

Stabilization of Ni2+ dimers in hexacyano Mo6 cluster-based Prussian blue derivatives: Experimental and theoretical investigations of magnetic properties

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Hexacyano molybdenum clusters chalcohalides and divalent cations (Zn^{2+} and Cu^{2+}) for the design of extended polymeric and supramolecular frameworks

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Abstract: Two new octahedral molybdenum cyanide cluster compounds, namely $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}\text{-}Mo_6B_{r6}Se_2(CN)_6].2H_2O$ **(1)** and $[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$ **(2)** (en = ethylenediamine), have been synthetized as single crystals. **1** was obtained by slow diffusion of a solution containing $[Mo_6Br_6Se_2(CN)_6]^{4-}$ cluster units into a solution of zinc acetate and ethylenediamine. **2** was obtained by slow diffusion of an ammonia solution of $[Mo_6Br_6Se_2(CN)_6]^{4-}$ cluster units into a solution of cupper chloride and ethylenediamine. Both compounds were structurally characterized by single-crystal X-ray diffraction analysis. **1** is a bimetallic one dimensional coordination compound and it crystallizes in the orthorhombic system ($P2_12_12_1$; Z = 4; a = 10.675(1) Å, b = 15.073(2) Å, c = 25.812(4) Å, V = 4153.3(1) $Å^3$ at T = 150 K). **2** is a bimetallic H bonded three dimensional compound and it crystallizes in the monoclinic system ($P2_1/c$; Z = 2; a = 9.4281(4) Å, b = 11.0220(5) Å, c = 21.1494(9) Å, β = 100.053(2)°, V = 2164.03(16) $Å^3$ at T = 296 K).

Keywords: Clusters compounds / Cyanides / Ethylenediamine / Divalent cation / Molybdenum / Single-crystal Structure / Extended Framework / Supramolecular Framework

1. INTRODUCTION

Prussian Blue is well known as a strong blue pigment for more than a century but its crystallographic structure was solved from single-crystal X-ray diffraction data only in 1977 by Ludi *et al.* [1]. The authors showed that the compound is based on trivalent and divalent Fe cations leading to $Fe^{III}_4[Fe^{II}(CN)_6]_3.xH_2O$ with x = 14-16. It crystallizes in the cubic system and is characterized by missing $[Fe^{II}(CN)_6]$ groups leading to a disordered structure. Following this discovery many works have been made in order to obtain Prussian Blue analogues. We can cite, among others, groups of Zhao in China or Verdaguer in France for their works, on one hand, on electroactive thin film of Pd^{+II}-based Prussian Blue analogues [2] and, on the other hand, on magnetic properties of Cr^{+III}–based compounds [3]. Thereafter, at the same time, the Fedorov group in Russia and the Long group in the United States had the brilliant idea to replace the $[M(CN)_6]^{3-/4-}$ complex by a $[Re_6S^i_8(CN)^a_6]^{3-/4-}$ cluster unit thinking that it would be possible to obtain new compounds with similar architecture than that of Prussian Blue due to similar orthogonal disposition of CN groups in iron complexes and in Re_6 cyanides. Enhanced porosity should result from the greater size of the hexacyano-clusters comparing to their mononuclear-based hexacyanides analogues [4-6]. It has been highlighted that the nature of the counter cations and their solvated species along with the charge of Re_6 cluster unit (3- or 4-) are the driving forces for the formation of structures with defined dimensionalities. Indeed a wide library of compounds with fascinating structures is reported in the literature [4-11]. Then, the Fedorov group, as well as the Kim group in Korea, continued the research on this topic and they obtained numerous compounds based on Re_6 metal atom cluster cyanides and transition metal complexed by chelating ligands [12-16]. Indeed, it is well known that reactions between $[Re_6Q^i_8(CN)^a_6]^{3-/4-}$ (Q = S, Se) and transition metals often lead to close-packed structure [9, 17] or interpenetrating frameworks [5, 18]. A way to prevent compact structures and meanwhile to favor porosity is to include large counter cations as ammoniu[1]m salt [19-21] or to use chelating ligands as ethylenediamine [22-23] which also permits to control the 0-, 1-, 2- or 3-D dimensionality of the resulting compounds. It is worth noting that when obtained compounds are molecular complexes, their structural

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cohesion is mainly ensured by hydrogen bonds [19, 24]. If extended polymeric compounds have been obtained in the chemistry of Re_6 octahedral clusters and more recently in the chemistry of Nb_6 octahedral clusters [25-27], very few is known about Mo_6 hexacyano homologous. Hitherto only one layered compound based on $[Mo_6Br^i_8(CN)^a_6]^{2-}$, namely $[trans\text{-}Cd(H_2O)_2][Mo_6Br_8(CN)_6]$, has been reported so far [28]. On the other hand, no extended polymeric frameworks based on $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$ (Q = S or Se) is reported. However $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$ (Q = S or Se) and $[Re_6Q^i_8(CN)^a_6]^{4-}$, which are both face capped units, are isoelectronic and they both carry a four minus charge. Consequently, the use of $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$ should lead to compounds exhibiting architectures closer to those of Re_6 compounds than those of Nb_6 edge bridged-based compounds. Two compounds based on $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$ are already reported in the literature [29]. These are $Cs_{0.4}K_{0.6}(Et_4N)_{11}[Mo_6Br_6S_2(CN)_6]_3$ and $Cs_{0.5}K_{0.5}(Et_4N)_{11}[Mo_6Br_6Se_2(CN)_6]_3$ in which the alkali metals and $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$ anions form a $\{M[Mo_6Br_6Q_2(CN)_6]_3\}^{11-}$ (M = Cs, K) framework with a topology related to that found in Super Prussian Blue Series [30-31], in particular cluster expanded Prussian Blue analogues [4-11]. In this frame, here we report the syntheses and crystal structures of two new compounds based on $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster unit and Zn^{2+} or Cu^{2+} cations complexed by ethylenediamine namely $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}Mo_6Br_6Se_2(CN)_6].2H_2O$ **(1)** and $[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$ **(2)** (en = ethylenediamine). **1** is a bimetallic one dimensional coordination compound while **2** is a bimetallic H bonded three dimensional compound. Structural correlations with their Re analogues are discussed.

2. EXPERIMENTAL

Commercially available reagents and solvents were used without further purification. **1** and **2** have been obtained following a multi-step synthesis. Indeed, first the $MoBr_2$ cluster compound is synthesized by placing Mo (Plansee) powder under Br_2 gas flow according to a described procedure [32]. Then, $MoBr_2$, CsBr (Alfa Aesar, 99.9%), Mo (Plansee) and Se (Alfa Aesar, 99.999%) are introduced in stoichiometric proportions in a vacuum sealed tube and heated at 900°C for two days to form $Cs_4[Mo_6Br_{12}Se_2]$ compound as previously described [29].
Elementary analyses for the heavy atoms have been done by Electron Dispersion Spectroscopy (EDS) with a scanning electron microscope JSM 7100F. Infrared red spectra were recorded on a Bruker Equinox 55 FTIR spectrometer on transmittance with KBr as reference.

$Cs_2K_2[Mo_6Br_6Se_2(CN)_6]$. 270 mg of KCN (4.1 mmol) were dissolved in 20 mL of methanol in a Schlenk tube. Then, 1g of $Cs_4[Mo_6Br_{12}Se_2]$ (0.45 mmol), prepared via solid state route at high temperature was added to the mixture and stirred 48h under reflux at 55°C. The resulting brown solution was filtered and methanol was evaporated almost to dryness. Then dicholoromethane was added to separate the excess of KCN and KBr by precipitation. This operation is repeated until there is no KCN and KBr anymore. Yield: 65% (0.5g, 0.29 mmol).
IR (cm^{-1}): 2113 (ν_{CN}).
EDS analysis, heavy atoms %: K, 11.2; Cs, 11.2; Mo, 33.2; Br, 33.6; Se, 10.8. Calcd for $Cs_2K_2[Mo_6Br_6Se_2(CN)_6]$: K, 11.1; Cs, 11.1; Mo, 33.3; Br, 33.3; Se, 11.1.

$[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}\text{-}Mo_6B_{r6}Se_2(CN)_6].2H_2O$ (1). In a narrow-diameter tube, a solution of 1.0 mg (0.58 µmol) of $Cs_2K_2[Mo_6Br_6Se_2(CN)_6]$ in 0.5 mL of water was allowed to diffuse into a solution of 3.5 mg of $Zn[OOCCH_3]_2.2H_2O$ (0.016 mmol) (Fluka Analytical, 99.5%) in 0.5 mL of water to which 0.09 mL (1.35 mmol) of ethylenediamine (Alfa Aesar, 99%) had been added. After 1 week dark red-brown crystals were obtained. Yield: 40% (0.04 mg, 0.22 µmol).
IR (cm^{-1}): 2109 and 2131 (ν_{CN}).
EDS analysis, heavy atoms %: Zn, 12.6 Mo, 38.8; Br, 36.9; Se, 11.7. calcd for $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}\text{-}Mo_6B_{r6}Se_2(CN)_6].2H_2O$: Zn, 12.5; Mo, 37.5; Br, 37.5; Se, 12.5.

$[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$ (2). In a narrow-diameter tube, a solution of 1.0 mg (0.58 µmol) of $Cs_2K_2[Mo_6Br_6Se_2(CN)_6]$ in 0.5 mL of water was allowed to diffuse into a solution of 3.5 mg of $CuCl_2.xH_2O$ (Aldrich) in 0.5 mL of ammonia (25%) to which 0.09 mL (1.35 mmol) of ethylenediamine (Alfa Aesar, 99%) had been added. After 3 weeks dark red-brown crystals were obtained.
$CuCl_2$ and ethylenediamine were solubilized in ammonia for creating a competition between ammonia and ethylenediamine around Cu^{2+} cation in order to slow down the reaction because at first attempts an amorphous precipitate formed very quickly without formation of a crystalline phase. Yield: 30% (0.3 mg, 0.17 µmol).
IR (cm^{-1}): 2104 (ν_{CN}).
EDS analysis, heavy atoms %: Cu, 13.3; Mo, 37.8; Br, 36.7; Se, 12.2. calcd for $[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$: Cu, 12.5; Mo, 37.5; Br, 37.5; Se, 12.5.

Crystal structure determinations. Crystallographic data, details on data collections and refinement parameters of the crystal structures are summarized in Table 1. Single-crystal X-ray diffraction data were collected at 150 K on a D8 VENTURE Bruker AXS diffractometer and processed with the APEX 3 [33] program suite for **1.** For **2**, data were collected at room temperature on an APEX-II Bruker AXS diffractometer and processed with the APEX 2 [34] program suite. For both compounds the X-ray wavelength used was the Mo-Kα (λ = 0.71073 Å). Frame integration and data reduction were carried out with the program SAINT [35]. The program SADABS [36] was then employed for multiscan-type absorption corrections.

Table 1. Crystal data and structure refinement parameters for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{14}H_{38}Zn_2N_{14}O_3Mo_6Br_6Se_2$	$C_{14}H_{40}Cu_2N_{14}O_4Mo_6Br_6Se_2$
Formula weight ($g.mol^{-1}$)	1786.28	1800.6
Crystal size (mm^3)	0.14 x 0.12 x 0.06	0.33 x 0.15 x 0.03
Crystal color	brown	brown
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$ (19)	$P2_1/c$ (14)
a (Å)	10.675(1)	9.4281(4)
b (Å)	15.073(2)	11.0220(5)
c (Å)	25.812(4)	21.1494(9)
β (°)		100.053(2)
Volume ($Å^3$)	4153(1)	2164.0(2)
Z	4	2
ρ(calcd.) ($g.cm^{-3}$)	2.86	2.76
μ (mm^{-1})	10.449	9.904
F(000)	3304	1668
λ (Å)	0.71073	0.71073
T (K)	150	296
2Θ range (°)	2.34 to 35.43	2.67 to 28.3
Collected reflections	48311	9883
Independent reflections	26337	5818
Observed reflections [$I > 2\sigma(I)$]	12243	3594
Data / restrains / refined parameters	26337 / 0 / 413	5818 / 0 / 217
Goodness-of-fit on F^2	0.959	1.023
$R_1, \omega R_2$	0.064, 0.125	0.044, 0.108
$R_1, \omega R_2$ (all data)	0.185, 0.153	0.094, 0.121
Large. diff. peak and hole (e. $Å^{-3}$)	2.513, -1.715	1.209, -1.202

The structure was determined by direct method using the SHELXT program [37], and refined with full-matrix least-square methods based on F^2 (SHELXL-2014) [38] with the aid of the WinGX plateform [39]. The final refinements included anisotropic displacement parameters for the non-hydrogen atoms. For both compounds the positions of the hydrogen atoms on the ethylenediamine groups were idealized by HFIX command.

3. RESULTS AND DISCUSSIONS

Synthesis. $K_2Cs_2[Mo_6Br_6Se_2(CN)_6]$ was synthetized and used as precursor because of its solubility and its stability in water contrary to $Cs_{0.5}K_{0.5}(Et_4N)_{11}[Mo_6Br_6Se_2(CN)_6]_3.16H_2O$ [29] which is precipitates in water at room temperature. Both **1** and **2** have been obtained as single-crystals.

Crystal structures. 1 crystallizes in the orthorhombic space group $P2_12_12_1$ with refined unit-cell parameters *a* = 10.675(1) Å, *b* = 15.073(2) Å, *c* = 25.812(4) Å and *V* = 4153(1) $Å^3$. **2** crystallizes in the monoclinic space group $P2_1/c$ with refined parameters *a* = 9.4281(4) Å, *b* = 11.0220(5) Å, *c* = 21.1494(9) Å, β = 100.053(2) ° and *V* = 2164.0(2) $Å^3$. All atoms fully occupy general Wyckoff positions [*i.e.* 4*a* and 4*e* for **1** and **2**, respectively (Table 2)] excepted face capping positions, randomly occupied by Br (75%) and Se (25%) as discussed below.

Both **1** and **2** are built up from a $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster unit where the face-capping positions of the octahedral cluster are randomly occupied by six bromine and two selenium atoms. The six apical positions are fully occupied by cyanide ligands as depicted in Figure 1. The presence of both bromine and selenium elements could not be distinguished by X-ray diffraction analyses but has been clearly observed and quantified by EDS analyses. Thus, the value of the Br/Se ratio was fixed at 0.75:0.25 during the refinement according to chemical analyses. The average Mo-Mo distances are 2.639(1) and 2.642(1) Å in **1** and **2**, respectively. The Mo-L (L = Br/Se) distances range from 2.572(1) to 2.629(1) Å in **1** and from 2.5590(9) to 2.6148(9) Å in **2**.

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

[{Zn(H$_2$O)(en)$_2$}{Zn(en)$_2$}-Mo$_6$B$_{r6}$Se$_2$(CN)$_6$].2H$_2$O **(1)**						
Atom	Site	x	y	z	Occ.	U(eq)
Mo1	4*a*	0.3872(1)	0.3871(1)	0.3371(1)	1	0.017(1)
Mo2	4*a*	0.5834(1)	0.4596(1)	0.2901(1)	1	0.018(1)
Mo3	4*a*	-0.3696(1)	0.0467(1)	0.2028(1)	1	0.019(1)
Mo4	4*a*	0.5653(1)	0.5979(1)	0.3528(1)	1	0.020(1)
Mo5	4*a*	0.5841(1)	0.4369(1)	0.3918(1)	1	0.019(1)
Mo6	4*a*	0.3705(1)	0.5248(1)	0.3992(1)	1	0.019(1)
Br1	4*a*	0.5997(1)	0.3011(1)	0.3289(1)	0.75	0.023(1)
Se1	4*a*	0.5997(1)	0.3011(1)	0.3289(1)	0.25	0.023(1)
Br2	4*a*	0.3873(1)	0.4084(1)	0.2369(1)	0.75	0.024(1)
Se2	4*a*	0.3873(1)	0.4084(1)	0.2369(1)	0.25	0.024(1)
Br3	4*a*	-0.1788(1)	-0.0237(1)	0.1561(1)	0.75	0.028(1)
Se3	4*a*	-0.1788(1)	-0.0237(1)	0.1561(1)	0.25	0.028(1)
Br4	4*a*	-0.3705(1)	0.1827(1)	0.1417(1)	0.75	0.028(1)
Se4	4*a*	-0.3705(1)	0.1827(1)	0.1417(1)	0.25	0.028(1)
Br5	4*a*	0.5637(1)	0.6197(1)	0.2525(1)	0.75	0.026(1)
Se5	4*a*	0.5637(1)	0.6197(1)	0.2525(1)	0.25	0.026(1)
Br6	4*a*	0.7726(1)	0.5082(1)	0.3450(1)	0.75	0.029(1)
Se6	4*a*	0.7726(1)	0.5082(1)	0.3450(1)	0.25	0.029(1)
Br7	4*a*	0.5652(1)	0.5738(1)	0.4521(1)	0.75	0.028(1)
Se7	4*a*	0.5652(1)	0.5738(1)	0.4521(1)	0.25	0.028(1)
Br8	4*a*	0.3888(1)	0.3655(1)	0.4368(1)	0.75	0.027(1)
Se8	4*a*	0.3888(1)	0.3655(1)	0.4368(1)	0.25	0.027(1)
C1	4*a*	0.2750(9)	0.2676(7)	0.3297(4)	1	0.024(2)
C2	4*a*	0.709(1)	0.4226(8)	0.2236(5)	1	0.032(2)
C3	4*a*	-0.247(1)	0.1093(7)	0.2617(5)	1	0.030(2)
C4	4*a*	0.663(1)	0.7257(7)	0.3644(5)	1	0.030(2)
C5	4*a*	0.710(1)	0.3704(7)	0.4487(5)	1	0.030(2)
C6	4*a*	0.241(1)	0.5568(7)	0.4659(5)	1	0.030(2)
C7	4*a*	0.029(3)	0.110(1)	0.4190(8)	1	0.133(8)
C8	4*a*	-0.026(3)	0.190(1)	0.4244(8)	1	0.33(8)
C9	4*a*	0.017(2)	0.203(1)	0.2016(7)	1	0.083(6)
C10	4*a*	0.048(2)	0.293(1)	0.2215(6)	1	0.072(6)
C11	4*a*	0.033(2)	0.375(1)	0.5774(8)	1	0.105(6)
C12	4*a*	0.090(2)	0.438(1)	0.6111(9)	1	0.105(6)
C13	4*a*	-0.058(2)	0.674(1)	0.4457(7)	1	0.081(6)
C14	4*a*	-0.115(2)	0.7143(9)	0.4965(7)	1	0.067(5)
N1	4*a*	0.205(1)	0.2122(7)	0.3272(4)	1	0.041(3)
N2	4*a*	0.768(1)	0.4105(8)	0.1892(5)	1	0.054(3)
N3	4*a*	-0.1857(9)	0.1395(6)	0.2922(4)	1	0.029(2)
N4	4*a*	0.709(1)	0.7925(7)	0.3723(4)	1	0.041(3)
N5	4*a*	0.775(1)	0.3414(7)	0.4767(5)	1	0.049(3)
N6	4*a*	0.190(1)	0.5697(7)	0.5008(4)	1	0.044(3)
N7	4*a*	0.031(1)	0.0737(7)	0.3643(6)	1	0.058(4)
N8	4*a*	-0.036(1)	0.2527(8)	0.3857(5)	1	0.052(3)
N9	4*a*	-0.017(1)	0.3048(8)	0.2706(4)	1	0.046(3)
N10	4*a*	0.055(1)	0.132 (1)	0.2410(5)	1	0.063(4)
N11	4*a*	0.029(1)	0.4065(8)	0.5199(5)	1	0.058(4)
N12	4*a*	0.037(1)	0.5241(9)	0.6087(4)	1	0.061(4)
N13	4*a*	-0.062(1)	0.5732(8)	0.4518(5)	1	0.055(3)
N14	4*a*	-0.049(1)	0.6816(8)	0.5399(5)	1	0.062(4)
O1	4*a*	-0.2024(9)	0.5036(8)	0.5501(5)	1	0.066(3)
O2	4*a*	-0.3539(9)	0.6308(6)	0.5878(4)	1	0.046(2)
O3	4*a*	0.8818(9)	0.9144(6)	0.4102(4)	1	0.046(2)
Zn1	4*a*	-0.0015(1)	0.1819(1)	0.3142(1)	1	0.028(1)
Zn2	4*a*	-0.0080(1)	0.5452(1)	0.5296(1)	1	0.034(1)

$[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$ **(2)**

Atom	Site	x	y	z	Occ.	U(eq)
Mo1	4*e*	0.4392(1)	0.4421(1)	0.5740(1)	1	0.024(1)
Mo2	4*e*	0.5908(1)	0.3512(1)	0.4916(1)	1	0.024(1)
Mo3	4*e*	0.6685(1)	0.5588(1)	0.5502(1)	1	0.024(1)
Br1	4*e*	0.3638(1)	0.2377(1)	0.5149(1)	0.75	0.036(1)
Se1	4*e*	0.3638(1)	0.2377(1)	0.5149(1)	0.25	0.036(1)
Br2	4*e*	0.8164(1)	0.4676(1)	0.4678(1)	0.75	0.037(1)
Se2	4*e*	0.8164(1)	0.4676(1)	0.4678(1)	0.25	0.037(1)
Br3	4*e*	0.5164(1)	0.6473(1)	0.6308(1)	0.75	0.034(1)
Se3	4*e*	0.5164(1)	0.6473(1)	0.6308(1)	0.25	0.034(1)
Br4	4*e*	0.6925(1)	0.3581(1)	0.6127(1)	0.75	0.039(1)
Se4	4*e*	0.6925(1)	0.3581(1)	0.6127(1)	0.25	0.039(1)
C1	4*e*	0.3658(8)	0.3684(7)	0.6605(4)	1	0.040(2)
C2	4*e*	0.6980(9)	0.1734(7)	0.4839(4)	1	0.040(2)
C3	4*e*	0.8657(7)	0.6238(6)	0.6125(4)	1	0.031(2)
C4	4*e*	0.705(1)	1.008(1)	0.6403(6)	1	0.091(4)
C5	4*e*	0.7338(9)	1.0707(9)	0.6984(6)	1	0.068(3)
C6	4*e*	1.279(1)	0.8858(9)	0.6953(5)	1	0.066(3)
C7	4*e*	1.3213(9)	1.0134(8)	0.5855(4)	1	0.056(2)
N1	4*e*	0.3186(9)	0.3259(7)	0.7019(4)	1	0.063(2)
N2	4*e*	0.7583(8)	0.0831(6)	0.4806(3)	1	0.056(2)
N3	4*e*	0.9638(7)	0.6511(6)	0.6477(3)	1	0.049(2)
N4	4*e*	0.8269(7)	0.9392(7)	0.6262(4)	1	0.077(3)
N5	4*e*	0.8810(7)	1.1233(6)	0.7101(3)	1	0.046(2)
N6	4*e*	1.11413(7)	0.8827(6)	0.6494(4)	1	0.057(2)
N7	4*e*	1.1978(6)	1.0760(6)	0.7267(3)	1	0.042(2)
O1	4*e*	1.0470(8)	1.1485(8)	0.5855(4)	1	0.104(3)
O2	4*e*	0.0225(7)	0.3780(7)	0.7057(4)	1	0.093(3)
Cu1	4*e*	1.0146(1)	1.0182(1)	0.6694(1)	1	0.045(1)

These distances are within the range observed in $Cs_{0.5}K_{0.5}(Et_4N)_{11}[Mo_6Br_6Se_2(CN)_6]_3$ [29] which is built up from the same $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster unit. Relevant selected bond lengths and angles are listed in Table 3.

The structure of **1** can be depicted by the association of one $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster unit with one $[Zn(H_2O)en_2]^{2+}$ and one $[Zn(en)_2]^{2+}$ groups. The $[Zn(H_2O)en_2]^{2+}$ groups and $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units form $[Mo_6Br_6Se_2(CN)^a_5CN\text{-}Zn(H_2O)en_2]^{2-}$ hetero-metallic complexes *via* C6N6-Zn2 bonds as represented in Figure 2. The latter are then interconnected through $[Zn(en)_2]^{2+}$ groups *via* C1N1-Zn1 and C3N3-Zn1 bonds to build infinite polymeric zigzag chains that spread along the *b* axis of the unit cell as depicted in Figure 3. The infinite chains are stacked along the *c* axis according to an ABAB stacking type. In the infrared spectra, two bands at 2109 and 2131cm^{-1} can be assigned to the bridging and terminal CN ligands, respectively.

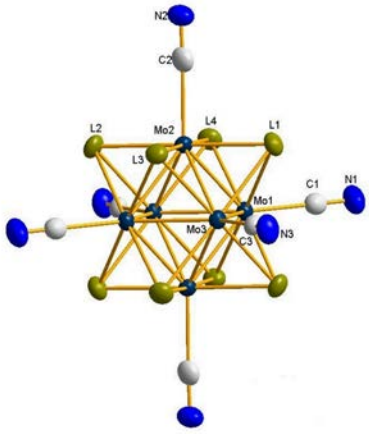


Figure 1. Representation of the $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster unit in **2**. L represents the Br/Se inner ligands. Displacement ellipsoids are shown at the 50 % probability level.

Table 3. Selected bond lengths (Å) and angles (°) for compounds **1**, **2** and $Cs_{0.5}K_{0.5}(Et_4N)_{11}[Mo_6Br_6Se_2(CN)_6]_3$.

1					
Mo1-Mo3$^{\#1}$	2.624(1)	Mo6-L3$^{\#1}$	2.599(1)	Mo1-C1-N1	171(1)
Mo1-Mo5	2.641(1)	Mo6-L4$^{\#1}$	2.612(1)	Mo2-C2-N2	174(1)
Mo1-Mo6	2.628(1)	Mo6-L7	2.595(1)	Mo3-C3-N3	178(1)
Mo2-Mo4	2.646(1)	Mo6-L8	2.597(1)	Mo4-C4-N4	177(1)
Mo2-Mo5	2.647(1)	Mo1-C1	2.17(1)	Mo5-C5-N5	177(1)
Mo3-Mo1$^{\#2}$	2.624(1)	Mo2-C2	2.25(1)	Mo6-C6-N6	177(1)
Mo3-Mo2$^{\#2}$	2.640(1)	Mo3-C3	2.22(1)	C1-N1-Zn1	144(1)
Mo3-Mo4$^{\#2}$	2.650(1)	Mo4-C4	2.21(1)	C3-N3-Zn1	147(1)
Mo4-Mo5	2.636(1)	Mo5-C5	2.23(1)	N1-Zn1-N3	170.8(4)
Mo4-Mo6	2.641(1)	Mo6-C6	2.20(1)	C6-N6-Zn2	140(1)
Mo5-Mo6	2.644(1)	C1-N1	1.13(1)	N6-Zn2-O1	171.5(4)
Mo1-L1	2.622(1)	C2-N2	1.11(2)		
Mo1-L2	2.605(1)	C3-N3	1.12(1)		
Mo1-L3	2.605(1)	C4-N4	1.14(1)		
Mo1-L8	2.594(1)	C5-N5	1.09(1)		
Mo2-L1	2.597(1)	C6-N6	1.12(2)		
Mo2-L2	2.620(1)	Zn1-N1	2.27(1)		
Mo2-L5	2.609(1)	Zn1-N3	2.14(1)		
Mo2-L6	2.572(1)	Zn1-N7	2.11(1)		
Mo3-L2$^{\#2}$	2.608(1)	Zn1-N8	2.16(1)		
Mo3-L3	2.594(1)	Zn1-N9	2.18(1)		
Mo3-L4	2.594(1)	Zn1-N10	2.12(1)		
Mo3-L5$^{\#2}$	2.614(1)	Zn2-N6	2.27(1)		
Mo4-L4$^{\#1}$	2.629(1)	Zn2-N11	2.14(1)		
Mo4-L5	2.609(2)	Zn2-N12	2.12(1)		
Mo4-L6	2.601(1)	Zn2-N13	2.13(1)		
Mo4-L7	2.588(2)	Zn2-N14	2.12(1)		
Mo5-L1	2.618(1)	Zn2-O1	2.23(1)		
Mo5-L6	2.581(1)				
Mo5-L7	2.592(1)				
Mo5-L8	2.617(1)				
2					
Mo1-Mo2	2.6379(8)	Mo1-C1	2.219(9)	Mo1-C1-N1	174.4(7)
Mo1-Mo3	2.6384(8)	Mo2-C2	2.223(8)	Mo2-C2-N2	177.6(7)
Mo1-Mo3$^{\#3}$	2.6471(8)	Mo3-C3	2.202(7)	Mo3-C3-N3	174.7(7)
Mo2-Mo3	2.6445(8)	C1-N1	1.150(9)		
Mo2-Mo3$^{\#3}$	2.6440(8)	C2-N2	1.155(9)		
Mo1-L1	2.6135(9)	C3-N3	1.123(9)		
Mo1-L2$^{\#3}$	2.6148(9)	Cu1-N4	2.039(7)		
Mo1-L3	2.6044(9)	Cu1-N5	2.012(6)		
Mo1-L4	2.5590(9)	Cu1-N6	2.003(7)		
Mo2-L1	2.5990(9)	Cu1-N7	2.031(6)		
Mo2-L2	2.6069(9)	Cu1-O1	2.343(7)		
Mo2-L3$^{\#3}$	2.6102(9)				
Mo2-L4	2.575(1)				
Mo3-L1$^{\#3}$	2.6224(9)				
Mo3-L2	2.6157(9)				
Mo3-L3	2.6018(9)				
Mo3-L4	2.5664(9)				
$Cs_{0.5}K_{0.5}(Et_4N)_{11}[Mo_6Br_6Se_2(CN)_6]_3$					
Mo1-Mo2	2.6532(8)	Mo2-C2	2.22(1)		
Mo2-Mo2	2.647(1)	C1-N1	1.11(2)		
Mo1-L1	2.6006(6)	C2-N2	1.12(1)		
Mo2-L1	2.6042(5)	Mo1-C1-N1	180.		
Mo1-C1	2.23(1)	Mo2-C2-N2	180.0(8)		

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

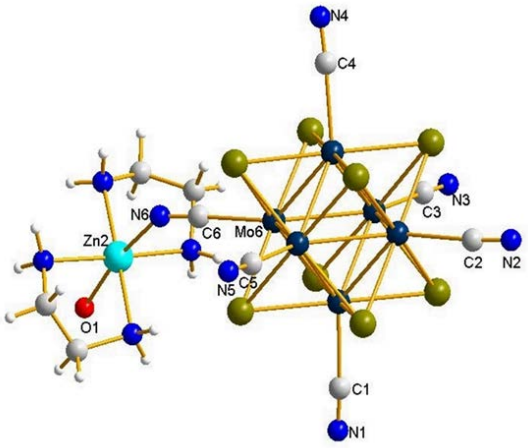


Figure 2. Representation of $[Mo_6Br_6Se_2(CN)^a{}_5CN\text{-}Zn(H_2O)en_2]^{2-}$ hetero-metallic complex in **1**.

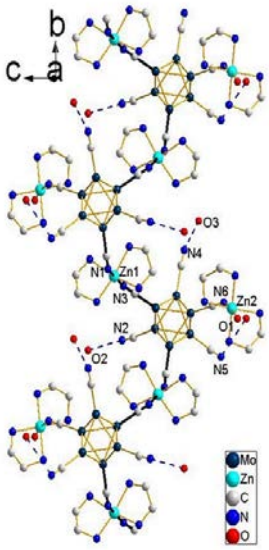


Figure 3. Representation of a one-dimensional polymeric chain in **1**. Dashed lines represent hydrogen bonds between free cyanides ligands and water molecules. The inner ligands and the H atoms on the ethylenediamine groups have been omitted for clarity.

Terminal cyanides ligands (*i.e*. C2N2, C4N4 and C5N5) are involved in weak interactions with (i) crystallization water molecules, (ii) water molecule of the $[Zn(H_2O)en_2]^{2+}$ groups and (iii) nitrogen atoms of an ethylenediamine group (N2-O2*cw* 2.8352(4); N4-O3*cw* 2.7943(2); N4-N12 3.36(2); N5-O1*w* 3.0912(3); N5-N11 3.09(2) Å). Beyond these interactions, the inter chains structural cohesion is also ensured by other hydrogen bonds between nitrogen atom of the ethylenediamine groups and crystallization water molecule (N7-O3*cw* 3.12(2); O3*cw*-N6 3.0922(3) Å), between nitrogen atoms of the ethylenediamine groups and inner ligands (N13-L6 3.42(1); N14-L4 3.50(1) Å), between crystallization water molecule and the water molecule of the $[Zn(H_2O)en_2]^{2+}$ groups (O1-O2cw 2.7092(2) Å) and between crystallization water molecules (O2*cw*-O3*cw* 2.9091(4) Å). The intra chain structural cohesion is ensured by coordination bonds between the $[Mo_6Br^i{}_6Se^i{}_2(CN)^a{}_6]^{4-}$ cluster unit and $Zn(en)_2$ groups. All the hydrogen bonds are listed in Table 4.

The structure of **1** is very similar to that of $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}\text{-}Re_6Te_8(CN)_6].3H_2O$ (**a**) [22-23] and to that of $[\{Mn(H_2O)(en)_2\}\{Mn(en)_2\}\text{-}Re_6Te_8(CN)_6].3H_2O$ (**b**) [40] which both crystallize in the monoclinic system, space group $P2_1/n$ with refined parameters a = 10.7689(6) Å, b = 16.5594(9) Å, c = 24.3631(14) Å, β = 92.070(1) °, V = 4341.8(4) Å^3 and a = 10.7940(1) Å, b = 16.8011(3) Å, c = 24.6467(5) Å, β = 92.055(1) °, V = 4466.8(1) Å^3 for **a** and **b**, respectively. The loss of symmetry from orthorhombic to monoclinic system is probably only due to the additional crystallization water molecule in the lattice because the size of both $[Mo_6Br^i{}_6Se^i{}_2(CN)^a{}_6]^{4-}$ and $[Re_6Te^i{}_8(CN)^a{}_6]^{4-}$ cluster units are close (approximatively 10.40 and 10.35 Å in diameter, respectively, according to a spherical shape model). In the $[M_6X^i{}_8(CN)^a{}_5CN\text{-}Zn(H_2O)en_2]^{2-}$ hetero-metallic complexes (M = Mo, Re ; X = Br, Se, Te), the Zn-N-(-C-M) distance in **1** is shorter than that in **a** [2.27(1) versus 2.339(6) Å] while it is equivalent to the Mn-N(-C-Re) [2.23(1) versus 2.26(2) Å] distance in **b**. The same trend is found for M^{2+}-OH_2 distances [2.23(1), 2.134(6) and 2.20(1) Å for **1**, **a** and **b**, respectively]. The average M^{2+}-N(-C-M) distances involved in $M^{2+}(en)_2$ bridges are 2.21(1), 2.216(6) and 2.24(1) Å in **1**, **a** and **b**, respectively. Consequently, the reason why the b parameter in **1** is significantly shorter than in **a** can only be explained by the difference between the Zn-N-C angles. Indeed, in **1**, the Zn-N-C angles are 144(1) and 147(1)° while they are 146.1(5) and 151.1(5)° in **a** which leads to an increase of the b parameter in **a**. If the c parameter is bigger in **1** than in **a** and **b**, is probably due to the additional crystallization water molecule which leads to stronger hydrogen bonds between the chains in both compounds **a** and **b**.

In **2**, Cu^{2+} is fully coordinated by two ethylenediamines groups and one H_2O molecule in a square-pyramidal coordination mode as depicted in Figure 4.

Table 4. List of hydrogen bonds (Å) in compounds **1** and **2**.

$[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}\text{-}Mo_6B_{r6}Se_2(CN)_6].2H_2O$ **(1)** (D-H---A) (Å)					
N2-H---O2cw	2.8352(4)	N5-H---N11	3.09(2)	N13-H---L6	3.42(1)
N4-H---O3cw	2.7943(2)	N7-H---O3cw	3.12(2)	N14-H---L4	3.50(1)
N4-H---N12	3.36(2)	O3cw-H---N12	3.83(2)	O2cw-H---O3	2.9091(4)
N5-H---O1	3.0912(3)	N9-H---L3	3.83(1)		
$[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$ **(2)** (D-H---A) (Å)					
N2-H---N6	3.0825(1)	N6-H---N3	3.0489(1)	O2-H---N1	2.8655(1)
N3-H---N5	3.1207(1)	N2-H---O1	3.2781(1)	O2-H---N5	3.1164(1)
N1-H---N7	3.0601(1)				

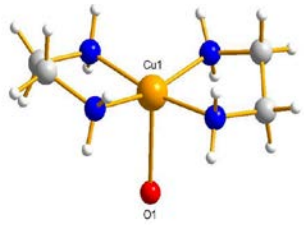


Figure 4. Representation of the Cu1 environment in **2**. Cu^{2+} is coordinated by two ethylenediamine groups and one H_2O molecule in a square-pyramidal coordination mode.

Square-pyramidal arrangement is common for Cu^{2+} and it is also found in other coordination polymers based on Re_6 cyanide clusters [41-42]. In **2**, the $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units are located on the vertices of the unit cell and in the middle of the faces defined by *b* and *c* parameters. The structure can be depicted as a AAA stacking type of hexagonal compact layers of $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units. Such a stacking generates prismatic sites in which the $[Cu(H_2O)(en)_2]^{2+}$ complexes cations are located (Figure 5a). It forms layers of cations intercalated between the cluster units layers (Figure 5b).

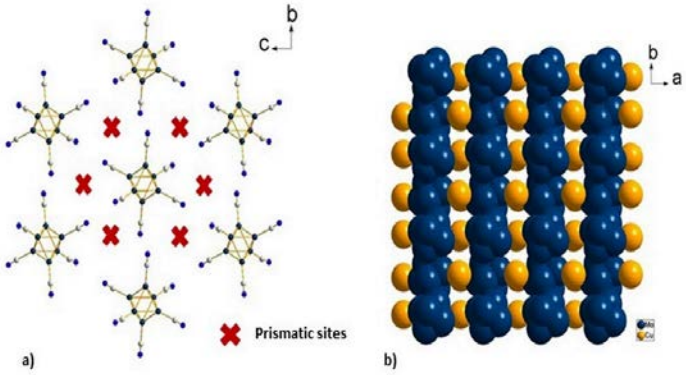


Figure 5. a) Projection in the (*b*, *c*) plane of the pseudo hexagonal compact arrangement of the $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units in **2**. The red cross represent the prismatic sites which are generated by the AAA stacking type of units. Inner ligands, $[Cu(H_2O)(en)_2]^{2+}$ complexes cations and crystallization water molecules have been omitted for clarity. b) Space filling model of the projection of the AAA stacking type of the $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units layers in the (*a*, *b*) plane evidencing the alternating of $[Cu(H_2O)(en)_2]^{2+}$ complexes cations layers and $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units layers. Only Mo_6 octahedral clusters and Cu^{2+} cations are represented for the sake of clarity.

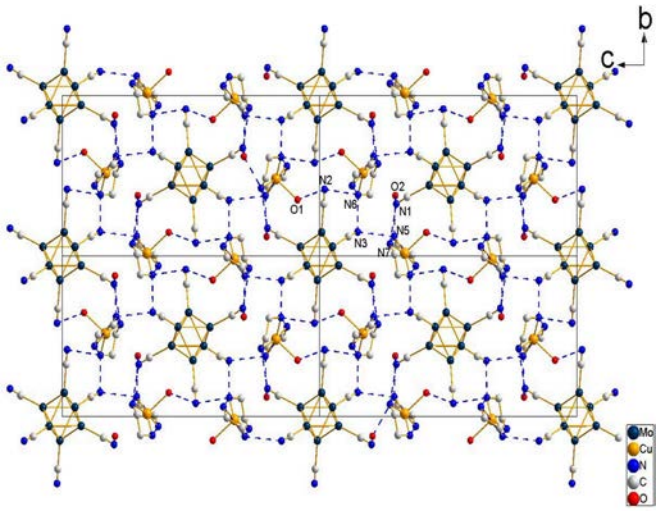


Figure 6. Projection in the (b, c) plane of a cluster units layer and the hydrogen bonds network between $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units, $[Cu(H_2O)(en)_2]^{2+}$ complexes cations and crystallization water molecules in **2**. H atoms of the ethylenediamine groups and inner ligands have been omitted for clarity.

In the infrared spectra, the single band at 2104 cm^{-1} indicates that all the CN ligands are free. Hence, the cations interact with $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units *via* hydrogen bonds between cyanides ligands and nitrogen atoms of ethylenediamine groups (N2-N6 3.0825(1); N3-N5 3.1207(1); N6-N3 3.0489(1); N1-N7 3.0601(1) Å) and between cyanides ligands and the water molecule of the $[Cu(H_2O)(en)_2]^{2+}$ complexes (N2-O1 3.2781(1) Å). Crystallization water molecules also strongly participate to the structural cohesion *via* hydrogen bonds with cyanides ligands (O2*cw*-N1 2.8655(1) Å) and with nitrogen atoms of ethylenediamine groups (O2*cw*-N5 3.1164(1) Å). These hydrogen bond distances are similar than those in $[Cu(En)_2(H_2O)_2][\{Cu(En)_2\}Re_6S_8(CN)_4(OH)_2].5.5H_2O$ and $[Cu(En)_2(H_2O)_2[\{Cu(En)_2\}Re_6Se_8(CN)_4(OH)_2].5H_2O$ [11b]. This hydrogen bonds (Table 4) network between $[Mo_6Br^i_6Se^i_2(CN)^a_6]^{4-}$ cluster units, $[Cu(H_2O)(en)_2]^{2+}$ complexes cations and crystallization water molecules (Figure 6) connects the cluster units layers together leading to a three-dimensional supramolecular framework as depicted in Figure 7.

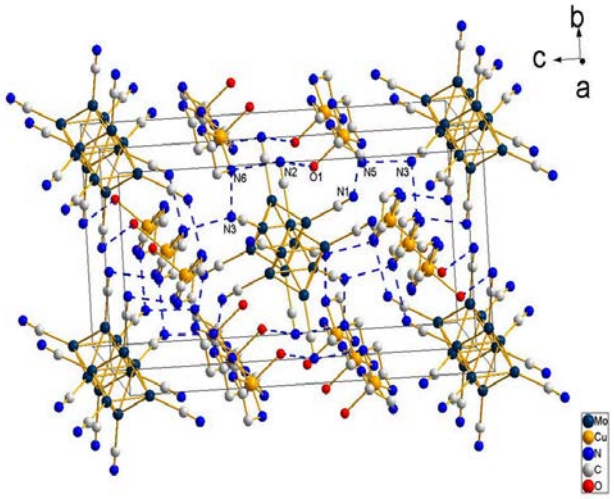


Figure 7. Representation of the hydrogen bonds allowing the connection between the cluster units layers and leading to a three-dimensional supramolecular framework. Inner ligands, hydrogen atoms and crystallization water molecules have been omitted for clarity.

The structure of **2** is strongly related to that of $[Ni(NH_3)_4(en)]_2[Re_6Te_8(CN)_6].2H_2O$ [22-23] which crystallizes in the monoclinic space group $P2_1/n$ with refined parameters a = 10.3607(7) Å, b = 10.6377(7) Å, c = 21.2875(14) Å, β = 97.170(1) ° and V = 2327.8(3) $Å^3$. In this compound, Ni^{2+} is fully coordinated by four ammonia molecules and one ethylenediamine group in an octahedral conformation type while in **2**, Cu^{2+} is fully coordinated by two ethylenediamine groups and one water molecule in a square-pyramidal conformation type. Square-pyramidal coordination type for Cu^{2+} is also found in $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6].5H_2O$ [42]. However, in the latter, a CN group of the cluster completes the coordination sphere of the Cu instead of a water molecule in **2**, leading to a neutral complex $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]$. In both compounds, the Cu-N(en) distances are close and range from 2.003(7) to 2.039(7) Å, in **2**, and from 2.011(6) to 2.037(4) Å, in $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6].5H_2O$.

CONCLUSION

Two new compounds $[\{Zn(H_2O)(en)_2\}\{Zn(en)_2\}$-$Mo_6B_{r6}Se_2(CN)_6].2H_2O$ **(1)** and $[\{Cu(H_2O)(en)_2\}_2Mo_6Br_6Se_2(CN)_6].2H_2O$ **(2)** (en = ethylenediamine) have been obtained by the reaction of $Cs_2K_2[Mo_6Br_6Se_2(CN)_6]$ with $Zn[OOCCH_3]_2.2H_2O$ and ethylenediamine, and with $CuCl_2.xH_2O$ and ethylenediamine for **1** and **2**, respectively. For the synthesis of **2,** ammonia has been used as solvant to organize a competition between ammonia and ethylenediamine as chelating ligands in order to slow down the reaction and induce crystallization. Both structures have been structurally characterized by single-crystal X-ray diffraction. **1** is a bimetallic one dimensional coordination compound while **2** is a bimetallic H bonded three dimensional compound. Structural cohesion of both compounds is mainly ensured by hydrogen bonds. The use of ethylenediamine as ligand permits hydrogen bonds especially between cyanides ligands and nitrogen atoms of ethylenediamine groups in both compounds which participate to the stability of the structures. Further work will consist in obtaining microcrystalline powder of both compounds to make characterizations as TGA and thermal dependent X-ray powder diffraction in order to study the thermal stability of the compounds and possible structural modifications.

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SUPPLEMENTARY MATERIAL

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein- Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD- 432616 and CSD-432617.

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