)	0.4109(2)	0.25	0.0438(9)
C1	3*b*	0.658(8)	0.658(8)	1/2	1.0	0.18(1)
N1	3*b*	0.748(6)	0.748(6)	1/2	1.0	0.18(1)
C2	6*c*	-0.086(2)	0.595(3)	0.442(1)	1.0	0.060(9)
N2	6*c*	-0.091(2)	0.587(3)	0.523(2)	1.0	0.081(9)
C3	3*b*	0.065(5)	0.065(5)	1/2	1.0	0.18(1)
N3	3*b*	-0.022(5)	-0.022(5)	1/2	1.0	0.18(1)
C4	6*c*	0.180(2)	0.520(2)	0.582(1)	1.0	0.045(8)
N4	6*c*	0.126(2)	0.564(3)	0.606(1)	1.0	0.045(7)
Cd1	3*a*	0	0.6152(1)	2/3	1.0	0.0300(6)
O1	6*c*	0.123(2)	0.807(2)	0.613(2)	1.0	0.11(1)
O2	6*c*	0.310(1)	0.850(2)	0.503(1)	1.0	0.074(8)
			5			
Mo1	3*b*	0.4938(2)	0.4938(2)	1/2	1.0	0.0341(5)
Mo2	6*c*	0.3758(1)	0.3316(2)	0.62665(9)	1.0	0.0282(4)
Mo3	3*b*	0.2134(2)	0.2134(2)	1/2	1.0	0.0283(5)
Mo4	6*c*	0.2751(1)	0.4313(1)	0.53613(9)	1.0	0.0249(4)
Br1	6*c*	0.4357(2)	0.5461(2)	0.6600(1)	0.75	0.0433(6)
Se1	6*c*	0.4357(2)	0.5461(2)	0.6600(1)	0.25	0.0433(6)
Br2	6*c*	0.1606(2)	0.2701(2)	0.6607(1)	0.75	0.0387(6)
Se2	6*c*	0.1606(2)	0.2701(2)	0.6607(1)	0.25	0.0387(6)
Br3	6*c*	0.1166(2)	0.3126(2)	0.4103(1)	0.75	0.0447(7)
Se3	6*c*	0.1166(2)	0.3126(2)	0.4103(1)	0.25	0.0447(7)
Br4	6*c*	0.3932(2)	0.5907(2)	0.4111(2)	0.75	0.0508(8)
Se4	6*c*	0.3932(2)	0.5907(2)	0.4111(2)	0.25	0.0508(8)
C1	3*b*	0.659(2)	0.659(2)	1/2	1.0	0.18(1)
N1	3*b*	0.745(3)	0.745(3)	1/2	1.0	0.18(1)
C2	6*c*	-0.088(2)	0.599(3)	0.445(1)	1.0	0.058(8)
N2	6*c*	-0.094(2)	0.584(2)	0.524(1)	1.0	0.070(8)
C3	3*b*	0.051(2)	0.051(2)	1/2	1.0	0.18(1)
N3	3*b*	-0.036(2)	-0.036(2)	½	1.0	0.18(1)
C4	6*c*	0.183(2)	0.521(2)	0.581(1)	1.0	0.048(8)
N4	6*c*	0.127(2)	0.563(2)	0.608(1)	1.0	0.052(7)
Cd1	3*a*	0	0.6132(1)	2/3	1.0	0.0318(5)
O1	6*c*	0.124(2)	0.805(2)	0.615(2)	1.0	0.10(1)
O2	6*c*	0.311(1)	0.840(1)	0.5025(8)	1.0	0.045(5)

Table S3B Selected bond lengths (Å) and angles (°) for compounds **4**, **5** and $Cs_{0.5}K_{0.5}(Et_4N)_{11}[Mo_6Br_6Q_2(CN)_6]$[13k]

4					
Mo1-Mo2	2.625(1)	Mo3-L2	2.594(3)	Mo1-C1-N1	180(9)
Mo1-Mo2$^{\#2}$	2.625(1)	Mo3-L2$^{\#2}$	2.594(3)	Mo2$^{\#4}$-C2-N2	170(3)
Mo1-Mo4	2.631(3)	Mo3-L3	2.581(4)	Mo3-C3-N3	180(7)
Mo1-Mo4$^{\#2}$	2.631(3)	Mo3-L3$^{\#2}$	2.581(4)	Mo4-C4-N4	178(2)
Mo2-Mo3	2.626(3)	Mo3-C3	1.96(3)	Cd1-N2-C2	150(2)
Mo2-Mo4	2.628(3)	Mo4-L1	2.577(3)	Cd1-N4-C4	169(2)
Mo2-Mo4$^{\#2}$	2.628(3)				
Mo3-Mo4	2.622(3)	Mo4-L2	2.594(3)		
Mo3-Mo4$^{\#2}$	2.622(3)	Mo4-L3	2.598(4)		
Mo1-L1	2.585(3)	Mo4-L4	2.598(3)		
Mo1-L1$^{\#2}$	2.585(3)	Mo4-C4	2.20(3)		
Mo1-L4	2.591(4)	Cd1-O1	2.35(2)		
Mo1-L4$^{\#2}$	2.591(4)	Cd1-O1$^{\#1}$	2.35(2)		
Mo1-C1	2.16(10)	Cd1-N2	2.30(2)		
Mo2-L1	2.580(3)	Cd1-N2$^{\#1}$	2.30(2)		
Mo2-L2	2.590(4)	Cd1-N4	2.26(2)		
Mo2-L3$^{\#2}$	2.593(3)	Cd1-N4$^{\#1}$	2.26(2)		
Mo2-L4$^{\#2}$	2.600(4)				
Mo2-C2$^{\#3}$	2.16(2)				
5					
Mo1-Mo2	2.635(2)	Mo3-L2	2.603(2)	Mo1-C1-N1	180(3)
Mo1-Mo2$^{\#2}$	2.635(2)	Mo3-L2$^{\#2}$	2.603(2)	Mo2$^{\#4}$-C2-N2	168(2)
Mo1-Mo4	2.642(3)	Mo3-L3	2.588(3)	Mo3-C3-N3	180(2)
Mo1-Mo4$^{\#2}$	2.642(2)	Mo3-L3$^{\#2}$	2.588(3)	Mo4-C4-N4	176(2)
Mo2-Mo3	2.638(2)	Mo3-C3	2.16(3)	Cd1-N2-C2	150(2)
Mo2-Mo4	2.638(3)	Mo4-L1	2.590(3)	Cd1-N4-C4	170(2)
Mo2-Mo4$^{\#2}$	2.643(2)	Mo4-L2	2.600(3)		
Mo3-Mo4	2.634(2)	Mo4-L3	2.603(3)		
Mo3-Mo4$^{\#2}$	2.634(3)	Mo4-L4	2.601(3)		
Mo1-L1	2.600(3)	Mo4-C4	2.19(3)		
Mo1-L1$^{\#2}$	2.600(3)	Cd1-O1	2.35(2)		
Mo1-L4	2.598(3)	Cd1-O1$^{\#1}$	2.35(3)		
Mo1-L4$^{\#2}$	2.598(3)	Cd1-N2	2.31(2)		
Mo1-C1	2.19(3)	Cd1-N2$^{\#1}$	2.31(2)		
Mo2-L1	2.589(3)	Cd1-N4	2.26(3)		
Mo2-L2	2.595(3)	Cd1-N4$^{\#1}$	2.26(3)		
Mo2-L3$^{\#2}$	2.596(3)				
Mo2-L4$^{\#2}$	2.601(3)				
Mo2-C2$^{\#3}$	2.21(2)				
		$Cs_{0.5}K_{0.5}(Et4N)_{11}[Mo_6Br_6Se_2(CN)_6]$			
Mo1-Mo2	2.6532(8)	C1-N1	1.11(2)		
Mo2-Mo2	2.647(1)	C2-N2	1.12(1)		
Mo1-L1	2.6006(6)	Mo1-C1-N1	180.		
Mo2-L1	2.6042(5)	Mo2-C2-N2	180.0(8)		
Mo1-C1	2.23(1)				
Mo2-C2	2.22(1)				

Symmetry transformations used to generate equivalent atoms: #1: -x, -x+y, -z+4/3 ; #2 : y, x, -z+1 ; #3 : -y+1, x-y+1, z+1/3 ; #4 : -x+y, -x+1, z-1/3 .

Fig S1. Asymmetric unit of **1**. Thermal ellipsoids are represented at the 50% probability level.

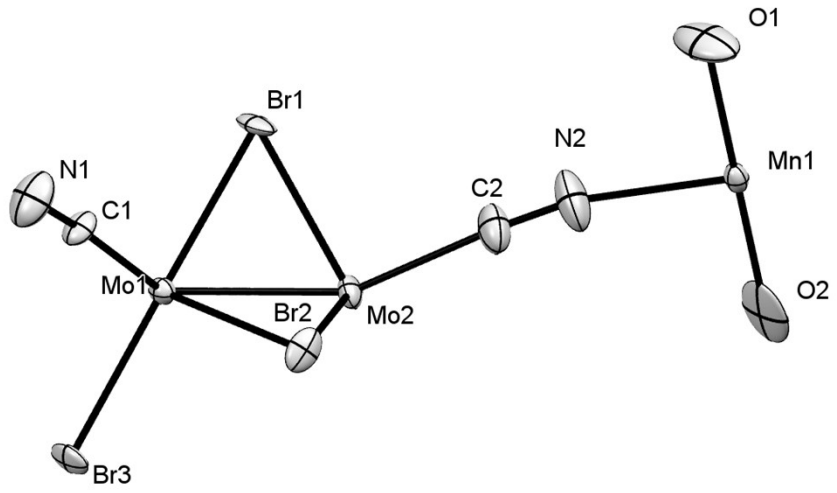

Fig S2. Asymmetric unit of **2**. Thermal ellipsoids are represented at the 50% probability level.

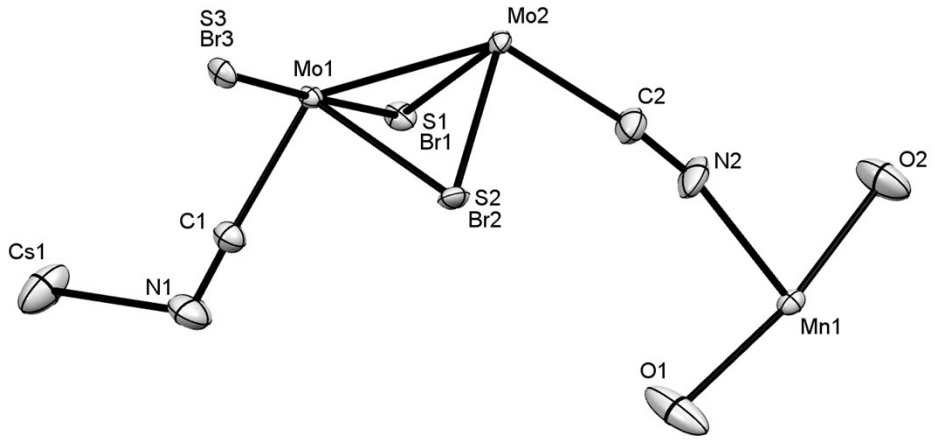

Fig S3. Asymmetric unit of **3**. Thermal ellipsoids are represented at the 50% probability level.

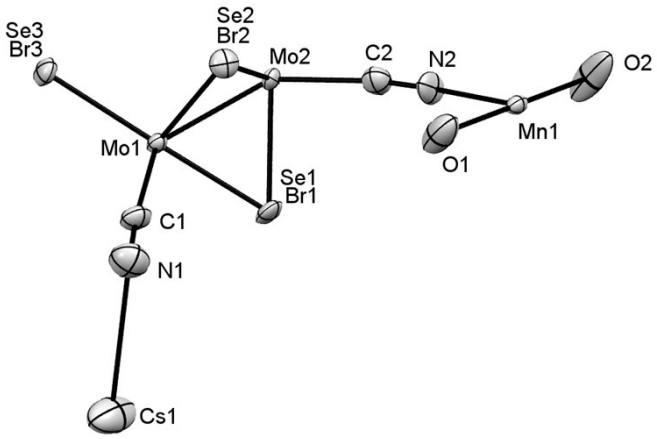

Fig S4. Asymmetric unit of **4**. Thermal ellipsoids are represented at the 50% probability level. . C1, C3, N1 and N3 were refined isotropically.

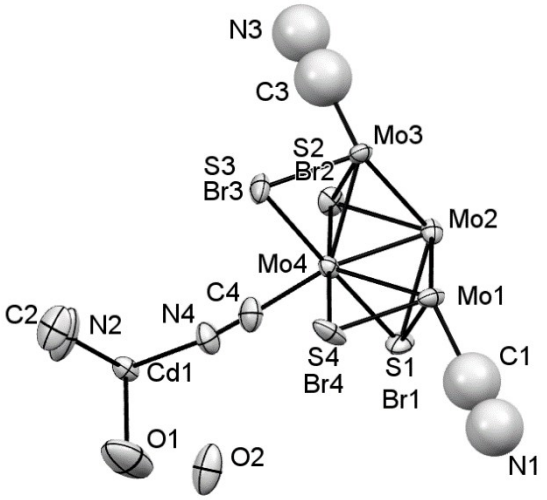

Fig S5. Asymmetric unit of **5**. Thermal ellipsoids are represented at the 50% probability level.

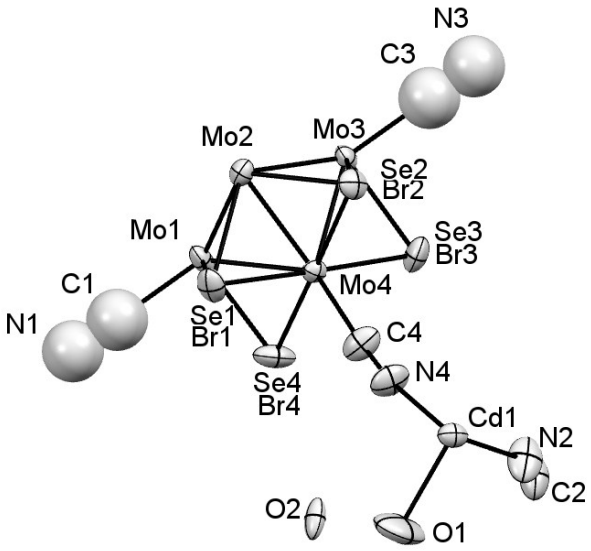

Table S4 Values of Curie constants for each possible configuration for Mn cations and for cluster unit in **3** and **4** (i.e. Mn^{II} in high or low spin environment; Mn^{III} in high or low spin environment and a paramagnetic (VEC = 23) or diamagnetic cluster (VEC = 24)). The values include the stoichiometric coefficients deduced from the structural refinements.

	MnII low spin	MnII high spin	MnIII low spin	MnIII high spin	diamagnetic cluster	paramagnetic cluster
n = number of unpaired electrons	1	5	2	4	0	1
(n(n+2))/8	0.375	4.375	1	3	0	0.375
C (3)*	0.255	2.975	0.32	0.96	0	0.375
C (4)**	0.3075	3.5875	0.18	0.54	0	0.375

* The refined leads to 0.68 Mn^{II} and 0.32 Mn^{III} for **3** and 0.82 Mn^{II} and 0.18 Mn^{III} for **4**. $C(3)_{MnIILS}$ = 0.68 × 0.375 = ,….. For all compound, there is one cluster unit per formula.

Table S5. Theoretical Curie constants for Cs_x[*trans*-($Mn^{II}_xMn^{III}_{1-x}$)$(H_2O)_2$][$Mo_6Br_6Q_2(CN)_6$] (Q = S (**3**) and Se (**4**)) calculated using the different possible combinations between $Mn^{II/III}$ low or high spin with diamagnetic or paramagnetic cluster. $C_{total}3 = 0.68\ C_{MnII} + 0.32\ C_{MnIII} + 1\ C_{Cluster}$; $C_{total}4 = 0.82\ C_{MnII} + 0.18\ C_{MnIII} + 1\ C_{Cluster}$

	A	B	C	D	E	F	G	H
Ctotal (3)	0.575	0.95	1.215	1.59	3.295	3.67	3.935	4.31
Ctotal (4)	0.4875	0.8625	0.8475	1.2225	3.7675	4.1425	4.1275	4.5025

A: Mn^{II}_{LS} + Mn^{III}_{LS} + diamagnetic cluster, B: Mn^{II}_{LS} + Mn^{III}_{LS} + paramagnetic cluster, C: Mn^{II}_{LS} + Mn^{III}_{HS} + diamagnetic cluster, D: Mn^{II}_{LS} + Mn^{III}_{HS} + paramagnetic cluster, E: Mn^{II}_{HS} + Mn^{III}_{LS} + diamagnetic cluster, F: Mn^{II}_{HS} + Mn^{III}_{LS} + paramagnetic cluster, G: Mn^{II}_{HS} + Mn^{III}_{HS} + diamagnetic cluster, H: Mn^{II}_{HS} + Mn^{III}_{HS} + paramagnetic cluster

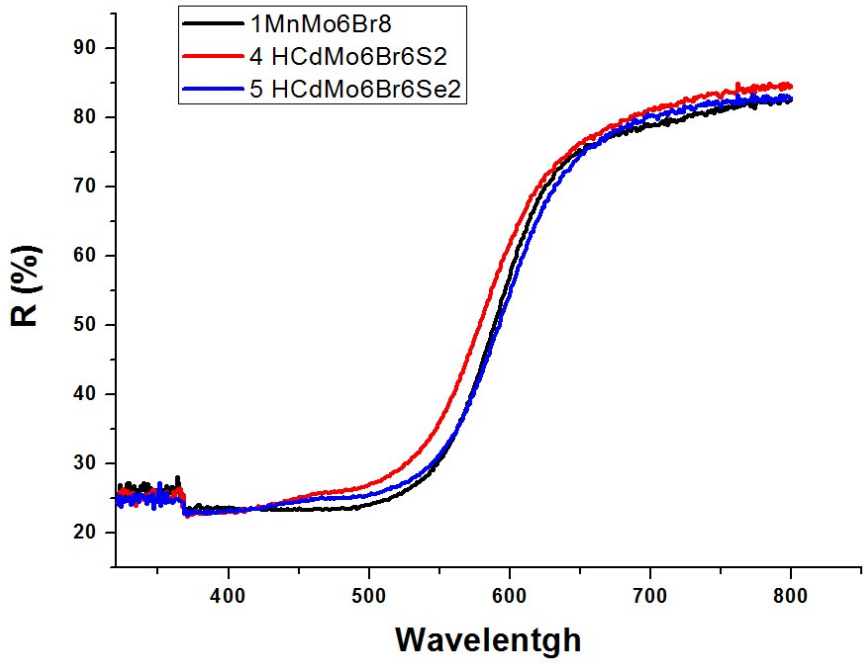

Fig S6. Reflectance spectra of **1**, **4** and **5**. These 3 compounds are based on Mo6 clusters with a 24 valence electrons concentration. The bump at around 360 nm is an artefact due to the automatic change of irradiation light.

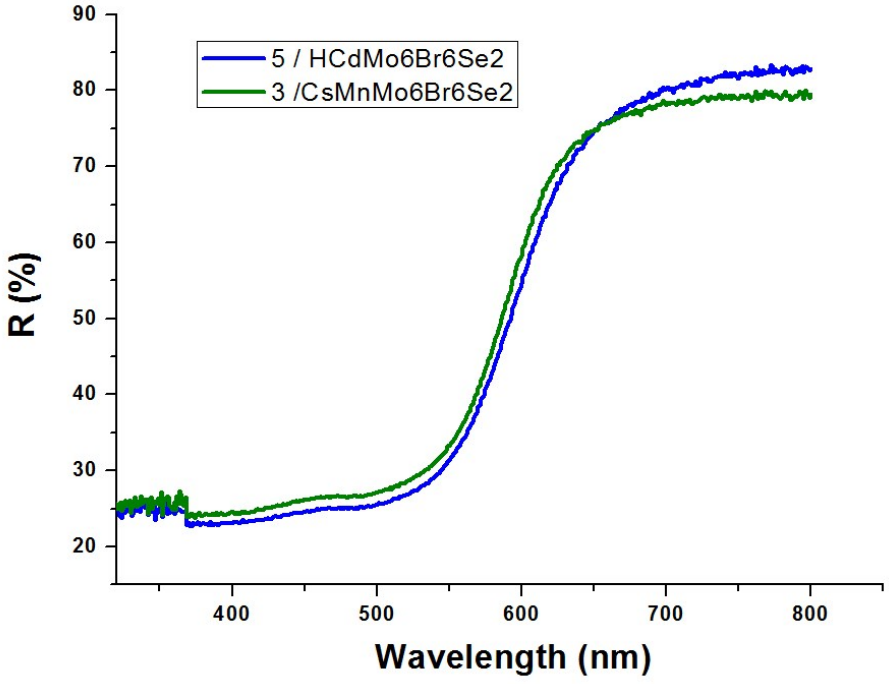

Fig S7. Reflectance spectra of **3** and **5**. **3** is based on $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{3-}$ with a 23 valence electrons concentration. **5** is based on $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ with a 24 valence electrons concentration. The bump at around 360 nm is an artefact due to the automatic change of irradiation light.

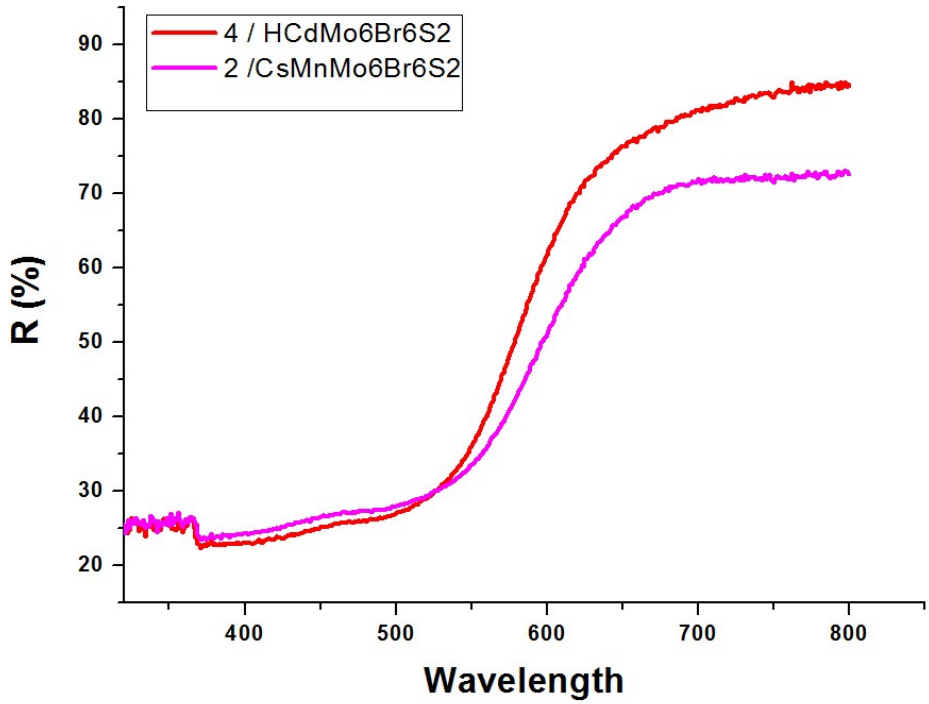

Fig S8. Reflectance spectra of **2** and **4**. **2** is based on $[Mo_6Br^i_6S^i_2(CN)^a_6]^{3-}$ with a 23 valence electrons concentration. **4** is based on $[Mo_6Br^i_6S^i_2(CN)^a_6]^{4-}$ with a 24 valence electrons concentration. The bump at around 360 nm is an artefact due to the automatic change of irradiation light.

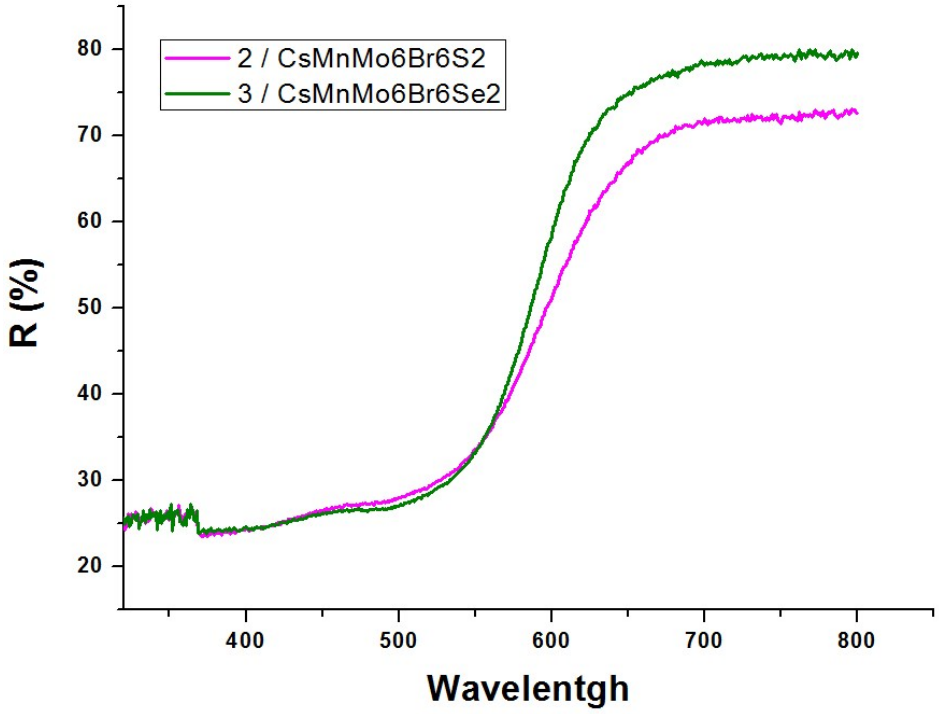

Fig S9. Reflectance spectra of **2** and **3**. **2** is based on $[Mo_6Br^i_6S^i_2(CN)^a_6]^{3-}$ with a 23 valence electrons concentration. **3** is based on $[Mo_6Br^i_6S^i_2(CN)^a_6]^{3-}$ with a 23 valence electrons concentration. The bump at around 360 nm is an artefact due to the automatic change of irradiation light.

Table S6 Compositions, charges, radius and volumes of face capped $[M_6Q^i_8(CN)^a_6]^{n-}$ and edge-bridged $[M_6Q^i_{12}(CN)^a_6]^{n-}$ reported in the literature

Anion	Charge	Radius of anion, Å	Volume of anion	Ref.
Type $[M_6Q_8(CN)_6]^{n-}$				
$[Re_6S_8(CN)_6]^{4-/3-}$	–4 / –3	6,65	387	[32]
$[Re_6Se_8(CN)_6]^{4-/3-}$	–4 / –3	6,65	416	[12a]
$[Re_6Te_8(CN)_6]^{4-/3-}$	–4 / –3	6,68	475	[15]
$[Mo_6S_8(CN)_6]^{7-}$	–7	6,77	401	[36]
$[Mo_6Se_8(CN)_6]^{7-/6-}$	–8 / –7 / –6	6,78	430	[36]
$[Re_{4,5}Mo_{1,5}S_8(CN)_6]^{5-}$	–5	6,68	393	[37]
$[Re_3Mo_3S_8(CN)_6]^{6-}$	–6	6,67	391	[34]
$[Mo_6Br_6S_2(CN)_6]^{4-}$	–4 / –3	6,73	425	[16]
$[Mo_6Br_6Se_2(CN)_6]^{4-}$	–4 / –3	6,76	427	[16]
$[Mo_6Br_8(CN)_6]^{2-}$	–2	6,74	423	[38]
$[W_6S_8(CN)_6]^{7-/6-/5-}$	–7	6,76	428	[39]
Type $[M_6Y_{12}(CN)_6]^{n-}$				
$[Nb_6Cl_{12}(CN)_6]^{4-}$	–4	7,03	480	[40]
$[Ta_6Cl_{12}(CN)_6]^{4-}$	–4	7,00	475	[41]
$[Nb_6Cl_9O_3(CN)_6]^{5-}$ (D_{3d})	–5	7,05	458	[40]
$[Nb_6Cl_9O_3(CN)_6]^{5-}$ (C_{2v})	–5	7,05	460	[11]
$[Nb_6Cl_4O_4(OH)_4(CN)_6]^{6-}$	–6	7,04	418	[42]

[1] The volume was estimated using Platon software.

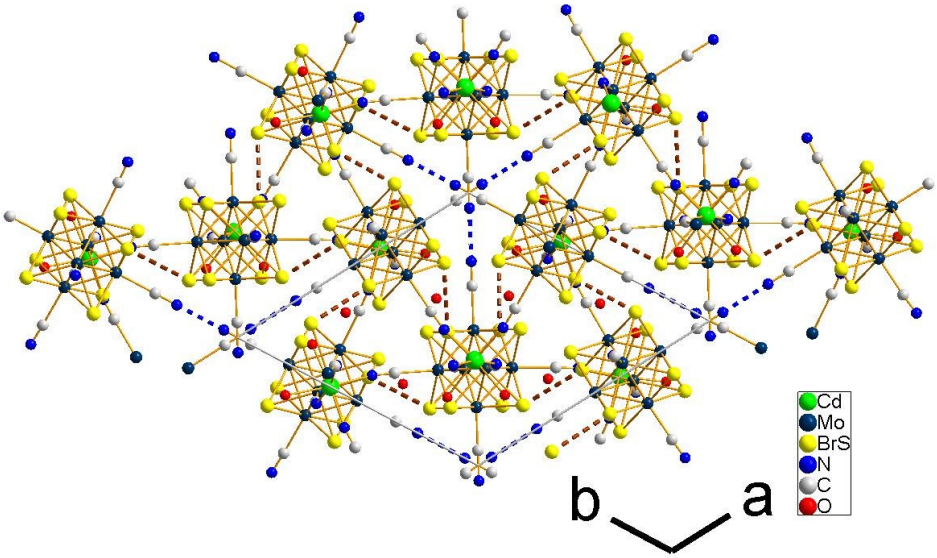

Fig. S10. Projection of the structure of **5** along the *c* axis. Ribons are linked together via Mo_6-C1N1-H-N3C3-Mo_6-bridges (dashed blue lines) and L1/L3 van der waals contact (dashed brown).