

# Supramolecular networks based on octacyanometallates of Mo and W

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**Abstract** – The self-assembly of cyano-bridged discrete coordination architectures and polymeric coordination networks based on  $[M(CN)_8]^{3-/4-}$  ( $M = Mo$  and  $W$ ) molecular building blocks has been systematically investigated in order to obtain some basic information useful for crystal engineering of supramolecular coordination networks. The research is illustrated by concentrating on the superstructural diversity that has been exhibited in 0D architectures generated by cis and trans octahedral precursors, 1D and 2D architectures generated by Cu(II) centres, as well as in 2D structure generated by octahedral node of  $[Mn(H_2O)_6]^{2+}$  and geometrically anisotropic  $[W(CN)_6(bpy)]^{2-}$  ( $bpy = 2,2'$ -bipyridine). *To cite this article: B. Sieklucka et al., C. R. Chimie 5 (2002) 639–649* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

supramolecular coordination compounds / coordination polymers / crystal engineering / octacyanometallates

**Résumé** – L'auto-assemblage d'architectures de coordination discrètes à ponts cyanure et de réseaux de coordination polymériques basés sur des briques moléculaires  $[M(CN)_8]^{3-/4-}$  ( $M = Mo$  et  $W$ ) a été étudié de manière systématique pour obtenir des informations de base utiles en ingénierie cristalline de réseaux de coordination supramoléculaires. Cette recherche est illustrée en considérant plus particulièrement la diversité structurale relevée dans des architectures 0D engendrées par des précurseurs octaédriques cis et trans, dans des architectures 1D et 2D engendrées par des centres Cu(II), ainsi que dans des structures 2D basées sur des nœuds octaédriques de  $[Mn(H_2O)_6]^{2+}$  et de  $[W(CN)_6(bpy)]^{2-}$  ( $bpy = 2,2'$ -bipyridine) géométriquement anisotrope. *Pour citer cet article: B. Sieklucka et al., C. R. Chimie 5 (2002) 639–649* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

composés de coordination supramoléculaire / polymères de coordination / ingénierie cristalline / octacyanométallates

## 1. Introduction

Inorganic supramolecular chemistry of octacyanometallate  $[M(CN)_8]^{3-/4-}$  ( $M = Mo$  and  $W$ ) molecular building blocks is currently an area of extensive research [1–8]. The driving force for the research in this field is the generation, by deliberate design, of functional molecular networks with predetermined structures and potential for technologically useful molecule-based electronic, magnetic and photomag-

netic applications. The design and control of the structure of multidimensional networks based on octacyanometallate  $[M(CN)_8]^{3-/4-}$  molecular building blocks is also the area of great fundamental structural interest and importance. We do not intend however to cover here the very important and expanding research area of the 'low-oxidation' organometallic chemistry of cyanometallates [9].

By means of crystal engineering, solid-state multimetal arrays can be constructed by using coordinative,

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$\pi$ - $\pi$  stacking, hydrogen bonds interactions, electrostatic forces and Van der Waals interactions [10–20]. The rational design of such molecular architectures may be achieved using  $[\text{M}(\text{CN})_8]^{3-/4-}$  as the bridging moiety to build a multidimensional structure with a second coordination centre by thoughtful choice of ligands, transition metals, and reaction conditions.

Our successful synthetic strategy leading to heteropolymetallic systems with extended structures consists in self-assembly processes involving substitutionally inert octacyanometallate anions or ligand-substituted octacyano complex  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  (bpy = 2,2'-bipyridine), and complex cations with labile coordination sites.

In each case, the information for the self-assembly of the entire structure is encoded into the individual building blocks due to their steric, topological and intermolecular bonding capabilities. Furthermore, the inherent coordination preferences of the metal cation used in the assembly process are coupled with the stereochemical non-rigidity of octacyanometallate moiety [21–24]. Polytopal rearrangements of three idealised eight-coordination geometries: square antiprism (SAPR-8), dodecahedron (DD-8) and bicapped trigonal prism (TPRS-8) are found to be barrierless.

As a part of our programme of crystal engineering, we are devising and studying octacyanometallate-based frameworks involving M–CN–M' linkage, in order to acquire the control over the way molecules assemble in the solid state. The control over the structure allows us to manipulate the properties of these supramolecular materials.

Herein, we will examine the structures according to the dimensionality of the observed structures based on  $[\text{M}(\text{CN})_8]^{3-/4-}$  molecular building blocks and cationic precursors: 0D architectures generated by cis and trans octahedral precursors, 1D and 2D architectures generated by Cu(II) centres, as well as 2D coordination polymer generated by octahedral node of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  and geometrically anisotropic  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$ .

## 2. 0D (discrete) architectures generated by cis and trans octahedral precursors

The possible structures that might result from the metal-directed self-assembly of cis-protected octahedral complexes of transition metals are molecular square and 1D zigzag chain [13]. We have used this strategy to synthesise hexanuclear cluster  $\{[\text{Mn}^{\text{II}}(\text{bpy})_2]_4[\text{M}^{\text{IV}}(\text{CN})_8]_2\} \cdot 8 \text{H}_2\text{O}$  (M = Mo, W) [25] and pentanuclear high-spin molecule  $[\text{Mn}^{\text{II}}(\text{bpy})_2][\text{Mn}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2][\text{W}^{\text{V}}(\text{CN})_6] \cdot 7 \text{H}_2\text{O}$  [26] based on *cis*- $[\text{Mn}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ . In the case of

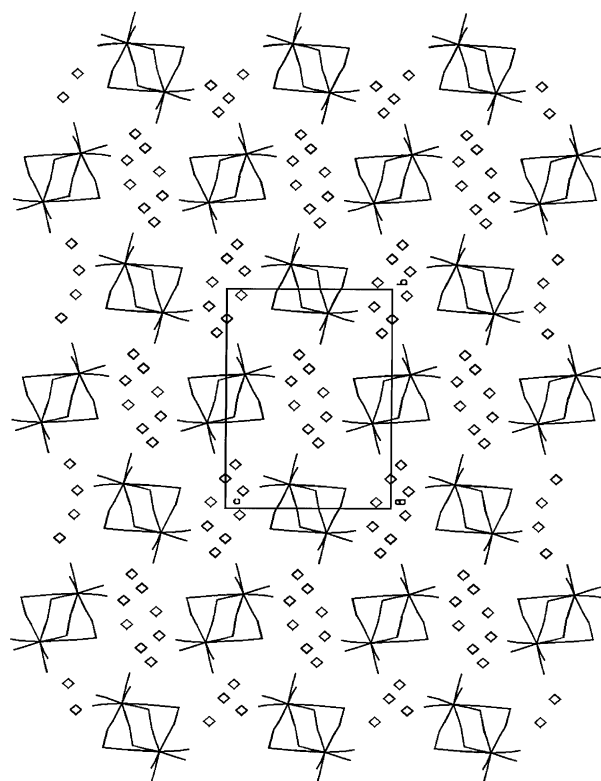


Fig. 1. The projection of  $\{[\text{Mn}^{\text{II}}(\text{bpy})_2]_4[\text{M}^{\text{IV}}(\text{CN})_8]_2\} \cdot 8 \text{H}_2\text{O}$  (M = Mo, W) on the *bc* crystallographic plane showing packing of the hexanuclear  $\text{Mn}_4\text{Mo}_2$  clusters (sticks) and  $\text{H}_2\text{O}$  molecules (diamonds). The cluster has octahedral geometry with four Mn centres at equatorial positions and two Mo centres at axial positions. 2,2'-bipyridyl ligands are omitted for clarity [25].

$[\text{M}^{\text{IV}}(\text{CN})_8]^{4-}$  building block, the hexanuclear cluster  $\{[\text{Mn}^{\text{II}}(\text{bpy})_2]_4[\text{Mo}^{\text{IV}}(\text{CN})_8]_2\} \cdot 8 \text{H}_2\text{O}$  has octahedral geometry (Fig. 1). The Mo centres located at the almost orthogonal axis to the plane of the four Mn centres have four bridging and four terminal cyano ligands arranged in square antiprismatic geometry. The molecule is realised by two, mutually perpendicular,  $\text{Mn}^{\text{II}}_2\text{Mo}^{\text{IV}}_2$  squares, sharing the Mo corners. The Mn atoms are hexacoordinate, having a distorted octahedral geometry with two bpy and two cis bent cyano-bridges. Each Mo atom has four bridging and four terminal cyano ligands arranged in a square antiprismatic geometry. The supramolecular architecture of the  $\text{Mn}^{\text{II}}_4\text{Mo}^{\text{IV}}_2$  lattice is controlled by CN-bridging, intra- and inter-molecular  $\pi$ - $\pi$  stacking (face-to-face and edge-to-face) interactions and extensive network of hydrogen bonds between terminal cyano ligands and the water molecules (Fig. 2).

The self-assembly of *cis*- $[\text{Mn}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  precursors results in formation of pentanuclear  $[\text{Mn}^{\text{II}}(\text{bpy})_2][\text{Mn}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2][\text{W}^{\text{V}}(\text{CN})_8] \cdot 7 \text{H}_2\text{O}$  molecule [26]. The pentanuclear molecule has the slightly distorted V-shape with two tungsten(V) atoms linked by single cyano bridges to three

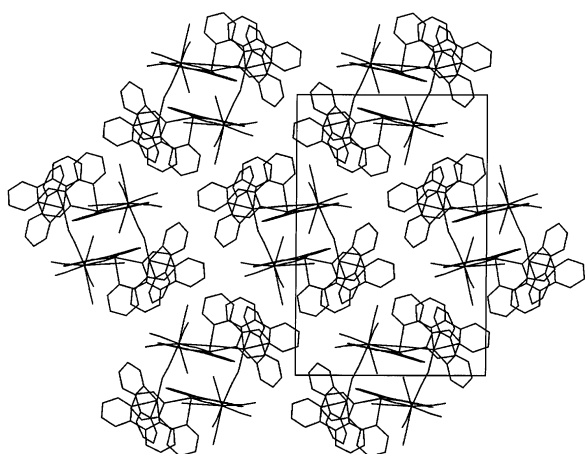


Fig. 2. The projection of  $\{[Mn^{II}(bpy)_2]_4[M^{IV}(CN)_8]_2\} \cdot 8 H_2O$  ( $M = Mo, W$ ) on the  $bc$  crystallographic plane showing  $\pi$ - $\pi$  stacking of bpy rings. Water molecules are omitted for clarity [25].

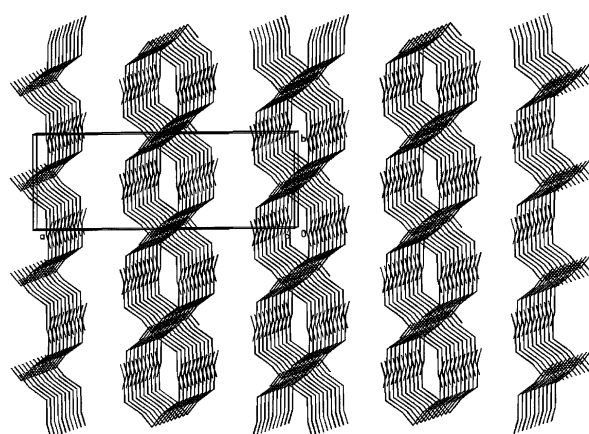


Fig. 4. Part of the X-ray structure of  $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)_2][W^V(CN)_8]_2 \cdot 7 H_2O$  showing column chain-like ordering of the molecules along the  $c$  crystallographic direction (the aromatic rings are omitted for clarity) [26].

manganese(II) centres in alternating sequence Mn–W–Mn–W–Mn (Fig. 3). In the molecule, the central  $[Mn(bpy)_2]^{2+}$  moiety is bound to two  $[W(CN)_8]^{3-}$  ions through a single cyano bridge. Each one of the  $[W(CN)_8]^{3-}$  is coordinated also to terminal  $[Mn(bpy)_2(H_2O)]^{2+}$  moiety through a single cyano bridge. The Mn atoms are hexacoordinate and present a distorted octahedral geometry.  $[Mn(bpy)_2]^{2+}$  moiety contains either two *cis* cyano bridges in the central Mn unit or single cyano bridge and aqua ligand in *cis* arrangement in the terminal one. Each W atom has two bridging and six terminal cyano ligands arranged

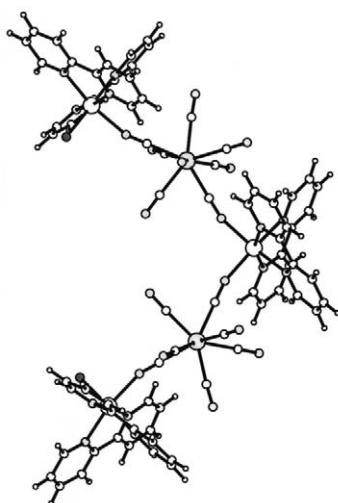


Fig. 3. View of  $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)_2][W^V(CN)_8]_2 \cdot 7 H_2O$  molecule along the  $a$  crystallographic direction; empty big spheres: Mn(II); grey big spheres: W(V); empty small spheres: C; grey small spheres: N; black small spheres: coordinated  $H_2O$  molecules [26].

in a square antiprismatic geometry slightly distorted towards bicapped trigonal prism geometry. The bridging CN ligands exhibit almost linear W–C–N units and significantly bent Mn–N–C sequences.

In the crystal, the V-shaped molecules are packed into infinite columns due to head-to-head and arm-to-arm  $\pi$ - $\pi$  stacking of the bpy rings of the terminal ('arms' of the pentamer) and central ('head' of the pentamer) Mn atoms of neighbouring molecules. Such an arrangement leads to a chain-like structure consisting of columns of pentamers clutched alternatively with their 'heads' and 'arms' (Fig. 4) forming linear tubes, where  $H_2O$  molecules are located (Fig. 5).

The complex exhibits intramolecular antiferromagnetic coupling between Mn(II) and W(V) centres, consistent with a ground state spin of  $S = 13/2$  and ferromagnetic long range transition at 0.66 K.

The preference for the formation of clusters in the self-assembly of *cis*- $[Mn^{II}(bpy)_2(H_2O)_2]^{2+}$  and  $[W(CN)_8]^{3-/4-}$  is enforced by the electroneutrality of resulting  $\{[Mn^{II}(bpy)_2]_4[M^{IV}(CN)_8]_2\} \cdot 8 H_2O$  and  $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)_2][W^V(CN)_6]_2 \cdot 7 H_2O$  products as well as to the  $\pi$ - $\pi$  stacking of bpy ligands, which seems to prevent the growth of the larger structures.

The self-assembly of  $[Co(tren)Cl_2]Cl$  [ $tren = tris(2\text{-aminoethylene})\text{amine}$ ] and  $K_4[W(CN)_8] \cdot 2 H_2O$  affords  $K_2\{[Co^{III}(tren)]_2[W^{IV}(CN)_8]_2\} \cdot 9 H_2O$  [27], containing tetranuclear square  $\{[Co(tren)]_2[W(CN)_8]_2\}^{2-}$  bridged by potassium ions into a two-dimensional array (Fig. 6). The tetranuclear square consists of alternating  $[Co^{III}(tren)]$  and  $[W^{IV}(CN)_8]$  corners. The Co(III) atoms are hexacoordinate and present a distorted octahedral geometry. Two *cis* bridging  $CN^-$  in  $[Co(tren)(NC)_2]^+$  exhibit bent Co–N–C sequences with the angle ranging from  $166(1)^\circ$  to  $173(1)^\circ$ . Each

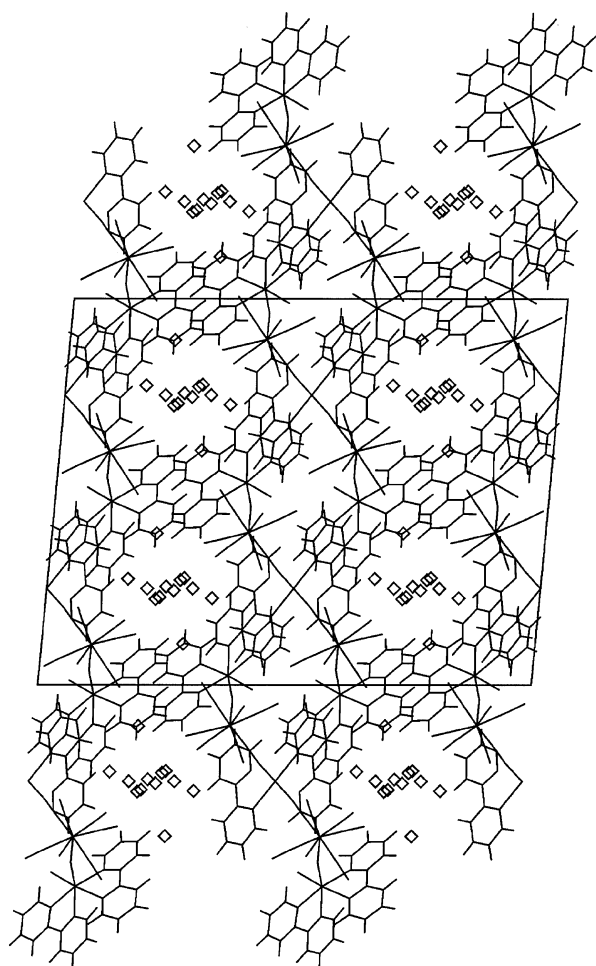


Fig. 5. Part of the X-ray structure of  $[\text{Mn}^{\text{II}}(\text{bpy})_2][\text{Mn}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2][\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot 7 \text{H}_2\text{O}$  showing the channels parallel to the  $b$  crystallographic direction, in which the lattice  $\text{H}_2\text{O}$  are located;  $\text{Mn}_3\text{W}_2$  molecules: sticks;  $\text{H}_2\text{O}$  molecules: diamonds [26].

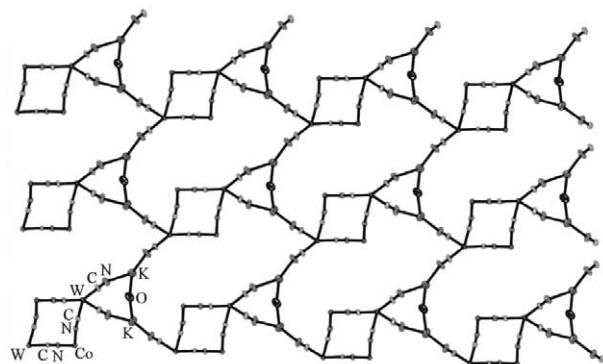


Fig. 6. View of the layer in  $\text{K}_2\{[\text{Co}^{\text{III}}(\text{tren})_2][\text{W}^{\text{IV}}(\text{CN})_8]_2\} \cdot 9 \text{H}_2\text{O}$  on the  $bc$  crystallographic plane, showing tetranuclear squares linked by potassium cations and bridging water molecules (the tren ligand, terminal CN ligands and non-bridging water molecules are omitted for clarity) [27].

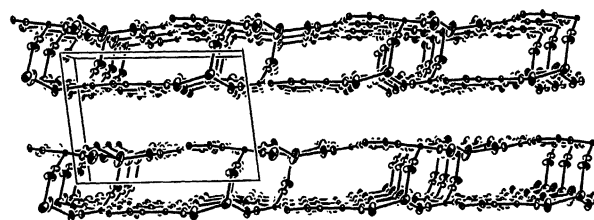


Fig. 7. Packing diagram of  $\text{K}_2\{[\text{Co}^{\text{III}}(\text{tren})_2][\text{W}^{\text{IV}}(\text{CN})_8]_2\} \cdot 9 \text{H}_2\text{O}$  along the  $b$  crystallographic direction, which shows bilayer arrangement of the crystal structure (the tren ligand, terminal CN ligands and water molecules are omitted for clarity) [27].

$\text{W}(\text{IV})$  centre has two bridging and six terminal cyano ligands arranged in a slightly distorted square antiprismatic geometry. The  $\{[\text{Co}(\text{tren})_2][\text{W}(\text{CN})_8]_2\}^{2-}$  squares are linked by potassium cations involving two terminal cyano ligands of each W centre to form a two-dimensional layer structure. The C–N–K bridges are significantly bent with the angle ranging from  $148(1)^\circ$  to  $164(1)^\circ$ . Formation of the layered structure by –CN–K–NC– linkage conforms to the analogous phenomena in some cyano-bridged networks based on hexacyanometalates [28, 29]. The  $\text{K}^+$  centres bind additionally to solvent water to give seven- and six-coordinate  $\text{K}^+$  ions. One of the water molecules forms the bridge between potassium ions leading to an additional triangular  $\text{WK}_2$  motif of the bridged layer. The given layer and neighbouring layer related by  $(-x, -y + 1, -z + 1)$  symmetry are linked in pairs by cyano groups coordinated to potassium ions. This results in formation of bilayers connected by centrosymmetric square units made of seven coordinated  $\text{K}^+$  and one of  $[\text{W}(\text{CN})_8]^{4-}$  corners of  $\{[\text{Co}(\text{tren})_2][\text{W}(\text{CN})_8]_2\}^{2-}$  square (Fig. 7). Layers are also linked through extensive network of hydrogen bonds involving interactions between cyano ligands, tris(2-aminoethylene)amine  $\text{NH}_2$  groups, and water molecules. The preference for the layered structure is attributed to the presence of potassium cations and hydrogen bonds, which are involved in aggregation with terminal cyano ligands. Therefore, the countercation and solvent can be used to control the dimensionality of the lattice.

The trans-directional bonding approach along with redox reactivity of  $\text{Pt}(\text{II})$  centre [30] has been applied by us to the construction of cyano-bridged  $[(\text{CN})_7\text{Mo}^{\text{IV}}-\text{CN}-\text{Pt}^{\text{IV}}(\text{en})_2-\text{NC}-\text{Mo}^{\text{IV}}(\text{CN})_7]^{4-}$  [31] ( $\text{en}$  = ethylenediamine) species. The trinuclear complex can be assembled by employing the inner-sphere electron-transfer process between  $\text{Pt}(\text{II})$  and  $[\text{Mo}(\text{CN})_8]^{3-}$ . On the process of crystallisation, the mixed-cation crystals of  $\text{Cs}_2[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][(\text{CN})_7\text{Mo}^{\text{IV}}-\text{CN}-\text{Pt}^{\text{IV}}(\text{en})_2-\text{NC}-\text{Mo}^{\text{IV}}(\text{CN})_7] \cdot 10 \text{H}_2\text{O}$  are formed.

In the trimeric anion, octacyanomolybdate(IV) units are bonded to  $[\text{Pt}^{\text{IV}}(\text{en})_2]$  moiety through trans



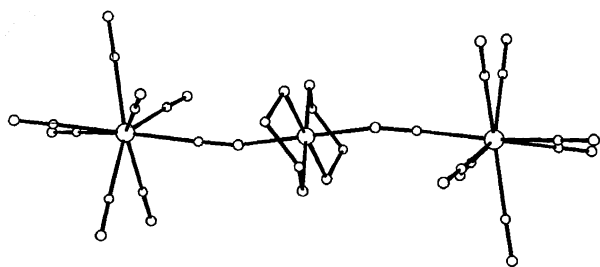


Fig. 8. View of the  $[(\text{CN})_7\text{Mo}^{\text{IV}}\text{-CN-Pt}^{\text{IV}}(\text{en})_2\text{-NC-Mo}^{\text{IV}}(\text{CN})_7]^{4+}$  trimeric species in  $\text{Cs}_2[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][(\text{CN})_7\text{Mo}^{\text{IV}}\text{-CN-Pt}^{\text{IV}}(\text{en})_2\text{-NC-Mo}^{\text{IV}}(\text{CN})_7] \cdot 10 \text{H}_2\text{O}$  showing bent cyano-bridges [31].

CN-bridges. The CN-bridges are characterised by bending of the Pt–N–C array (Fig. 8). The  $[\text{Mo}(\text{CN})_8]^{4-}$  has strongly distorted antiprismatic shape. The extended crystal structure reveals the alternating columns of trimers and isolated  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$  cations (Fig. 9). The important feature of the network is the presence of large  $\text{Cs}^+$  cations trapped within the ‘cage’ formed by Cl, N and O atoms of  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ , terminal CN ligands and water molecules, respectively. This arrangement indicates a crucial role of  $\text{Cs}^+$  in stabilisation of the structure in addition to the three-dimensional hydrogen bonds network.

The reaction of *trans*-directing  $[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]^+$   $[\text{salenH}_2 = N,N'$ -bis(salicylidene)ethylenediamine] with  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  resulted in the formation of  $[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]_3[\text{W}^{\text{V}}(\text{CN})_8] \cdot \text{H}_2\text{O}$  [32] discrete species. The complex consists of trinuclear anion  $\{[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]_2[\text{W}^{\text{V}}(\text{CN})_8]\}^-$  and  $[\text{Mn}^{\text{III}}(\text{salen})\text{-}$

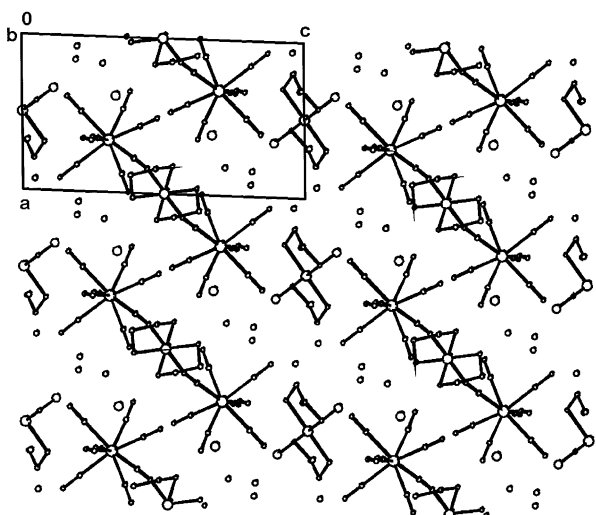


Fig. 9. Packing diagram of  $\text{Cs}_2[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][(\text{CN})_7\text{Mo}^{\text{IV}}\text{-CN-Pt}^{\text{IV}}(\text{en})_2\text{-NC-Mo}^{\text{IV}}(\text{CN})_7] \cdot 10 \text{H}_2\text{O}$  along the *b* crystallographic direction, showing  $[(\text{CN})_7\text{Mo}^{\text{IV}}\text{-CN-Pt}^{\text{IV}}(\text{en})_2\text{-NC-Mo}^{\text{IV}}(\text{CN})_7]^{4-}$  trimeric cyano-bridged species,  $[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2]^{2+}$  and  $\text{Cs}^+$  cations and lattice  $\text{H}_2\text{O}$  molecules [31].

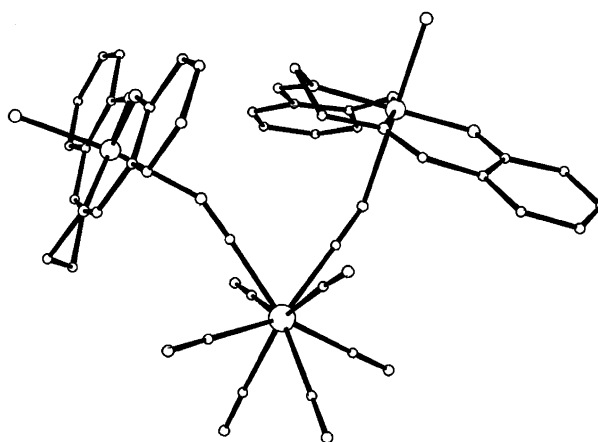


Fig. 10. The structure of  $\{[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]_2[\text{W}^{\text{V}}(\text{CN})_8]\}^-$  anion showing bent cyano-bridges [32].

$\text{H}_2\text{O}]^+$  counteranion. Within the trinuclear unit, the W centre (template) of distorted square antiprism geometry has six terminal and two bridging cyano ligands, whereas the  $[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}(\text{NC})]^+$  units display a distorted octahedral geometry (Fig. 10). The W centre is linked to two  $[\text{Mn}(\text{salen})\text{H}_2\text{O}]^+$  moieties through its two adjacent cyano corners of triangular face of SAPR-8. The Mn–N–C sequences are exceptionally long and strongly bent. In the crystal, the V-shaped trinuclear anions and isolated  $[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]^+$  cations are packed separately into infinite columns due to face-to-face  $\pi$ – $\pi$  stacking of the salen rings. Such an arrangement leads to a broken wave-like structure (Fig. 11). The complex exhibits intramolecular antiferromagnetic coupling between Mn(III) and W(V) centres consistent with a ground state spin of  $S = 7/2$  and ferromagnetic long range transition with  $T_N = 6 \text{K}$ .

### 3. 1D and 2D architectures generated by square-pyramidal Cu(II) centre

The strategy of exploiting square-pyramidal geometry of Cu(II) centre to generate cyano-bridged structures by connecting with octacyanotungstates(IV,V) has yielded 1D and 2D coordination polymers, with various Cu(II) moieties and architectures. The nature of the coordination of terminal ligand and the charge and geometry of octacyanides are the primary factors that determine the topology of the network.

The self-assembly of  $[\text{Cu}^{\text{II}}(\text{dien})(\text{H}_2\text{O})_2]^{2+}$  (dien = diethylenetriamine) and  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  in aqueous solution generates the one-dimensional chain  $\{[\text{W}^{\text{V}}\text{-CN-Cu}^{\text{II}}(\text{dien})\text{-NC}]_4^{5+}\}_n$  whose 5+ charge is balanced by isolated  $[\text{W}(\text{CN})_8]^{3-}$  and  $\text{Na}^+$  counterions in  $\text{Na}\{[\text{Cu}^{\text{II}}(\text{dien})]_4[\text{W}^{\text{V}}(\text{CN})_8]\}[\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot 8 \text{H}_2\text{O}$  [33]. The core of the chain (Fig. 12) is based on (i) square

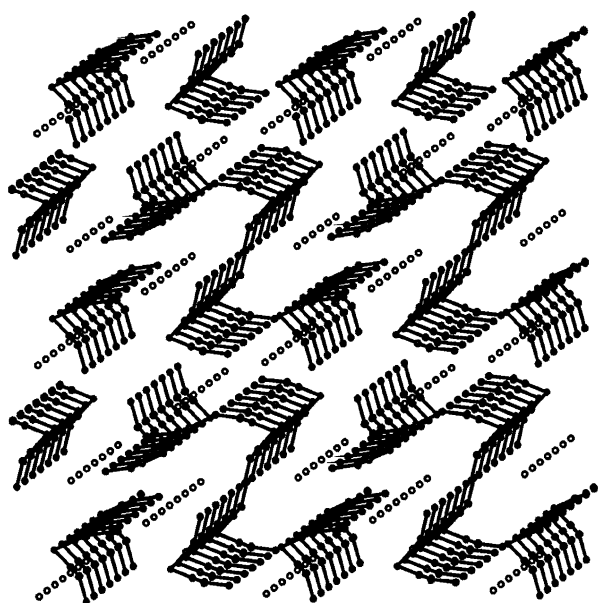


Fig. 11. Perspective view of packing diagram of  $[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]_3[\text{W}^{\text{V}}(\text{CN})_8]\cdot\text{H}_2\text{O}$  along the  $a$  crystallographic direction. Only the skeleton of  $\{[\text{Mn}^{\text{III}}(\text{salen})\text{H}_2\text{O}]_2[\text{W}^{\text{V}}(\text{CN})_8]\}^-$  and Mn centres of  $[\text{Mn}(\text{salen})(\text{H}_2\text{O})]^+$  counteranions (separated empty spheres) are shown. Salen ligands and  $\text{H}_2\text{O}$  molecules are omitted for clarity [32].

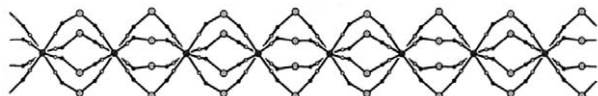


Fig. 12. Projection of the backbone of the chain  $\{\text{M}^{\text{V}}[-\text{CN}-\text{Cu}^{\text{II}}(\text{dien})-\text{NC}-]_4\}_n$  in  $\text{Na}\{[\text{Cu}^{\text{II}}(\text{dien})]_4[\text{M}^{\text{V}}(\text{CN})_8]\} [\text{M}^{\text{V}}(\text{CN})_8]_2\cdot 8\text{H}_2\text{O}$  ( $\text{M} = \text{Mo}, \text{W}$ ), along the  $b$  crystallographic direction; black big spheres:  $\text{W}(\text{V})$ , grey big spheres:  $\text{Cu}(\text{II})$ , black small spheres:  $\text{N}$ , grey small spheres:  $\text{C}$  [33].

antiprismatic  $[\text{W}(\text{CN})_8]^{3-}$  with all cyano ligands involved in bridging to eight adjacent  $\text{Cu}(\text{II})$  sites and (ii)  $[\text{Cu}(\text{dien})(\text{NC})_2]$  units of square pyramidal geometry, where N-bonded cyanides occupy the axial and equatorial sites. The exact match of parallel squares of N-donors of the cyanides of  $\text{W}(\text{V})$  sites to the squares of  $\text{Cu}(\text{II})$  sites gives rise to a unique quadruple W-knotted cord pattern, formed by four bent threads of  $-\text{CN}-\text{Cu}(\text{dien})-\text{NC}-$  sequences knotted at the  $\text{W}(\text{V})$  centres. The geometry and orientation of copper centres limit the propagation of the polymer to one direction converging all threads to the neighbouring tungsten node of the chain.

Within the chain, the bridging  $[\text{W}(\text{CN})_8]^{3-}$  anion has slightly distorted square antiprismatic  $D_{4d}$  local geometry. The copper presents a square pyramidal (SPY-5) coordination, where the three nitrogen donors of dien ligand occupy the equatorial positions. The 5-coordination of the Cu centre is completed by two

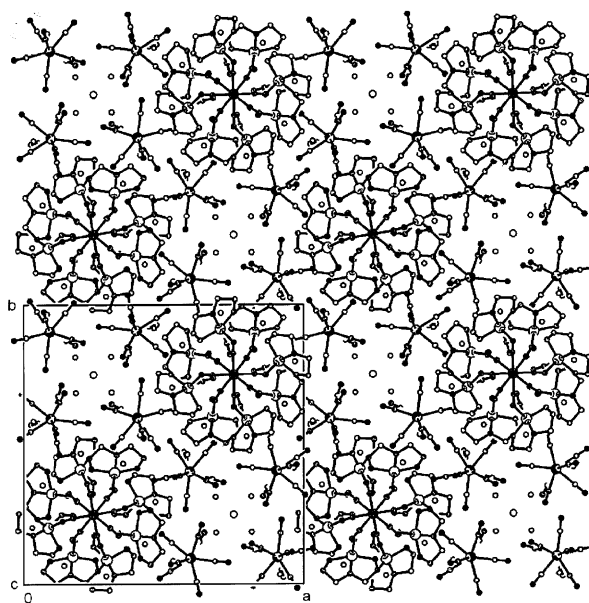


Fig. 13. Projection of compound  $\text{Na}\{[\text{Cu}^{\text{II}}(\text{dien})]_4[\text{M}^{\text{V}}(\text{CN})_8]\} [\text{M}^{\text{V}}(\text{CN})_8]_2\cdot 8\text{H}_2\text{O}$  ( $\text{M} = \text{Mo}, \text{W}$ ) along the  $c$  crystallographic direction showing the chain, non-bridging  $[\text{M}(\text{CN})_8]^{3-}$  anions,  $\text{Na}^+$  cations and lattice water molecules: view parallel to the axis of the chain and perpendicular to the square planes of bridging  $[\text{M}(\text{CN})_8]^{n-}$  square antiprisms [33].

N-donors of CN bridges from two  $\text{W}$  centres. The cyanide groups show different geometries: being short coordinated in the equatorial position of copper, but significantly longer at the axial position of the pyramidal  $\text{Cu}$ . These two sets of distances are related to two different non-linear geometries of  $\text{W}-\text{C}-\text{N}-\text{Cu}$  unit: being less bent in equatorial short CN bridges and significantly more bent in axial long CN bridges. These two distinguishable types of  $\text{M}-\text{CN}-\text{Cu}$  ( $\text{M} = \text{nd}$  cation) linkages are common for cyano-bridged assemblies based on (SPY-5) copper complexes [34]. The projection of the molecular entity in the lattice is presented in Fig. 13. The isolated  $[\text{W}(\text{CN})_8]^{3-}$  ions are distorted from  $D_{4d}$  geometry. The  $\text{Na}^+$  cations are located within the ‘cages’ formed by N atoms of isolated  $[\text{W}(\text{CN})_8]^{3-}$  and oxygen atoms of  $\text{H}_2\text{O}$ . The lattice molecules of water are located within the ‘tubes’ formed by isolated  $[\text{W}(\text{CN})_8]^{3-}$ , parallel to the  $c$  axis, and around tungsten knots of the chain. They participate in the extensive hydrogen-bonding network between themselves, with the nitrogen atoms of the  $[\text{W}(\text{CN})_8]^{3-}$  anion and with the hydrogen atoms of the dien N-H groups. The molybdenum analogue  $\text{Na}\{[\text{Cu}^{\text{II}}(\text{dien})]_4[\text{Mo}^{\text{V}}(\text{CN})_8]\} [\text{Mo}^{\text{V}}(\text{CN})_8]_2\cdot 8\text{H}_2\text{O}$  was found to be isomorphous.

The magnetic behaviour is the one of two isolated paramagnetic  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  entities and of  $\text{WCu}_4$  pentanuclear units, with a weak ferromagnetic intra-unit interaction between  $\text{W}$  and  $\text{Cu}$  and a very weak anti-

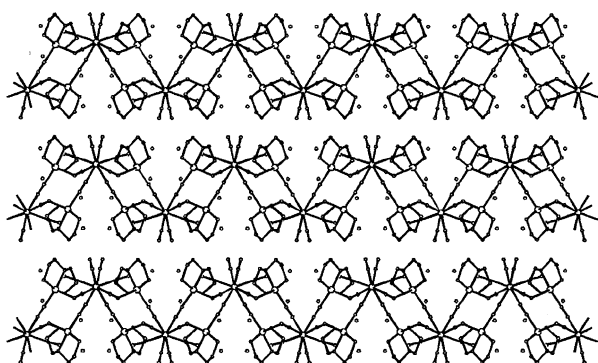


Fig. 14. Packing diagram of  $\{[\text{Cu}^{\text{II}}(\text{dien})_2][\text{M}^{\text{IV}}(\text{CN})_8] \cdot 4 \text{H}_2\text{O}\}_n$  ( $\text{M} = \text{Mo}, \text{W}$ ) along the  $b$  crystallographic direction showing 2-dimensional cyano-bridged polymeric layers and lattice  $\text{H}_2\text{O}$  molecules (dots) [35].

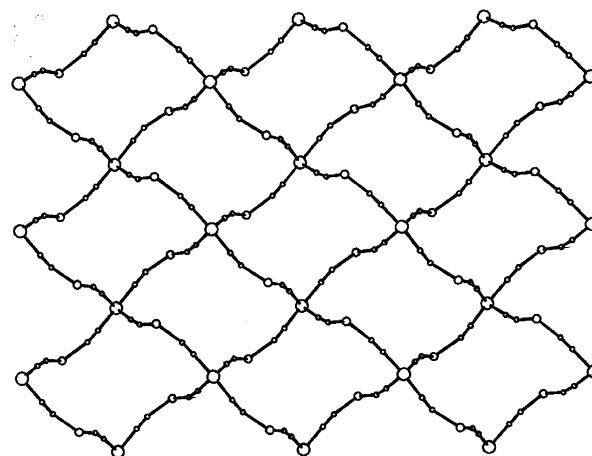


Fig. 15. View of the square-grid pattern in  $\{[\text{Cu}^{\text{II}}(\text{dien})_2][\text{M}^{\text{IV}}(\text{CN})_8] \cdot 4 \text{H}_2\text{O}\}_n$  ( $\text{M} = \text{Mo}, \text{W}$ ) on the  $ab$  crystallographic plane; big empty spheres:  $\text{M}(\text{IV})$ ; medium empty spheres:  $\text{Cu}(\text{II})$ ; small spheres:  $\text{C}, \text{N}$  [35].

ferromagnetic interaction between the  $\text{WCu}_4$  units. The weak ferromagnetic interaction is due to the orthogonality of the  $\text{W}(\text{d}_{z^2})$  and  $\text{Cu}(\text{d}_{x^2-y^2})$ -type orbitals through the long  $\text{W}-\text{C}-\text{N}-\text{Cu}$  pathway, whereas the very weak antiferromagnetic coupling can be assigned to a weak overlap  $\text{W}(\text{d}_{z^2})$  and  $\text{Cu}(\text{d}_{x^2-y^2})$ -type magnetic orbitals over the short  $\text{W}-\text{C}-\text{N}-\text{Cu}$  pathway.

The self-assembly of  $[\text{Cu}^{\text{II}}(\text{dien})(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{W}^{\text{IV}}(\text{CN})_8]^{4-}$  in aqueous solution generates 2D layers of  $\{[\text{Cu}^{\text{II}}(\text{dien})_2][\text{W}^{\text{IV}}(\text{CN})_8] \cdot 4 \text{H}_2\text{O}\}_n$  [35]. The crystal structure of  $\{[\text{Cu}^{\text{II}}(\text{dien})_2][\text{W}^{\text{IV}}(\text{CN})_8] \cdot 4 \text{H}_2\text{O}\}_n$  (Fig. 14) comprises strongly folded layers of square grid pattern (Fig. 15). Four tungsten centres are located at the corners and four Cu centres on the edges of the squares. The structure of the layer resembles of the egg holder with two W and two Cu atoms at the corners of the bottom and top, respectively. Each  $[\text{W}^{\text{IV}}(\text{CN})_8]^{4-}$  of square antiprismatic geometry links four Cu centres. The four cyano bridges are formed by  $\text{CN}^-$  groups occupying the corners of two adjacent triangular faces of SAPR-8. The  $[\text{Cu}(\text{dien})(\text{NC})_2]$  units are of square pyramidal geometry with N-bonded cyanides occupying one axial and one equatorial site. Similarly, as in  $\text{Na}\{[\text{Cu}^{\text{II}}(\text{dien})]_4[\text{W}^{\text{V}}(\text{CN})_8]\}[\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot 8 \text{H}_2\text{O}$ , the equatorial bridge is shorter and less bent than the axial one. The remaining four terminal  $\text{CN}^-$  ligands of  $[\text{W}^{\text{IV}}(\text{CN})_8]^{4-}$ , standing out of the layer, as well as  $\text{RNH}_2$  groups from dien ligand and lattice water molecules are involved in the extensive network of hydrogen bonds stabilizing 3-dimensional architecture. The molybdenum analogue  $[\text{Cu}^{\text{II}}(\text{dien})_2][\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 4 \text{H}_2\text{O}$  was found to be isomorphous.

We have demonstrated that by controlling the charge of octacyanometalate moiety,  $\text{Na}\{[\text{Cu}^{\text{II}}(\text{dien})]_4[\text{M}^{\text{V}}(\text{CN})_8]\}[\text{M}^{\text{V}}(\text{CN})_8]_2 \cdot 8 \text{H}_2\text{O}$  with 1D chain  $\{[\text{M}^{\text{V}}(-\text{CN}-\text{Cu}^{\text{II}}(\text{dien})-\text{NC}-)]_n^{5+}\}$ , or 2D  $[\text{Cu}^{\text{II}}(\text{dien})_2][\text{M}^{\text{IV}}(\text{CN})_8] \cdot 4 \text{H}_2\text{O}$  neutral layers may be generated. In

the self-assembly process of  $[\text{Cu}^{\text{II}}(\text{dien})(\text{H}_2\text{O})_2]^{2+}$  and octacyanometalates, the interplay of charges and geometry of cationic and anionic building blocks are important factors influencing the topology of coordination polymers formed.

In order to elucidate the influence of the degree of chelation of terminal ligand, the  $[\text{Cu}(\text{tetren})]^{2+}$  (tetren = tetraethylenepentaamine) complex has been reacted with  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  in aqueous solution at different pH [35]. The  $[\text{Cu}(\text{tetren})]^{2+}$  is the single source of pre-programmed  $\text{Cu}(\text{II})$  centres formed by protonation of N atoms of tetren ligand: penta-coordinated  $[\text{Cu}(\text{tetren})]^{2+}$  at  $\text{pH} > 6$ , tri-coordinated  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)]^{4+}$  in the pH range 3–5 and aqua complex of  $\text{Cu}(\text{II})$  formed by the release of fully protonated tetren ligand at  $\text{pH} < 2$ .

The crystal structure analysis of the  $[\text{Cu}(\text{tetren})](\text{ClO}_4)_2$  precursor reveals that  $[\text{Cu}(\text{tetren})]^{2+}$  cation of distorted trigonal bipyramidal geometry has significantly longer terminal equatorial  $\text{Cu}-\text{N}$  bonds compared to the remaining central  $\text{Cu}-\text{N}$  bonds [36]. The geometry of coordinatively saturated  $[\text{Cu}(\text{tetren})]^{2+}$  precursor implies that in the self-assembly process the terminal  $\text{N}-\text{Cu}$  bonds would be the first to be broken in favour of cyano bridges formation. Indeed, the reaction between  $[\text{Cu}(\text{tetren})]^{2+}$  and  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  in  $\text{Cu}:\text{W} = 3:2$  molar ratio in aqueous solution at  $\text{pH} 7.0$  affords the assembly of  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)]^{4+}$ . However, the obtained  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)]_4[\text{W}^{\text{IV}}(\text{CN})_8]_4 \cdot 10 \text{H}_2\text{O}$  contains spontaneously reduced tungsten(IV) centre. The structure of generated compound is unique with cyano-bridged  $\text{W}_2\text{Cu}_2$  squares joined by single cyano bridges into infinite one-dimensional polymer of necklace pattern (Fig. 16) [35]. The  $\text{W}_2\text{Cu}_2$  squares with alternative  $\text{W}-\text{Cu}$  corners comprise two different

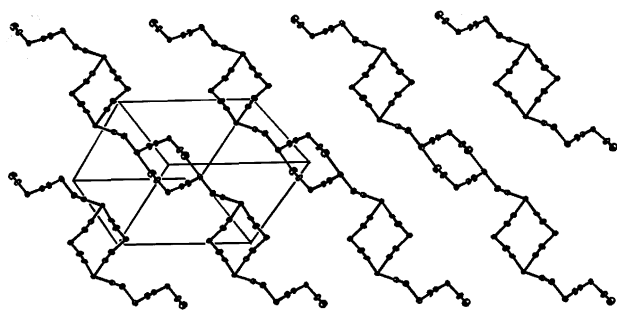


Fig. 16. Cyano-bridged skeleton of 1D polymer of necklace pattern in  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)_4][\text{W}^{\text{IV}}(\text{CN})_8]_4 \cdot 10 \text{H}_2\text{O}$  ( $\text{pH} = 7$ ). The skeleton is formed by  $\text{W}_2\text{Cu}_2$  squares joined through  $\text{CN}^-$  bridges. Lattice  $\text{H}_2\text{O}$  molecules are omitted for clarity [35].

types. The one  $\text{W}_2\text{Cu}_2$  subunit contains W centres of distorted dodecahedral (DD-8) geometry with three bridging cyano ligands and penta-coordinated Cu centres, whereas the other one consists of W centres with two bridging cyano ligands and hexa-coordinated Cu centres. The blocking tetren ligand is coordinated by three central nitrogen donor atoms to Cu atoms in equatorial positions, while the remaining terminal nitrogens of tetren are protonated and uncoordinated. The  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)(\text{NC})_2]^{2+}$  units are of square pyramidal geometry with bent N-bonded cyanides occupying the axial and equatorial sites. The *mer*- $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)(\text{NC})_3]^+$  units are of distorted octahedral geometry with almost linear equatorial and strongly bent axial cyano bridges. The terminal amino groups of tetren ligand, terminal cyano ligands, and water molecules are involved in hydrogen bonds strengthening the internal structure of the chain.

The same molecular building blocks:  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)]^{4+}$  and either  $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$  or  $[\text{W}^{\text{IV}}(\text{CN})_8]^{4-}$  in  $\text{Cu}:\text{W} = 3:2$  molar ratio generates at  $\text{pH} 3.5$  another type of the network superstructure:  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)]_4[\text{W}^{\text{IV}}(\text{CN})_8]_4 \cdot 10 \text{H}_2\text{O}$  assembly forms unique 1D chain of long and short brick three-row wall pattern (Fig. 17) [35]. The wall comprises the fused  $\text{W}_2\text{Cu}_2$  squares forming the central row and of  $\text{W}_3\text{Cu}_3$  distorted rectangles forming two external rows. The W centres comprise two different types of distorted square anti-

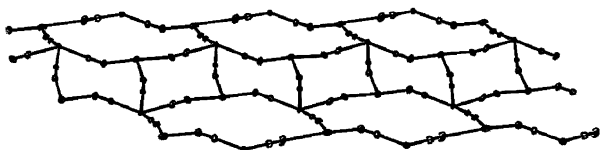


Fig. 17. Cyano-bridged skeleton of 1D polymer of long and short brick three-row wall pattern in  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)_4][\text{W}^{\text{IV}}(\text{CN})_8]_4 \cdot 10 \text{H}_2\text{O}$  ( $\text{pH} = 3.5$ ). The central row is formed by  $\text{W}_2\text{Cu}_2$  squares and the external rows are formed by  $\text{W}_3\text{Cu}_3$  distorted rectangles. Lattice  $\text{H}_2\text{O}$  molecules are omitted for clarity [35].

prismatic structure:  $\text{W}_2\text{Cu}_2$  subunit contains W centres with four bridging cyano ligands, whereas  $\text{W}_3\text{Cu}_3$  rectangle contains W centres with four and two bridging cyano ligands. Cu sites are hexa-coordinated with *mer*-tetren $\text{H}_2$  ligand. The *mer*- $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)(\text{NC})_3]^+$  in  $\text{W}_2\text{Cu}_2$  subunit has bent cyano bridges, one equatorial and two axial ones.  $\text{W}_3\text{Cu}_3$  rectangle contains *mer*- $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)(\text{NC})_3]^+$  present in  $\text{W}_2\text{Cu}_2$  as well as Cu site of short and almost linear equatorial CN bridge and significantly bent two axial bridges. The terminal cyano ligands of  $[\text{W}(\text{CN})_8]^{4-}$  are presumably involved in the network of hydrogen bonds linking parallel chains through the lattice water molecules.

Both compounds of the formula  $[\text{Cu}^{\text{II}}(\text{tetrenH}_2)]_4[\text{W}^{\text{IV}}(\text{CN})_8]_4 \cdot 10 \text{H}_2\text{O}$  obtained for different pH conditions exemplify the structural supramolecular isomerism [13]: the components of the network remain the same but they have a different superstructure. The networks are effectively different compounds. The preference for the either structural supramolecular isomer can be attributed to the substitutional reactivity of  $[\text{Cu}(\text{tetren})]^{2+}$  at different pH. Therefore, the pH can be used to control the topology of the assemblies.

The self-assembly of  $[\text{W}(\text{CN})_8]^{3-}$  and  $[\text{Cu}(\text{tetren})]^{2+}$  in acidic aqueous solution generates  $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2 \text{H}_2\text{O}\}_n$  [36]. The  $[\text{Cu}(\text{tetren})]^{2+}$  complex ion provides the pre-programmed bare Cu(II) centres formed by release of fully protonated tetren ligand. The  $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2 \text{H}_2\text{O}\}_n$  consists of anionic double-layers  $\{\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4\}_n$ , the charge of which is balanced by tetren $\text{H}_5^{5+}$  cations (Fig. 18). Each  $[\text{W}(\text{CN})_8]^{3-}$  of bicapped trigonal prism geometry links five Cu centres, coordinated by (NC)

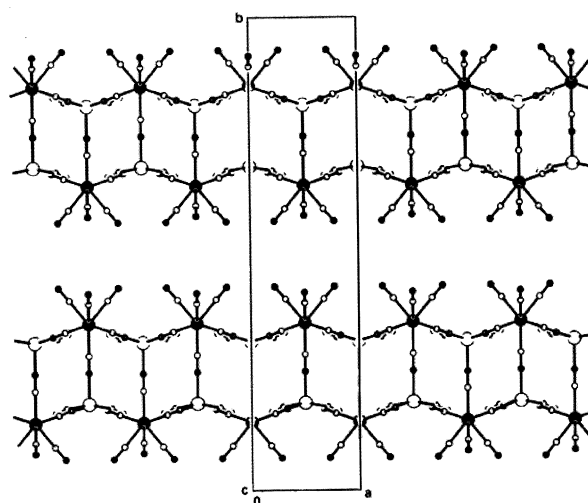


Fig. 18. Projection of double layers in  $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2 \text{H}_2\text{O}\}_n$  on the  $ab$  crystallographic plane: big black spheres: M(IV); big empty spheres: Cu(II); small black spheres: N; small empty spheres: C. The disordered tetren $\text{H}_5^{5+}$  cations and  $\text{H}_2\text{O}$  molecules are omitted for clarity [36].



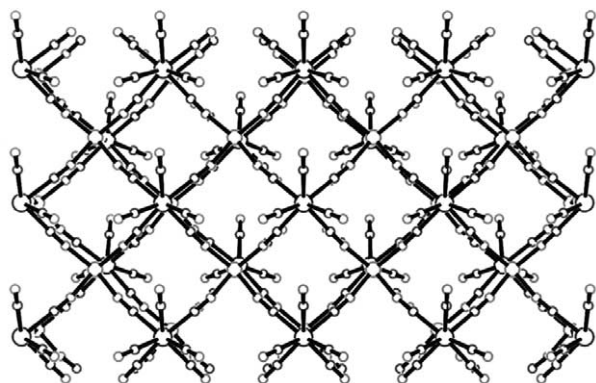


Fig. 19. Projection on the *ac* crystallographic plane showing square-grid pattern of single double-layer in  $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4 [\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2 \text{H}_2\text{O}\}_n$ . The disordered tetren $\text{H}_5^{5+}$  cations and  $\text{H}_2\text{O}$  molecules are omitted for clarity [36].

bridges in a square pyramid. Four slightly bent equatorial cyanide bridges Cu–N–C gives rise to the square-grid pattern of the single layer, while the practically linear axial  $\text{CN}^-$  bridge joins two layers and thus forms the double-layer (Fig. 19). In consequence, the double-layer is realised by the two stacked sheets of edge sharing Cu–(NC–W) $_5$  square-pyramids of antiparallel orientation. The cation and the inferred water molecules lie in planes between the Cu–W double layers.

The remaining three terminal CN ligands of  $[\text{W}(\text{CN})_8]^{3-}$ , standing out of the layer, are presumably involved in the extensive network of hydrogen bonds linking parallel double-layers through the lattice water molecules and are undoubtedly significant in construction of the system. The  $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4 [\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2 \text{H}_2\text{O}\}_n$  exhibits soft ferromagnetic behaviour, with an ordering temperature  $T_C$  of 34K. The ferromagnetic coupling can be rationalised in terms of the interactions of unpaired electrons originating from the mutually orthogonal  $3d_{x^2-y^2}$  orbital of Cu(II) and the mixture of  $5d_{z^2}$  and  $5d_{x^2-y^2}$  ground state orbitals of the W(V) centre of bicapped trigonal prism geometry along both types of Cu–NC–W bridge.

#### 4. 2D coordination polymer generated by octahedral node of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and geometrically anisotropic $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$

For highly symmetrical  $[\text{M}(\text{CN})_8]^{n-}$  units, the design and synthesis of geometrically and magnetically anisotropic polynuclear systems encounter large difficulties [4b, 37]. These observations prompted us to explore the possibility of lowering the symmetry of

octacoordinated cyano building block by using the molecular precursor related to the octacyanotungstate(IV) geometrically anisotropic  $[\text{W}^{\text{IV}}(\text{CN})_6(\text{bpy})]^{2-}$  complex [38, 39]. Our strategy is convergent on the new synthetic approach based on the replacement of a highly symmetrical hexacyanoferrate(III) ion by lower symmetry  $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{phen})]^-$  [40] (phen = 1,10-orthophenanthroline) and  $[\text{Fe}^{\text{III}}(\text{CN})_4(\text{bpy})]^-$  [41] precursors. In  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$ , which is not compatible with cubic geometry of hexacyano moieties, two coordination sites are occupied by bpy ligand acting as terminal coordinator and participating in secondary  $\pi$ -stacking interactions. Therefore,  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  has the advantage of the formation of anisotropic, directional network over the homoleptic hexacyano complexes producing the highly symmetrical three-dimensional arrays.

To gain the evidence on the binding modes of  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  with transition metal centres, we have studied the reaction of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  with  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$ , and obtained the two-dimensional basket weave-like [11,13] coordination polymer  $\{[\text{fac}-(\text{H}_2\text{O})_3\text{Mn}^{\text{II}}-(\mu\text{-NC})_3\text{-W}^{\text{IV}}(\text{CN})_3(\text{bpy})] \cdot 4.5 \text{H}_2\text{O}\}_n$  [42] of  $4.8^2$  topology [43]. There is only one previous example of such topology observed in a 2D parallel interpenetrated network of coordination polymer formed between  $\text{Cd}(\text{NO}_3)_2$  and 2,4-bis(4-pirydyl)-1,3,5-triazine (dpt),  $[\text{Cd}_2(\text{NO}_3)_4(\text{dpt})_2(\text{MeCN})]_\infty$ , which exists as a doubly interpenetrated  $4.8^2$  two-dimensional sheet in the solid state [44].

The self-assembly reaction of the  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  precursor with  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  in aqueous solution yields a novel two-dimensional coordination polymer  $\{[\text{fac}-(\text{H}_2\text{O})_3\text{Mn}^{\text{II}}-(\mu\text{-NC})_3\text{-W}^{\text{IV}}(\text{CN})_3(\text{bpy})] \cdot 4.5 \text{H}_2\text{O}\}_n$ . The crystal structure of  $\{[\text{fac}-(\text{H}_2\text{O})_3\text{Mn}^{\text{II}}-(\mu\text{-NC})_3\text{-W}^{\text{IV}}(\text{CN})_3(\text{bpy})] \cdot 4.5 \text{H}_2\text{O}\}_n$  consists of neutral thick waved layers and separated by crystallisation water molecules (Fig. 20). Within each layer,  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  forms three single cyano-bridges to three *fac*- $[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_3]$  (Fig. 21). Each *fac*- $[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_3]$  is linked to three  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$ . The CN-bridges are significantly bent. The Mn and W centres linked alternatively by single cyano bridge afford spatially distorted small tetranuclear  $\text{W}_2\text{Mn}_2(\mu\text{-CN})_4$  and large octanuclear  $\text{W}_4\text{Mn}_4(\mu\text{-CN})_8$  polygons that run along the layer. The face-to-face  $\pi$ -stacked  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  pairs control the formation of polygons and give rise to the basket weave-like pattern (Fig. 22). Aqua ligands of *fac*- $[\text{Mn}(\text{NC})_3(\text{H}_2\text{O})_3]$  and non-bridging cyano ligands of  $[\text{W}(\text{CN})_6(\text{bpy})]^{2-}$  are involved in the extensive network of hydrogen bonds linking parallel layers through the crystallisation water molecules and are significant in the construction of the system.

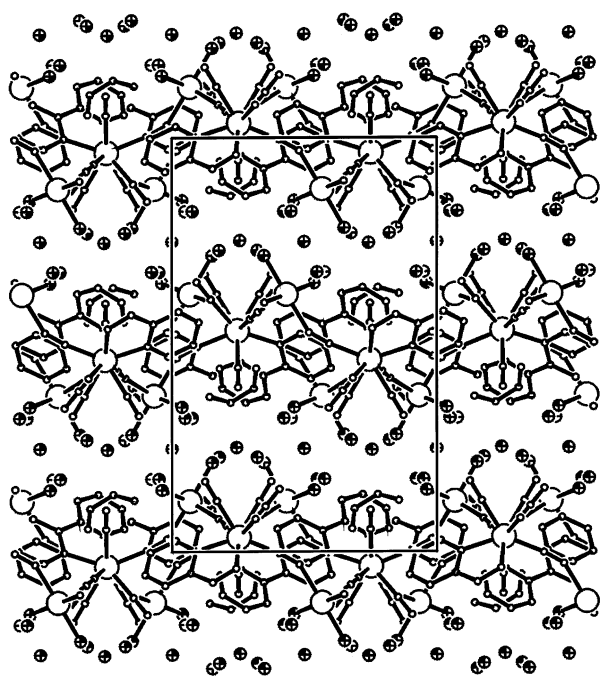


Fig. 20. Packing diagram of  $\{[fac-(H_2O)_3Mn^{II}-(\mu-NC)_3-W^{IV}(CN)_3bpy] \cdot 4.5 H_2O\}_n$  along the  $b$  crystallographic direction, showing the thick wavy layers separated by crystallisation water molecules [42].

## 5. Conclusions

We have demonstrated the principles of self-assembly applied towards the design and synthesis of discrete coordination architectures and polymeric coordination networks based on  $[M(CN)_8]^{3-/4-}$  and cationic complexes as templates and nodes. The rational design of supramolecular structure exploits coordinative,  $\pi$ - $\pi$ -stacking, hydrogen bonds interactions, electrostatic forces, and Van der Waals interactions. The systematic approach to increasing an understanding of the fundamental and subtle factors that control the architectures in the solid state has resulted in design, isolation, and characterisation of a number of novel compounds. Our results serve to emphasise the difficulty in predictably preparing coordination networks.

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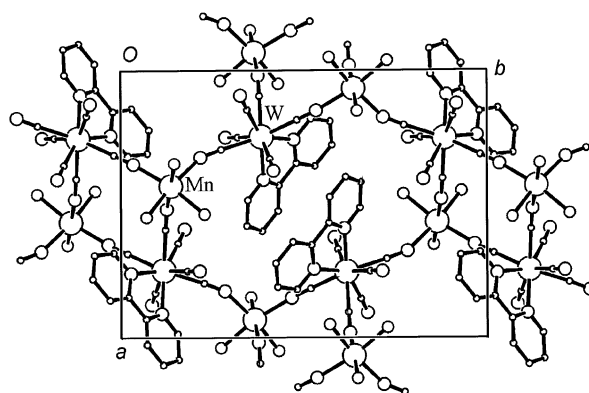


Fig. 21. View of a representative section of the 2D lattice of  $\{[fac-(H_2O)_3Mn^{II}-(\mu-NC)_3-W^{IV}(CN)_3bpy] \cdot 4.5 H_2O\}_n$  parallel to the  $ab$  crystallographic plane. The layer is built of tetranuclear  $W_2Mn_2$  and octanuclear  $W_4Mn_4$  polygons [42].

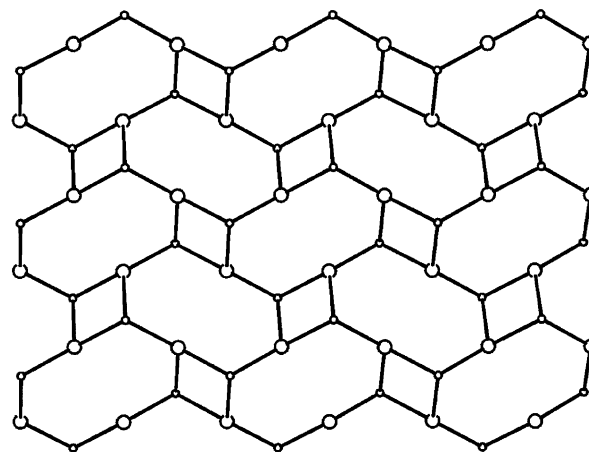


Fig. 22. Basket weave-like pattern ( $4,8^2$  topology) of  $\{[fac-(H_2O)_3Mn^{II}-(\mu-NC)_3-W^{IV}(CN)_3bpy] \cdot 4.5 H_2O\}_n$  [42].

The control over these materials is far from satisfactory. However, as our understanding increases about the numerous factors involved, supramolecular octacyanometallate-based coordination synthesis is likely to develop considerably further.

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