

CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Novel 'Anti-Prussian Blue' Structure Based on Zn^{2+} Nodes and $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ Heterometallic Cluster Spacers and its Rearrangement to Prussian Blue

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Alexander V. Virovets^{*a,b}, Yakov M. Gayfulin^a, Eugenia V. Peresyphkina^{a,b}, Yuri V. Mironov^{a,b}, Nikolay G. Naumov^{a,b}

The reaction between ZnCl_2 and aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ is controlled by the concentration of NH_3 . High concentration of NH_3 favors the formation of $[\text{Zn}(\text{NH}_3)_4]_8\{\text{Zn}[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]_3\} \cdot 9\text{H}_2\text{O}$ with an ideal primitive cubic 3D network of Zn^{2+} cations joint by cyanocluster anions as unprecedented bulky linear spacers. The low concentration of NH_3 leads to the formation of usual Prussian blue structure $[\text{Zn}(\text{NH}_3)_4]_2[\text{ZnRe}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ with alternating octahedral Zn^{2+} and cyanocluster nodes. Both compounds contain paramagnetic cluster anion with $g=2.279$ and 2.280 , respectively. Powder diffraction studies prove that the former compound transforms into the latter after an exposure of polycrystalline sample in air.

Introduction

The chemistry of coordination polymers has been intensively developing during last years¹ due to their potential usage as molecular sieves and gas storage containers.² Owing to their stability and rigid geometry, mono- and polynuclear cyanocomplexes of transition metals are suitable to serve as the secondary building units (SBU) for obtaining 2D and 3D frameworks *via* coordination of *d*- or *f*-metal cations to the nitrogen atoms of CN-groups.³ Therefore the transition metal cyanometallates in general can be regarded as coordination polymers, where central atoms of cyanocomplexes (*nodes*) are connected to almost linear cyano *spacers*. Presumably the very first coordination polymer discovered in the beginning of 18th century was inorganic pigment, so-called Prussian blue (Prussian-blue, PB) known in two forms, soluble $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ and insoluble $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$.⁴ It gave the name to an entire class consisting now of hundreds compounds. The PB-type compounds can be used as cathode materials,⁵ electrochemical receptors and sensors,⁶ magnetic materials,⁷ antidotes for Cs and Tl in medicine.⁸ The 3D coordination network in PB-type compounds can be treated as a combination of the octahedral $\text{M}^{2+}/\text{M}^{3+}$ nodes

connected by the CN spacers into an ideal or a distorted primitive cubic network. According to the topological approach⁹ that during last years was successfully applied to the coordination polymers, the primitive cubic network corresponds to so-called **pcu** topological type.¹⁰ Therefore, in general all cyanometallates with **pcu** net could be regarded as PB analogues.

The expansion of PB-type structure (and, generally, the **pcu** net) was expected to give larger cavities that would allow incorporation of guest molecules. In fact, the expansion of any framework is possible by modification of a node and/or a spacer. Since 1998 the octahedral high-valence cluster complexes with terminal cyanogroups (cyanoclusters) were found to be able to form 2D and 3D coordination polymers similarly to mononuclear cyanocomplexes.¹¹ The first series of PB-type cyanocluster-based compounds of general formula $\text{M}_4[\text{Re}_6\text{X}_8(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Ga}^{3+}, \text{Fe}^{3+}$; $\text{X} = \text{Se}, \text{Te}$) was obtained in 2001.¹² The authors replaced relatively small $[\text{Fe}(\text{CN})_6]^{4-}$ node with the larger $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$ one (N...N separation of ~ 6.2 vs ~ 10.2 Å) and keeping the **pcu** net topology unchanged succeeded in a '*direct expansion of Prussian blue*'. Further modification of an anionic node is

possible when cyanocluster complexes $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$ or $[\text{Nb}_6\text{Cl}_9\text{O}_3(\text{CN})_6]^{5-}$ are used that are even larger because of longer metal-metal distances.¹³ The other way is to replace the mononuclear cationic node by the polynuclear one, e.g., by the binuclear $[\text{Co}_2(\mu\text{-H}_2\text{O})_4]^{4+}$ or $[\text{Zr}_6\text{BCl}_{12}]^{2+}$.¹⁴ To elongate the spacers one can connect two terminal nitrogen atoms of the neighboring cyanoclusters e.g. with $[\text{M}(\text{H}_2\text{O})_4]^{2+}$ or $[\text{ML}]^{2+}$ square planar complex cations (L = chelate ligand) to give NC-M(H₂O)₄-CN or NC-M(L)-CN spacers instead of much shorter CN group. Using this concept the **pcu** net was obtained porous enough to allow double interpenetration of the $[\{\text{M}(\text{H}_2\text{O})_4\}_3\text{W}_6\text{S}_8(\text{CN})_6]$ networks (M = Mn, Fe, Co)¹⁵. A ‘superexpanded Prussian-blue analogue’¹⁶ was reported for $(\text{H}_3\text{O})_2[\text{Fe}(\text{CN})_6(\text{Mn}(\text{salen}))_6\text{Nb}_6\text{Cl}_{12}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (*salen* = 2,2’-(ethane-1,2-diylbis(azanylylidenemethanylylidene))diphenolate), the first mixed cyanocluster and mononuclear cyanocomplex network spaced by bulky NC-Mn(*salen*)-CN units. The resulting nets yet belongs to the **pcu** type, but consists of only anionic nodes, while in the ‘classical PB’ type the cationic and anionic nodes alternate like counter ions in NaCl structure. Despite this fact, authors¹⁶ attribute the structure to PB-type.

Here we demonstrate another possibility to construct expanded PB-type network. We synthesized two novel 3D cyanometallates based on recently discovered paramagnetic cluster $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ anion¹⁷ and Zn^{2+} cations, $[\text{Zn}(\text{NH}_3)_4]_8\{\text{Zn}[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]_3\} \cdot 8\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{NH}_3)_4]_2[\text{ZnRe}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (**2**) and observed irreversible transformation of **1** into **2**. Structure of **2** can be attributed to classical PB-type, while in the **pcu** net of **1** octahedrally coordinated *cationic* nodes are linked by linear *anionic* cluster spacers. Compared to ‘superexpanded Prussian-blue analogue’, the cations and the anions in **1** as well as their topological roles of node and spacer are permuted that allows us to call this structure type *anti-Prussian blue*.

Experimental

Materials and spectroscopic studies

The starting cluster salt $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ was prepared as described¹⁷. Other reagents were purchased from commercial sources and used without further purification.

IR spectra in KBr pellets were recorded on a Bruker Scimitar FTS 2000 spectrometer in the range 4000-375 cm^{-1} . Elemental analysis was made on a Euro EA3000 analyzer. Energy dispersion spectroscopy (EDS) was performed on an electron microscope Hitachi TM-3000 equipped by Bruker Nano EDS analyzer. EPR spectra of powdered samples were recorded on Varian E-109 EPR spectrometer in X-band at 300 K. Diphenylpicryl-hydrozil (DPPH) was used as standard of g-value with $g = 2.0036$. Simulation of EPR spectra was made by Bruker Simfoniya program. Powder X-Ray diffraction patterns of the synthesized compounds were recorded using Philips PW1820/1710 diffractometer (Cu K α radiation, graphite monochromator, silicon plate used as an external standard).

Obtaining of single crystals of

$[\text{Zn}(\text{NH}_3)_4]_8\{\text{Zn}[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]_3\} \cdot 9\text{H}_2\text{O}$ (**1**)

Solution of ZnCl_2 (10 mg, 0.075 mmol) in 2 ml of concentrated aqueous ammonia (25%) was layered on 2 ml of aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ (10 mg, 0.006 mmol) in a thin glass tube. The tube was tightly closed. Cubic brown crystals have grown at the wall of the tube. Yield: 8 mg (80%). EDS: Zn:Re:Mo:S = 3,0:3,0:2,9:8,2. IR (cm^{-1} , Fig.S1 in ESI): $\nu(\text{OH})$, $\nu_{\text{a,s}}(\text{NH}_3)$ 3200–3500 (broad band); $\nu(\text{CN})$ 2100; $\delta(\text{HOH})$ 1643; $\delta_s(\text{HNNH})$ 1263, 1115; $\rho_t(\text{NH}_3)$ 714 (broad band); $\nu(\text{MS})$ 418.

Synthesis of **1**, microcrystalline powder samples

Solution of ZnCl_2 (50 mg, 0.373 mmol) in concentrated ammonia was mixed with aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ (50 mg, 0.031 mmol). The resulting brown precipitate was centrifuged and left in a mother solution to protect it from decay. The phase was identified by X-ray powder diffraction. Yield: 45 mg (90%).

Obtaining of single crystals of

$[\text{Zn}(\text{NH}_3)_4]_2[\text{ZnRe}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (**2**)

Solution of ZnCl_2 (10 mg, 0.075 mmol) in 2 ml of diluted ammonia was layered on 2 ml of aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ (10 mg, 0.006 mmol) in a glass tube. The tube with the mother solution was left unsealed in air. A few cubic brown crystals of **2** grow together with microcrystalline powder. Yield of the bulk product: 9 mg (95%). EDS: Zn:Re:Mo:S = 3,1:3,0:2,9:8,1. IR (cm^{-1} , Fig.S1 in ESI): $\nu(\text{OH})$ 3572; $\nu_{\text{a}}(\text{NH}_3)$ 3331; $\nu_{\text{s}}(\text{NH}_3)$ 3254, 3198; $\nu(\text{CN})$ 2112; $\delta(\text{HOH})$ 1604; $\delta_s(\text{HNNH})$ 1236; $\rho_t(\text{NH}_3)$ 637; $\nu(\text{MS})$ 422.

Synthesis of **2**, microcrystalline powder samples

The wet brown microcrystalline powder of compound **1** was taken from the mother solution and kept in air for about 20 minutes. After drying the brown powder of compound **2** was formed. The phase was identified by X-ray powder diffraction.

Single crystal diffraction studies

Diffraction data for **1** and **2** were obtained by the standard technique using Bruker Apex2 Duo diffractometer equipped with CCD detector using MoK α radiation (graphite monochromator). Crystallographic data and details of the diffraction experiments are given in Table 1. Absorption corrections were applied empirically using SADABS program.¹⁸ Both structures were solved by direct methods and refined with the full-matrix least-squares method on F^2 with SHELXTL programs set.¹⁹ Hydrogen atoms of coordinated NH_3 molecules were refined in riding-on-pivot-atom model. Due to the high symmetry all metal positions in the cluster cores were approximated as 50%Mo+50%Re with the use of corresponding EXYZ and EADP instructions.

Table 1. Crystallographic data and details of diffraction experiments for $[\text{Zn}(\text{NH}_3)_4]_8\{\text{Zn}[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]_3\} \cdot 9\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{NH}_3)_4]_2[\text{ZnRe}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (**2**).

	1	2
Deposition no.	ICSD- 428694	ICSD- 428695
Chemical formula	$\text{C}_{18}\text{H}_{114}\text{Mo}_9\text{N}_{50}\text{O}_9\text{Re}_9\text{S}_{24}\text{Zn}_9$	$\text{C}_6\text{H}_{28}\text{Mo}_3\text{N}_{14}\text{O}_2\text{Re}_3\text{S}_8\text{Zn}_3$
Molecular weight	5072.62	1627.43
Space group	$Pm\bar{3}m$	$Fm\bar{3}m$
$a/\text{\AA}$	14.9831(3)	14.774(2)
Cell volume / \AA^3	3363.61(12)	3224.5(9)
Z	1	4
T / K	150	150
$D_x / \text{g cm}^{-3}$	2.504	3.352
$\mu (\text{MoK}\alpha) / \text{mm}^{-1}$	10.850	15.080
$T_{\text{min}}, T_{\text{max}}$	0.228 – 0.266	0.589 – 0.746
Crystal size / mm	$0.12 \times 0.11 \times 0.07$	$0.08 \times 0.08 \times 0.08$
Habitus	truncated cube	prism
2θ range / deg.	1.92 – 30.50	2.39 – 30.76
Index range	$-3 \leq h \leq 21$	$-20 \leq h \leq 19$
	$-17 \leq k \leq 12$	$-20 \leq k \leq 21$
	$-10 \leq l \leq 19$	$-19 \leq l \leq 20$
Total reflections	6480	8428
Unique reflections	1090	300
R_{int}	0.0483	0.0555
Observed reflections	855	250
No. of parameters	47	23
$R_1 (F_o > 4\sigma(F_o))$	0.0380	0.0433
wR_2 (all)	0.1217	0.1079
GooF (all)	1.123	1.178
$\Delta\rho$ min/max, $e^{-\text{\AA}^{-3}}$	-7.980 / 2.629	-3.959 / 4.090

Relatively poor quality of crystal of **2** resulted in some chemically meaningless residual density peaks in proximity of heavy atoms. Partial occupancy of solvent water molecule was revealed after refinement of the displacement parameter (a.d.p.) for corresponding oxygen atom. Its occupancy factor of 0.33 was assigned to give a reasonable value of isotropic a.d.p. Our attempts to localize the hydrogen atoms of all solvent water molecules failed.

The CIF files containing all details of structure determination and full tables of geometrical parameters have been deposited in the Crystal Structure Depot at FIZ Karlsruhe, under the deposition codes given in Table 1, and can be obtained free of charge from http://www.fiz-karlsruhe.de/obtaining_crystal_structure_data.html.

Powder diffraction study of transformation of **1** to **2**.

The microcrystalline powder of compound **1** was centrifuged and placed on the silica cuvette with small amount of mother solution. Due to high instability of **1** towards aeration the cuvette was quickly cooled down by the liquid nitrogen and mounted on the powder X-ray diffractometer. A series of powder patterns were recorded one after another in 2θ range of 16 to 18°. Every measurement took about 400 sec.

Results and discussion

Reaction between solution of ZnCl_2 in concentrated ammonia and aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ resulted in the compound $[\text{Zn}(\text{NH}_3)_4]_8\{\text{Zn}[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]_3\} \cdot 9\text{H}_2\text{O}$ (**1**).

Crystals suitable for single-crystal X-ray structural analysis can be obtained by slow diffusion of starting solutions in the sealed glass tube, while the microcrystalline powder readily precipitates after direct mixing of solutions.

The cyanocluster anion $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ in **1** has a structure typical for $[\text{M}_6(\mu_3\text{-X})_8(\text{CN})_6]^{q-}$ clusters. High site symmetry of the cluster anions (D_{4h}) resulted in the slightly distorted Re_3Mo_3 octahedral core where Re and Mo atoms are statistically distributed over the metal sites. All M-M distances are almost equal (Table 2, Table S1 in ESI). Metal core is surrounded by a cube of eight capping sulfur atoms. Each metal atom coordinates one CN group *via* carbon atom to give nearly linear Zn-NC-M fragment (Fig. 1).

Table 2. Main bond distances (\AA) in **1** and **2** compared to $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ (*).

Bond	1	2	*
M-M	2.6230(8), 2.6248(10)	2.6374(17)	2.6273(8)
M-S	2.427(3), 2.439(2)	2.426(4)	2.439(2)
M-C	2.145(14), 2.17(3)	2.23(3)	2.173(13)
Zn- N_{CN}	2.35(3)	2.194(19)	-
Zn- N_{NH_3}	1.994(10), 2.04(2)	2.16(3)	-

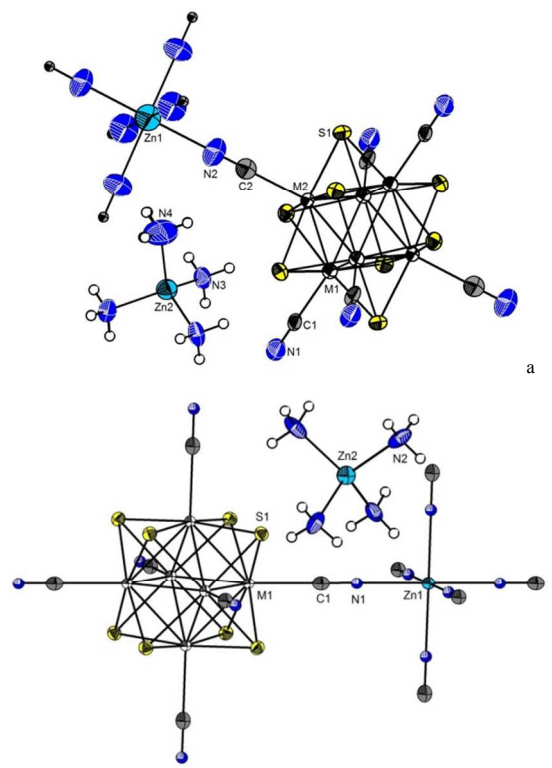


Figure 1. Structure of cations and anions in **1** (a) and **2** (b), a.d.p. ellipsoids at 50% probability level. Positions of M1 and M2 correspond to 50%Re+50%Mo.

There are two types of Zn^{2+} cations in the structure of **1**. One of them coordinates six nitrogen atoms of CN groups forming an ideal octahedron, while the other belongs to the extra-framework tetrahedral $[\text{Zn}(\text{NH}_3)_4]^{2+}$ cations (Fig. 1a). The cyanocluster anion, in turn, uses only two terminal nitrogen atoms in *trans* positions to connect neighbouring Zn^{2+} cations. Therefore the ideal **pcu** net in **1** is realized with the

cyanocluster anions playing role of linear bulky *spacers* joining the cationic nodes (Fig. 2a). In contrast to the previously described ‘*superextended Prussian blue*’,¹⁶ where *anionic* nodes are connected via *cationic* spacers, we can call the structure of **1** *anti-Prussian blue*.

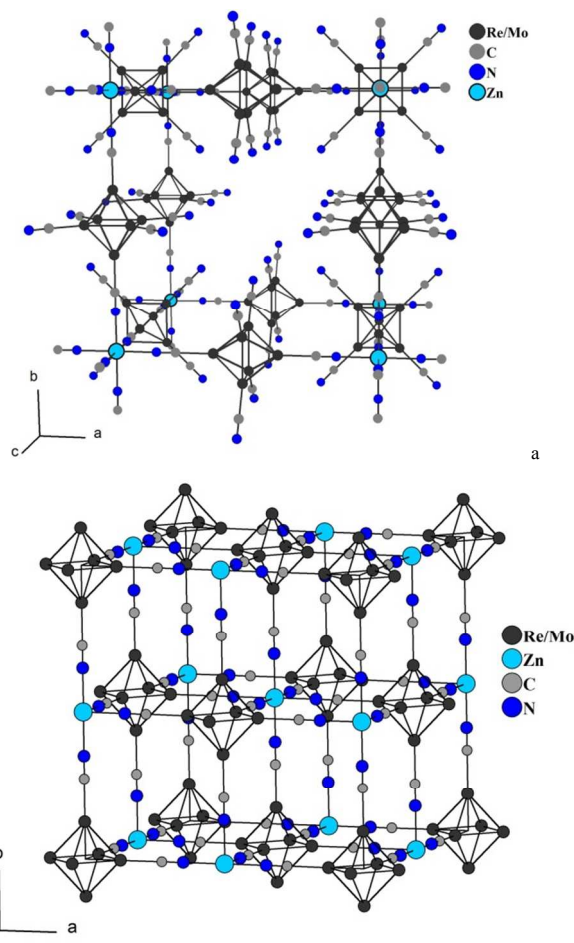


Figure 2. Crystal packing in **1** (a) and **2** (b). Sulfur atoms of cluster anions, extra-framework cations and solvent water molecules are omitted for clarity.

In the overwhelming majority of known 2D and 3D coordination polymers based on the cyanoclusters, the cluster anions play a role of the nodes. The rare exceptions, when they play a role of spacers, like in **1**, are $[\text{Cu}_2(\textit{threo-tab})_3(\text{NH}_3)][\text{Re}_6\text{Te}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, $[\text{Cu}_2(\textit{threo-tab})_3(\text{NH}_3)][\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (*threo-tab* = 1,2,3,4-tetraaminobutane) and $\text{K}[\text{Nd}(\mu\text{-C}_4\text{H}_{10}\text{O}_4)(\text{H}_2\text{O})_4\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ ($\text{C}_4\text{H}_{10}\text{O}_4$ = butan-1,2,3,4-tetraol),²⁰ where the hexanuclear cyanocluster anion uses only two *trans*-CN groups to coordinate Cu^{2+} cations. A combination of the cyanocluster spacer with *threo-tab* or butan-1,2,3,4-tetraol spacers links the Cu^{2+} nodes in a distorted square planar (**sql**) 2D net. In the structure of $[(\text{Cu}_2(\text{NH}_3)(\textit{threo-tab})_2)_2\{\text{Re}_4\text{Te}_4(\text{CN})_{12}\}_2] \cdot 8\text{H}_2\text{O}$ ^{20b} the **sql** net is formed in a similar way by a combination of *threo-tab* and tetranuclear cyanocluster spacers. The hexanuclear cyanocluster anion plays a role of a *non-linear* spacer coordinating the Cu^{2+} cations by

two *cis*-CN groups in $[\text{Cu}(\textit{threo-tab})(\text{H}_2\text{O})_2][\text{Re}_6\text{Te}_8(\text{CN})_6] \cdot 12.5\text{H}_2\text{O}$ ^{20a} giving rise to 2D **hcb** net. All these structures feature by additional organic spacers besides the cyanoclusters. Thus, the structure of **1** is evidently the first 3D coordination polymer based on only cyanocluster spacers in the family of CN-bridged coordination polymers based on metal chalcogenide clusters.

The powder diffraction pattern for microcrystalline sample of **1** surprisingly gave the pattern that did not agree with **1**. Our attempts to reproduce **1** by slow diffusion in the unsealed glass tube resulted in the polycrystalline powder together with a few single crystals of rather poor quality. Single crystal X-ray structural analysis revealed the compound $[\text{Zn}(\text{NH}_3)_4][\text{ZnRe}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (**2**). The polycrystalline powder was also identified as **2** according to powder diffraction pattern.

The structure of **2** belongs to the ‘classical’ Prussian blue type with the cluster anions and Zn^{2+} cations alternating like in NaCl structure (Fig. 2b). Both anionic and cationic positions in the resulting **pcu** net are fully occupied in contrast to a wide class of defect PB structures as, for example, insoluble Prussian blue, $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$. It becomes possible due to the presence of extra-framework $[\text{Zn}(\text{NH}_3)_4]^{2+}$ cations that, together with water molecules, fill the cavities (Fig. 1b). The metal-metal bond distances in highly symmetrical (O_h) cluster anion are close to those found in **1** (Table 2, Table S1 in the SI).

Surprisingly, the theoretical powder diffraction pattern of **2** coincided with those earlier registered for polycrystalline sample of **1**. This fact showed that **1** irreversibly transforms into **2** when the freshly prepared powder sample of **1** is exposed in air, whereas the compound **2** is stable in air at room temperature. One can assume that the presence of oxygen in the unsealed tube can drive the oxidation of the cluster core. The EPR spectra for both **1** and **2** (Fig. S2 in SI) do not confirm this hypothesis being in a good agreement with the paramagnetic cluster core, and the presence of 23 cluster valence electrons. The calculated values of g factor for **1** and **2** (2.279 and 2.280, respectively) are similar to those found for $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ (2.279).

The facts that **1** transforms into **2** and these compounds both have in total Zn:cluster ratio 3:1, similar Bravais cell parameters and the same **pcu** topology of 3D network, drawn us to the conclusion that they might be structurally interrelated. Nevertheless the frameworks in **1** and **2** differ both in Zn:cluster ratio (1:3 and 1:1) and in charge (-16 and -4 per formula unit). The distance between nodes in **1** is almost twice longer (equal to $a = 14.98 \text{ \AA}$) than in **2** (equal to $a/2 = 7.39 \text{ \AA}$, Table 1). In other words, **1** possesses more porous **pcu** net adopting fourfold amount of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ counteractions relative to **2**. The total content of NH_3 in **2** is less than in **1**, 8 vs 10.67 molecules per cluster anion. Consequently, the loss of NH_3 can be the driving force for the transformation **1**→**2** that is accordingly irreversible. However, it seems possible to stabilize the anti-Prussian blue structure by using stable voluminous cations.

A closer look at the structure **1** shows that it can hardly be re-arranged to **2**, for example, by the migration and further coordination of Zn^{2+} cations to the cluster anions. We can therefore suppose that **1** and **2** cannot form solid solutions, and the process **1**→**2** is not topotaxial. To prove that structural transformation **1**→**2** would rather be impossible in the solid state we left relatively large crystal of **1** in air and regularly checked the unit cell on single crystal diffractometer. We noticed that unit cell kept unchanged, and the diffraction pattern slowly fades within 1-2 weeks. The crystal slowly decomposed without cracking apparently due to the loss of solvent water molecules. At that no any sign of **1**→**2** transformation was observed.

According to X-ray powder diffraction study complete transformation process **1**→**2** takes about 20 min in wet freshly prepared microcrystalline samples. The intensity of strong reflection (022) belonging to **1** gradually decreases, while the reflection (022) characteristic of **2** simultaneously appears and its intensity increases (Fig. 3).

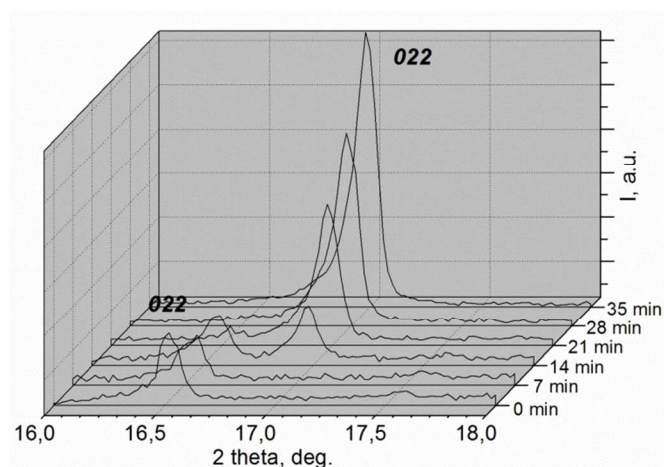


Figure 3. Evolution of the XRD pattern of compound **1** in the proximity of characteristic (022) reflection during the transformation into compound **2**.

Since we do not detect any ‘intermediate’ crystalline phase between **1** and **2** the process is proved to be non-topotaxial chemical reaction. Additionally we also do not observe the increase of the background that would indicate the formation of amorphous phase. Therefore the transformation **1**→**2** is possible only in the mother solution, and the driving force of this process is the loss of NH_3 .

Conclusions

We found that the chemical reaction between ammonia solution of ZnCl_2 and aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]\cdot 8\text{H}_2\text{O}$ is controlled by the concentration of NH_3 . High concentration favours the formation of compound **1** with novel anti-Prussian blue structure, where cationic Zn^{2+} nodes are joint by cluster anions as spacers forming highly porous primitive cubic (pcu) framework. The lower concentration of NH_3 leads to the formation of the compound **2** with ‘classical’ Prussian blue structure. The compound **1** can be prepared by slow diffusion

of reactants in sealed vessels and is stable at room temperature in the mother solution, while **2** can be obtained in the unsealed system or by exposing wet powder of **1** in air. At the same time relatively large dried crystal of **1** can be kept at room temperature, but gradually decomposes. Transformation of **1** into **2** requires dramatic structural re-arrangement and therefore can only undergo via non-topotaxial chemical reaction in the mother solution as proved by microcrystalline powder diffraction study.

Acknowledgements

This work is supported by the grant of the Government of the Russian Federation (PN 14.Z50.31.0006, leading scientist Prof. M. Schröder). Authors are grateful to Dr. V. A. Nadolnny (NIIC SB RAS, Novosibirsk, Russia) for EPR spectra recording.

Notes and references

^a Nikolaev Institute of Inorganic Chemistry SB RAS, Ak.Lavrentyev prosp. 3, Novosibirsk 630090, Russia.

^b Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russia.

*To whom correspondence should be addressed. Present address: Lst. Prof. Dr. M. Scheer, Institut für Anorganische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany. E-mail: avvirovets@yahoo.com

Electronic Supplementary Information (ESI) available: IR and EPR spectra, full table of bond distances in **1** and **2**, crystallographic data in CIF format. See DOI: 10.1039/b000000x/

- (a) Batten, S. R.; Neville, S. M.; Turner, D. R., *Coordination polymers: Design, analysis and application*. ed.; Cambridge, UK: Royal Society of Chemistry.: 2009; (b) Champness, N. R., *Dalton Trans.* **2006**, (7), 877-880; (c) Janiak, C.; Vieth, J. K., *New J. Chem.* **2010**, 34, (11), 2366-2388; (d) O’Keeffe, M., *Chem. Soc. Rev.* **2009**, 38, (5), 1215-1217; (e) Tranchemontagne, D. J.; Mendoza-Cortez, J. L.; O’Keeffe, M.; Yaghi, O. M., *Chem. Soc. Rev.* **2009**, 38, (5), 1257-1283; (f) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O’Keeffe, M.; Yaghi, O. M., *Account. Chem. Res.* **2010**, 43, (1), 58-67; (g) Leong, W. L.; Vittal, J. J., *Chem. Rev.* **2011**, 111, (2), 688-764; (h) Stock, N.; Biswas, S., *Chem. Rev.* **2011**, 112, (2), 933-969.
- (a) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., *Nature* **2003**, 423, (6941), 705-715; (b) O’Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M., *J. Solid State Chem.* **2000**, 152, (1), 3-20; (c) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M., *Science* **2002**, 295, (5554), 469-472.
- (a) Dunbar, K. R.; Heintz, R. A. *Progr. Inorg. Chem.* **1997**, 45, 284-391; (b) Shatruk, M.; Avendano, C.; Dunbar, K. R. *Progr. Inorg. Chem.* **2009**, 56, 155-334.
- Keggin, J. F.; Miles, F. D., *Nature* **1936**, 137, 577-578.

- 5 Moritomo, Y., Takachi, M., Kurihara, Y., Matsuda, T. *Adv. Mat. Sci. Eng.* **2013**, 1-17.
- 6 (a) Chen, X.; Wu, G.; Cai, Z.; Oyama, M.; Chen, X. *Microchim. Acta* **2014**, 181, (7-8), 689-705; (b) Wang, J. *Chem. Rev.* **2008**, 108, (2), 814-825; (c) Boyer, J. L., Kuhlman, M. L., Rauchfuss, T. B. *Acc. Chem. Res.* **2007**, 40, (4), 233-242.
- 7 (a) Verdaguer, M., Bleuzen, A., Marvaud, V., Vaissermann, J., Seuleiman, M., Desplanches, C., Scuiller, A., Train, C., Garde, R., Gelly, G., Lomenech, C., Rosenman, I., Veillet, P., Cartier, C., Villain, F. *Coord. Chem. Rev.* **1999**, 190-192, 1023-1047; Sato, O., Iyoda, T., Fujishima, A., Hashimoto, K. *Science* **1996**, 271, (5262) 704-705; (c) Ohkoshi, S., Tokoro, H. *Acc. Chem. Res.* **2012**, 45, (10), 1749-1758; (d) Bleuzen, A., Marvaud, V., Mathoniere, C., Sieklucka, B., Verdaguer, M. *Inorg. Chem.* **2009**, 48, (8), 3453-3466.
- 8 (a) Lestaevél, P., Racine, R., Bensoussan, H., Rouas, C., Gueguen, Y., Dublineau, I., Bertho, J. M., Gourmelon, P., Jourdain, J. R., Souidi, M. *Medecine Nucleaire-Imagerie Fonctionnelle et Metabolique.* **2010**, 34, (2), 108-118; (b) Melo, D. R., Lipsztein, J. L., Leggett, R., Bertelli, L., Guilmette, R. *Health Physics.* **2014**, 106, (5), 592-597; (c) Galvan-Arzate, S., Santamaria, A. *Toxicology Lett.* **1998**, 99, (1), 1-13.
- 9 (a) O'Keeffe, M.; Yaghi, O. M., *Chem. Rev.* **2012**, 112, (2), 675-702; (b) Alexandrov, E. V.; Blatov, V. A.; Kochetkov, A. V.; Proserpio, D. M., *Cryst. Eng. Comm.* **2011**, 13, (12), 3947-3958; (c) Blatov, V. A.; Proserpio, D. M., *Modern Methods of Crystal Structure Prediction*. In Oganov, A. R., Ed. Wiley-VCH: Weinheim: 2011.
- 10 O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M., *Acc. Chem. Res.* **2008**, 41, (12), 1782-1789.
- 11 (a) Naumov, N. G.; Virovets, A. V.; Sokolov, M. N.; Artemkina, S. B.; Fedorov, V. E., *Angew. Chem. Int. Ed.* **1998**, 37, (13-14), 1943-1945; (b) Beauvais, L. G.; Shores, M. P.; Long, J. R., *Chem. Mater.* **1998**, 10, (12), 3783-3786.
- 12 (a) Shores, M. P.; Beauvais, L. G.; Long, J. R., *J. Am. Chem. Soc.* **1999**, 121, (4), 775-779; (b) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R., *J. Am. Chem. Soc.* **2001**, 123, (33), 8022-8032.
- 13 (a) Naumov, N. G.; Cordier, S.; Perrin, C., *Solid State Sci.* **2005**, 7, (12), 1517-1521; (b) Yan, B.; Zhou, H.; Lachgar, A., *Inorg. Chem.* **2003**, 42, (26), 8818-8822.
- 14 (a) Naumov, N. G.; Sokolov, M. N.; Imoto, H.; Saito, T.; Fedorov, V. E., *J. Struct. Chem.* **1991**, 42, (2), 326-330; (b) Shores, M. P.; Beauvais, L. G.; Long, J. R., *J. Am. Chem. Soc.* **2000**, 122, (12), 2763-2772; (c) Beauvais, L. G.; Long, J. R., *Inorg. Chem.* **2006**, 45, (1), 236-243.
- 15 Jin, S.; DiSalvo, F. J., *Chem. Mater.* **2002**, 14, (8), 3448-3457.
- 16 Zhang, J.; Lachgar, A., *J. Am. Chem. Soc.* **2007**, 129, (2), 250-251.
- 17 Gayfulin, Y. M.; Naumov, N. G.; Rizhikov, M. R.; Smolentsev, A. I.; Nadolinny, V. A.; Mironov, Y. V., *Chem. Commun.* **2013**, 49, (85), 10019-10021.
- 18 *SADABS*, Bruker AXS Inc.: Madison, Wisconsin, USA, 2013.
- 19 *Bruker (2005) SHELXTL Structure Determination Programs Ver. 6.22*, Bruker AXS Inc.: Madison, Wisconsin, USA, 2005.
- 20 (a) Mironov, Y. V.; Naumov, N. G.; Brylev, K. A.; Efremova, O. A.; Fedorov, V. E.; Hegetschweiler, K., *Angew. Chem. Int. Ed.* **2004**, 43, (10), 1297-1300; (b) Mironov, Y. V.; Naumov, N. G.; Brylev, K. A.; Efremova, O. A.; Fedorov, V. E.; Hegetschweiler, K., *Russ. J. Coord. Chem.* **2005**, 31, (4), 269-281; (c) Tarasenko, M. S.; Ledneva, A. Y.; Naumov, D. Y.; Naumov, N. G.; Fedorov, V. E., *J. Struct. Chem.* **2011**, 52, (1), 172-179.

The reaction between ZnCl_2 and aqueous solution of $\text{CaK}_4[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ is controlled by the concentration of NH_3 . High concentration of NH_3 favors the formation of $[\text{Zn}(\text{NH}_3)_4]_8\{\text{Zn}[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]_3\} \cdot 9\text{H}_2\text{O}$ with an ideal primitive cubic 3D network of Zn^{2+} cations joint by cyanocluster anions as unprecedented bulky linear spacers. The low concentration of NH_3 leads to the formation of usual Prussian blue structure $[\text{Zn}(\text{NH}_3)_4]_2[\text{ZnRe}_3\text{Mo}_3\text{S}_8(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ with alternating octahedral Zn^{2+} and cyanocluster nodes. Both compounds contain paramagnetic cluster anion with $g=2.279$ and 2.280 , respectively. Powder diffraction studies prove that the former compound transforms into the latter after an exposure of wet polycrystalline sample in air.