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Review

Engineering of octacyanometalate-based coordination networks towards functionality

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Contents

Abstract

The design and construction of new supramolecular coordination compounds based on octacyanometalate $[M(CN)_8]^{3-/4-}$ (M = Mo and W) building blocks of potential utility as functional materials has received considerable attention over the recent years. The research in this field has resulted in the cyano-bridged polynuclear octacyanometalate-based molecules and polymeric coordination networks which behave like molecular magnets and photo-induced magnetic materials. This article surveys the superstructural complexity of some coordination frameworks built by multidirectional non-rigid octacyanometalate anions as linkers in self-assembly with convergent Mn(II,III), Co(III), Cu(II) and Pt(II) complexes with polyamine, diimine and Schiff-base blocking ligands. The role of intermolecular directional forces in propagation of M–CN–M′ linkages into the architectures of various dimensionalities and topologies is pointed out. The network topologies are outlined and the structure/property relationship is discussed.

Keywords: Crystal engineering; Octacyanomolybdate; Octacyanotungstate; Magnetic properties; Cyano bridge; Crystal structures

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1. Introduction

Over a hundred years ago, in 1904, Chilesotti synthesized a new cyano complex, $K_4[Mo(CN)_8]\cdot 2H_2O$ [1]. He observed that after the irradiation by sunlight, the aqueous solution of octacyanomolybdate(IV) turned red and released HCN. A few years later, in 1910, Rosenheim et al. investigated the photosensitivity of $[Mo(CN)_8]^{3-}$ ion [2]. The same behaviour of $[W(CN)_8]^{3-}$ was noticed by Olsson [3]. In 1924, Collenberg observed that the irradiation of $[Mo(CN)_8]^{4-}$ in alkaline solution results in replacing up to maximum four

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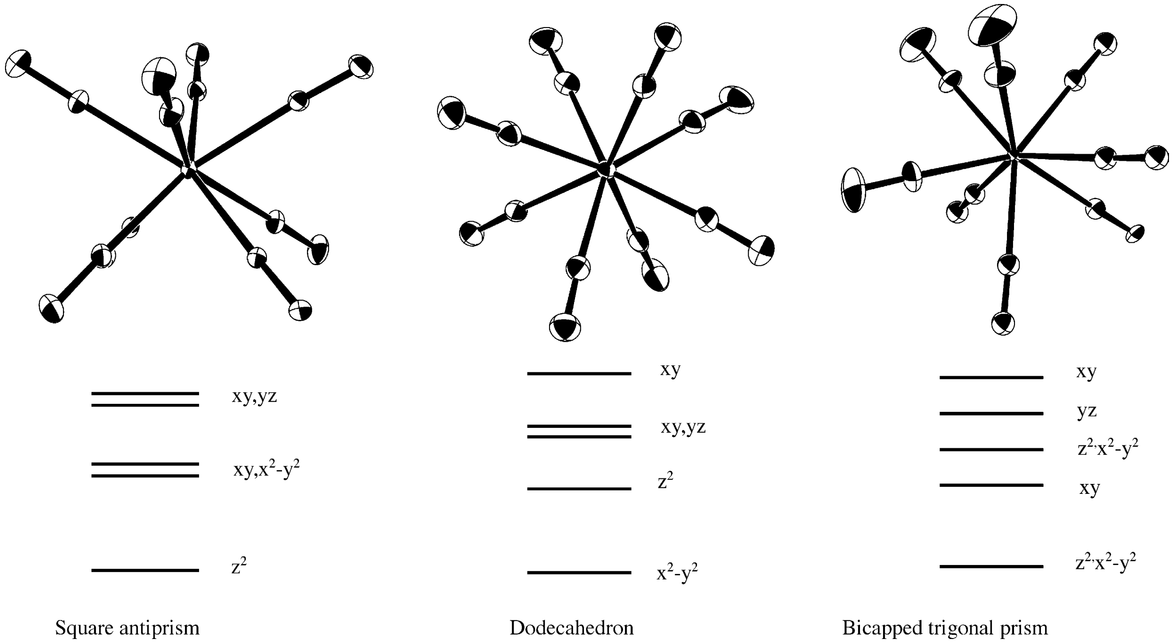


Plate 1.

CN^- ligands by OH^- ions [4]. Since then, the reactivity and photoreactivity of octacyanometalates have been studied till early nineties [5].

Recently, the octacyanometalate of Mo and W redox couples, offering eight cyano ligands potentially able to form cyano-bridged networks with 3d metal centres, have opened the new very attractive subject in crystal engineering. Their appealing new topologies, interesting structural features and collective properties are very promising material of potential applications in modern information storage technology, optical devices and microelectronics or as nano-porous materials. The research in this field has resulted in high-nuclearity octacyanometalate-based molecules and polymeric coordination networks of magnetic and photomagnetic properties, built by Mn(II) [6–23], Co(II), Co(III) [10,18,24–27], Mn(III) [28,29], Cu(II) [30–48] and Ni(II) [15,49–51] centres.

The design of such molecular architectures is based on the widely employed building block (tecton) methodology in solution [52] consisting in the substitution of the labile coordination sites in cationic complexes by the octacyanometalate anions acting as ligands. The formation of coordinate M–CN–M′ bonds between mononuclear molecular precursors is accompanied by intermolecular π–π stacking, hydrogen bonding and electrostatic interactions.

The topology of self-assembled coordination network is encoded into the individual building blocks due to their steric, topological and intermolecular bonding capabilities. In particular, the inherent coordination preferences of the metal cationic building blocks used in the assembly process are coupled with the stereochemical non-rigidity and coordination versatility of octacyanometalate moiety [53]. The octacyanometalate anions display three idealized basic geometries: square antiprism (SAPR-8, D_{4d}), dodecahedron (DD-8, D_{2d}) or bicapped trigonal prism (TPRS-8, C_{2v}) (Chart 1). The spatial configuration and therefore the exact ordering of the d-levels is very sensitive to the crystallographic environment, i.e. counterions and/or solvent. Moreover, polytopal rearrangements of SAPR-8, DD-8 and TPRS-8 geometries are found to be barrierless [54].

This review will focus on the $[M(CN)_8]^{3-/4-}$ (M = Mo and W) complex ions in constructing coordination networks with Mn(II), Mn(III), Co(III), Cu(II) and Pt(II) convergent precursor centres. The convergent cationic 3d complexes contain blocking polydentate ligands and labile ligands at *cis* or *trans* positions. This enables the propagation of polymeric framework into the required directions favouring low-dimensional architectures. Generally, our synthetic strategy and crystal engineering is based on exploring (i) different oxidation states of octacyanometalates precursors related to two possible ground spin states: $S = 0$ or 1/2 for M(IV) and M(V), respectively; (ii) the metal-to-metal charge-transfer transition (MMCT) leading to the photomagnetic systems.

The different coordination geometry along with the degree of chelation of cationic tectons as well as octacyanometalate coordination functionality leads to a range of diverse molecules and coordination polymers resulting in the adoption of 0-D, 1-D or 2-D distinct topologies. In the case of *cis*-protected octahedral cationic tectons of Mn(II) and Co(III) either architectures based on a 0-D molecular square or fragment of 1-D zigzag chain are formed. The use of simple salen ligand [salen = the *N*,*N*′-ethylenebis(salicylideneaminato) dianion] and its *trans*-protected Mn^{III} complexes leads to either the $Mn_3^{II}W^{V}$ molecules or the $\{Mn_3^{II}Mo^{IV}\}_n$–1-D zigzag chains. Steric hindrance at Schiff-base 3-OMesalophen [3-OMesalophen = the *N*,*N*′-*o*-phenylenebis(3-methoxy-salicylideneaminato) dianion] ligand results in the formation of 0-D $\{Mn^{III}W^{V}\}^{2-}$ anions. The aliphatic polyamine copper(II) tectons with $[N_3]$ donor atom sets lead to the construction of a family of related 1-D and 2-D coordination polymers. The release of the fully protonated polyamine ligands produces 2-D polymers with Cu(II) centres coordinatively saturated solely by CN bridges supplied by $[W(CN)_8]^{3-}$ ions.

A logical extension of the building-block approach is to combine the pre-organized multinuclear supramolecular coordination compound formed by 3d-metal centres bridged by organic linear *spacer* ligands with octacyanometalate moiety. In case of polynuclear $\{[Cu(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ (4,4′-bpy = 4,4′-bipyridine), the self-assembly results in the 2-D network, which is built of infinite Cu^{II} chains cross-linked by octacyanotungstate units.

The application of square planar Pt(II) complexes in the reactions with octacyanometalates(V) affords the ionic as well as cyano-bridged mixed-valence systems. The formation of trinuclear cyano-bridged M^{V}–CN–Pt^{IV}–NC–M^{V} complex in the inner-sphere redox requires the overcoming of stereochemical barrier created by octacyanometalate(V) moiety and, depending on the condition employed, the different reaction pathways for W(V) and Mo(V) are observed.

Each of these different coordination networks will be discussed and the structures that are observed, spectroscopic properties and magnetostructural correlations described and compared.

2. Architectures of octacyanometalate-based networks

2.1. Coordination networks based on Mn(II) complexes

The weak and moderate field Mn(II) octahedral complexes are particularly attractive as building blocks in formation of magnetic coordination networks due to their $3d^5$ electronic configuration leading to high electronic spin $S = 5/2$, generally good electrochemical stability as well as substitutional lability [55]. The formation of cyano-bridged bimetallic octacyanometalate(V,IV)-manganese(II) compounds dependent on the reaction conditions (i.e. solvent, blocking ligands or charge balancing ions) have been reported by a few other groups [6–19]. The use of $Mn^{II}(ClO_4)_2$-$[M^{V}(CN)_8]^{3-}$ substrates in alcoholic media leads to the formation of pentadecanuclear cyano-bridged clusters $[Mn_9{}^{II}Mn_6{}^{V}]$ with high spin ground state [6–8]. In contrast, the aqueous solution of these building blocks produces the extended 3-D coordination networks: $\{Mn_6{}^{V}(H_2O)_9[W^{V}(CN)_8]_4\cdot 13H_2O\}_n$ [9], characterized by a long-range ordering temperature $T_C = 54$ K, as well as paramagnetic $\{Mn_2{}^{II}(H_2O)_4[W^{IV}(CN)_8]\cdot 4H_2O\}_n$ [10] compound able to intercalate selectively ammonia and small primary amines. The incorporation of Cs^+ and CH_3COO^- counterions and/or addition of blocking ligand molecules result in totally different 3-D architectures: $\{[Mn_2{}^{II}(H_2O)_2(CH_3CO_2)][W^{V}(CN)_8]\cdot 2H_2O\}_n$ ($T_C = 40$ K) [11], $\{Mn_2{}^{II}Cs_{0.5}[W^{V}(CN)_8](CH_3CO_2)_{1.5}(H_2O)\}_n$ ($T_C = 45$ K) [11], $\{[Mn^{II}(pym)(H_2O)]_2[Mn^{II}(H_2O)_2][W^{V}(CN)_8]_2(pym)_2\cdot 2H_2O\}_n$ (pym = pyrimidine) ($T_C = 47$ K) [12], $\{Cs[Mn^{II}(3\text{-CNpy})_2][W^{V}(CN)_8]\cdot H_2O\}_n$ (3-CNpy = 3-cyanopyridine) ($T_C = 35$ K) [13] and $\{\mu\text{-bpym-}[Mn^{II}(H_2O)]_2\text{-}\mu\text{-}[(NC)_6M^{IV}(CN)_2]\}_n$ (bpym = bipyrimidine) [14]. The use of *trans*-protected cationic complexes favouring the 1-D architectures gives rise to the formation of cyano-bridged chain assemblies $\{[Mn^{II}L]_2[Nb^{IV}(CN)_8](H_2O)\cdot 5H_2O\}_n$ and $[Mn_2{}^{II}L_2(H_2O)_2][Mo^{IV}(CN)_8]\cdot 5H_2O$ (L = macrocyclic ligands) [15,16]. The latter compound has revealed the photomagnetic effect in solid state resulting in the appearance of Mn(II)–Mo(V) antiferromagnetic interaction.

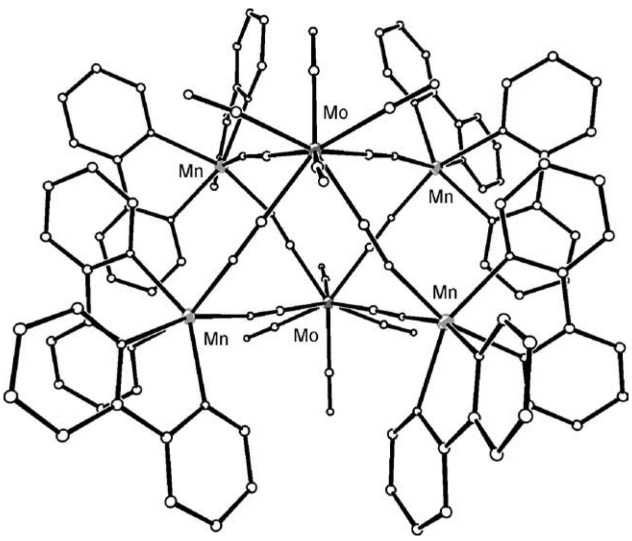


Fig. 1. The molecular structure of $[Mn^{II}(bpy)_2]_4[Mo^{IV}(CN)_8]_2\cdot 8H_2O$ (**1**) (adapted from Ref. [20]).

We were particularly interested in metal-directed self-assembly of *cis*-protected octahedral complexes leading to the formation of either molecular square or zigzag chain [52d]. Such polynuclear molecules or one-dimensional chains can be regarded as potential single-molecule magnets (SMM) [56] or single-chain magnets (SChM), respectively [57]. We have chosen *cis*-$[Mn(bpy)_2(H_2O)_2]^{2+}$ complex (bpy = 2,2′-bipyridyl), which reacted with $[M(CN)_8]^{4-}$ and $[W(CN)_8]^{3-}$ anions in aqueous solution to give two original 0-D cyano-bridged architectures: $[Mn^{II}(bpy)_2]_4[M^{IV}(CN)_8]_2\cdot 8H_2O$ [M = Mo (**1**), W (**2**)] [20] and $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\cdot 7H_2O$ (**3**) [21], respectively.

The crystal structure of **1** is built of cyano-bridged hexanuclear clusters $Mn_4{}^{II}Mo_2{}^{IV}$ of octahedral geometry (Fig. 1). The $[Mo(CN)_8]^{4-}$ moieties located at the axial sites coordinate four Mn centres located in equatorial sites. The molecule is realized then by two, mutually perpendicular, $Mn_2{}^{II}Mn_2{}^{IV}$ squares sharing the Mo corners. Four cyano bridges and four terminal cyano ligands of each $[Mo(CN)_8]^{4-}$ moiety are arranged in square antiprismatic geometry. The cyano-bridges

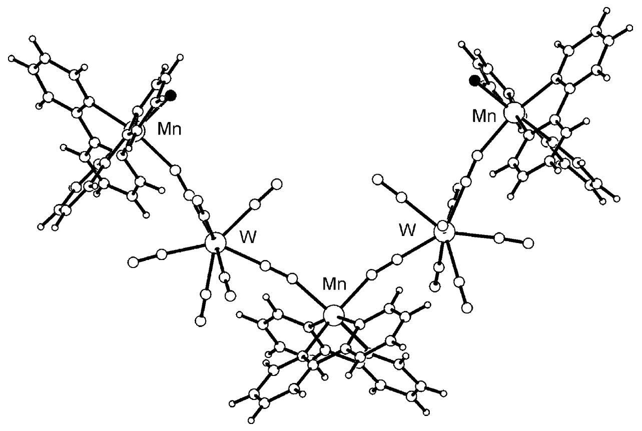


Fig. 2. The molecular structure of $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2 \cdot 7H_2O$ (**3**) (adapted from Ref. [21]).

are formed by the neighbouring ligands of the square wall of square antiprism. The Mn atoms retains a distorted octahedral geometry with two bpy ligands and bent cyano-bridges arranged in *cis*-positions. The supramolecular architecture of the $Mn_4^{II}Mn_2^{IV}$ lattice is controlled by CN-bridging, intra- and inter-molecular π–π stacking (face-to-face and edge-to-face) interactions and extensive network of hydrogen bonds between terminal cyano ligands and the water molecules. The compounds **1** and **2** are isostructural and generally reveal paramagnetic behaviour. At very low temperature antiferromagnetic intra- or intermolecular interactions are observed. The irradiated solids of $\{[Mn(bpy)_2]_4[M(CN)_8]_2\} \cdot 8H_2O$ display irreversible (**1**) or reversible (**2**) photo-induced magnetic modifications. The irradiation ($\lambda = 337$–357 nm) at 5 K in SQUID cavity results in formation of $Mn_2^{I}Mn_2^{II}Mn_2^{IV}$ photoproduct. The irradiation in the ambient conditions, in the presence of O_2, causes photodecomposition of cluster into $[Mn^{II}(bpy)_2(CN)_2]$ and $[M^{VI}(CN)_4(O_2)]$ [22].

The structure of **3** consists of V-shaped cyano-bridged pentanuclear molecules $Mn_3^{II}W_2^{II}$. Two W atoms are linked by single bent cyano bridges to three Mn centres in alternating sequence Mn–W–Mn–W–Mn (Fig. 2). In the molecule, the central $[Mn(bpy)_2]^{2+}$ moiety is bound to two $[W(CN)_8]^{3-}$ ions of distorted square antiprism geometry. Each of the $[W(CN)_8]^{3-}$ is coordinated also to terminal $[Mn(bpy)_2(H_2O)]^{2+}$ moieties. The cyano-bridges are formed by the two remote ligands with the C_{br}–W–C_{br} angle of 126.4°. The case hexacoordinated $[Mn(bpy)_2(NC)_2]$ or $[Mn(bpy)_2(NC)(H_2O)]^{+}$ moieties retain distorted octahedral geometry with ligand sets arranged in *cis*-geometry. In the crystal lattice the V-shaped molecules are packed into infinite columns due to π–π stacking of the bpy rings of the terminal and central Mn atoms of neighbouring molecules. Such arrangement leads to the existence of linear tubes, where H_2O molecules are located (Fig. 3). The compound **3** exhibits intramolecular antiferromagnetic coupling between Mn(II) and W(V) centres consistent with a ground state spin of $S = 13/2$ and intermolecular ferromagnetic coupling leading to the long-range magnetic ordering below 0.66 K.

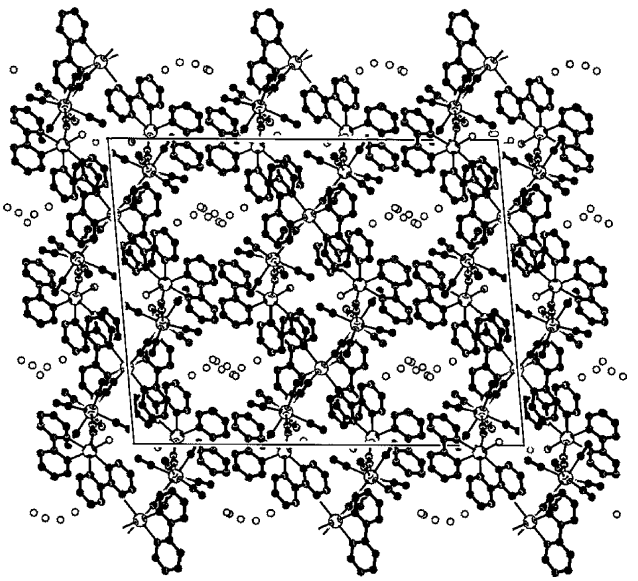


Fig. 3. π–π Stacking of bpy rings and the channels containing crystallization water molecules in $\{[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\} \cdot 7H_2O$ (**3**) (adapted from Ref. [21]).

The $Mn_4^{II}Mn_2^{IV}$ clusters are built of two cross-linked $Mn_2^{II}Mn_2^{IV}$ squares, while V-shaped $Mn_3^{II}W_2^{V}$ molecules can be considered as short-range chains, where propagation has been stopped at $Mn^{II}{:}W^{V} = 3{:}2$ stoichiometry. The 0-D topologies of **1–3** are assured by the electroneutrality as well as by the π–π stacking of bpy ligands, which seems to prevent the growth of the higher-dimensionality structures. It has also been reported recently by another group, that the change of reaction media from aqueous to DMF solution results in the formation of 1-D $\{[Mn^{II}(bpy)_2(DMF)_2]_2[M^{V}(CN)_8]_2[Mn^{II}(DMF)_4]\}_n$ architecture [17,18]. The presence of *O*-coordinated DMF led to the cyano-bridged chains consisting of $\{Mn_2W_2\}$ molecular squares joined by *trans*-$[Mn^{II}(NC)_2(DMF)_4]$ moieties. The compounds present long-range magnetic phase-transitions near 3 K with some glassy spin character of the W analogue.

In our investigation of octacyanometalate-based coordination networks we have also explored the possibility of lowering the symmetry of octacoordinated cyano building block by using the molecular precursor related to the octacyanotungstate(IV)—geometrically anisotropic $[W^{IV}(CN)_6(bpy)]^{2-}$ complex [58,59]. In $[W(CN)_6(bpy)]^{2-}$, which is not compatible with cubic geometry of hexacyano moieties, two coordination sites are occupied by bpy molecule acting as terminal blocking ligand and participating in secondary π–π stacking interactions. Therefore, $[W(CN)_6(bpy)]^{2-}$ has the advantage of formation of anisotropic, directional network over the homoleptic hexa- as well as octacyanocomplexes. Our strategy was similar to the synthetic approach based on the replacement of a highly symmetrical hexacyanoferrate(III) ion by lower symmetry $[Fe^{III}(CN)_4(phen)]^{-}$ [60], and $[Fe^{III}(CN)_4(bpy)]^{-}$ [61] precursors.

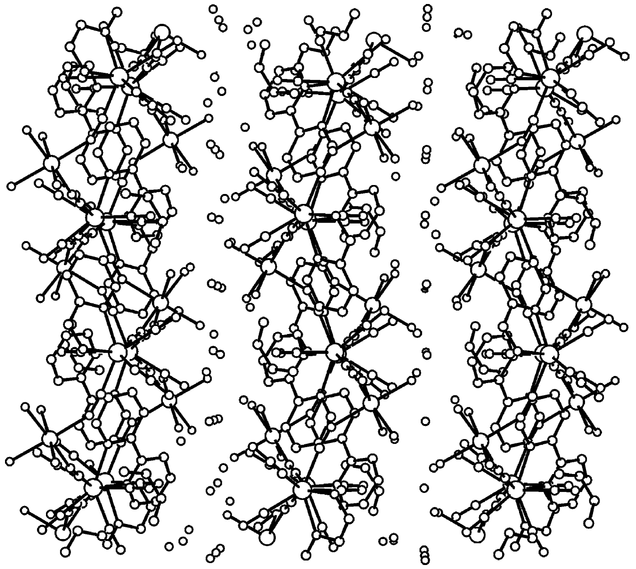


Fig. 4. Waved layers separated by crystallisation water molecules in $\{[fac\text{-}(H_2O)_3Mn^{II}\text{-}(\mu\text{-}NC)_3\text{-}W^{IV}(CN)_3(bpy)]\cdot 4.5H_2O\}_n$ (**4**). View along the *b* axis (adapted from Ref. [23]).

The self-assembly reaction of $[W(CN)_6(bpy)]^{2-}$ precursor with $[Mn(H_2O)_6]^{2+}$ in aqueous solution yielded two-dimensional coordination polymer $\{[fac\text{-}(H_2O)_3Mn^{II}\text{-}(\mu\text{-}NC)_3\text{-}W^{IV}(CN)_3(bpy)]\cdot 4.5H_2O\}_n$ (**4**) [23]. The crystal structure of **4** consists of neutral thick waved layers separated by crystallisation water molecules (Fig. 4). Within the layer, $[W(CN)_6(bpy)]^{2-}$ units form three bent cyano-bridges towards three $[Mn^{II}(H_2O)_3]$, whereas $[Mn^{II}(H_2O)_3]$ moieties are linked to three $[W(CN)_6(bpy)]^{2-}$ (Fig. 5). The cyano-bridges are formed by the three ligands with the angles C_{br}–W–C_{br} of 138.5°, 109.3° and 80.7°. Such coordination, along with face-to-face π–π stacked $[W(CN)_6(bpy)]^{2-}$ pairs, leads to the coexistence of spatially distorted small tetranuclear $W_2Mn_2(\mu\text{-}CN)_4$ and large octanuclear $W_4Mn_4(\mu\text{-}CN)_8$ polygons along the layer. The compound **4** is one of the first examples realizing the two dimensional basket weave-like pattern of $4,8^2$ topology (Fig. 6) [62]. The notation of $4,8^2$ topology for the regular and semi-regular 2-D networks means that in each node of the network one square motif neighbours two octagonal motifs [52d,63]. Aqua ligands of $[Mn(NC)_3(H_2O)_3]$ and non-bridging cyano ligands of $[W(CN)_6(bpy)]^{2-}$ are involved in the extensive network of hydrogen bonds linking parallel layers through the crystallisation water molecules being significant in construction of the system.

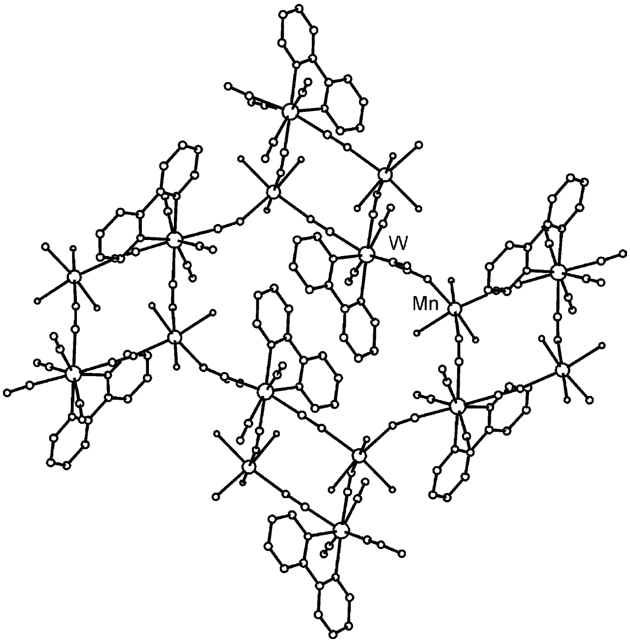


Fig. 5. Octanuclear Mn_4W_4 and tetranuclear Mn_2W_2 polygons in $\{[fac\text{-}(H_2O)_3Mn^{II}\text{-}(\mu\text{-}NC)_3\text{-}W^{IV}(CN)_3(bpy)]\cdot 4.5H_2O\}_n$ (**4**) (adapted from Ref. [23]).

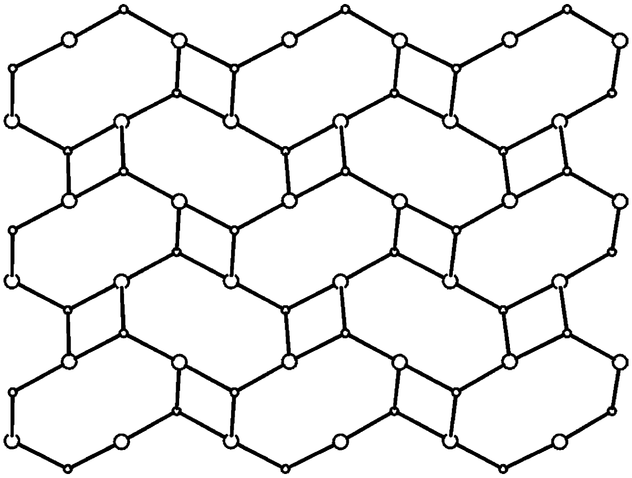


Fig. 6. $4,8^2$ topology of 2-D architectures of $\{[fac\text{-}(H_2O)_3Mn^{II}\text{-}(\mu\text{-}NC)_3\text{-}W^{IV}(CN)_3(bpy)]\cdot 4.5H_2O\}_n$ (**4**) (adapted from Ref. [23]).

2.2. *Coordination networks based on Co(II) and Co(III) complexes*

Cobalt(II) and cobalt(III) complexes continue to attract attention as building blocks in construction of functional materials, which may act as nano-switches or memory devices. The Co(II,III) coordination networks can reveal bistability properties involving the reversible intermetallic spin-transition or low-spin ⇔ high-spin transitions under the action of temperature, pressure or visible light irradiation. In some cases simultaneous presence of Co(III) and Co(II) in bimetallic networks is required for the observation of spin-transition phenomenon [64]. Moreover, high-spin cobalt(II) complexes reveal significant internal magnetic anisotropy and introduce the additional anisotropy feature into the coordination network. In particular, the presence of magnetic hysteresis loop, as required experimental evidence for the SMMs or SChMs [56,57], can be observed.

Only a few examples of cobalt-octacyanometalate coordination networks have been reported until now [10,18,24–27].

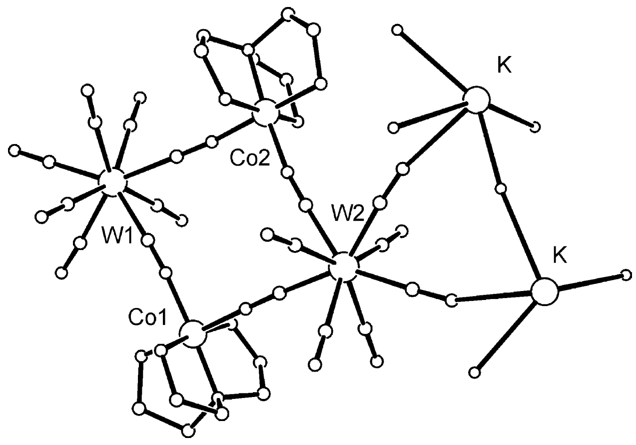


Fig. 7. Co_2W_2 square in $K_2\{[Co^{III}(tren)]_2[W^{IV}(CN)_8]_2\}\cdot 9H_2O$ (**5**) (adapted from Ref. [27]).

The slow diffusion of aqueous solutions of $Co^{II}(NO_3)_2$ and appropriate octacyanotungstate gave two 3-D cyano-bridged networks: (i) $\{[W^V(CN)_2]_2[(\mu\text{-}CN)_4Co^{II}(H_2O)_2]_3\cdot 4H_2O\}_n$ [24] characterised by $T_C = 18$ K as well as magnetic hysteresis loop of coercive field $H_c = 600$ Oe and remnant magnetisation M_r equal to ca. 50% of magnetisation at saturation and (ii) paramagnetic $\{Co_2{}^{II}(H_2O)_4[W^{IV}(CN)_8]\cdot 4H_2O\}_n$ [10,24,25], isostructural to manganese(II) analogue and of similar properties (vide supra). In DMF solution, 1-D architecture of $\{[Co_3{}^{II}(DMF)_{12}][W^V(CN)_8]_2\}_n$ is formed [18]. The compound is characterised by ferromagnetic long-range ordering with glassy spin behaviour below 7.3 K and magnetic hysteresis loop of $H_c = 907$ Oe at 2 K. It has been reported also that the mixing of $Co^{II}Cl_2$, $Cs_3[W^V(CN)_8]$ and 3-cyanopyridine affords 2-D network of $Cs^I\{[Co^{II}(3\text{-}CNpy)_2][W^V(CN)_8]\}\cdot H_2O$ [26]. It is the first example of Co^{II}–W^V based compound exhibiting the *charge-transfer-induced spin-transition* (CTIST) between $Co^{II}(S = 3/2)W^V(S = 1/2)$ (high-spin, HS) high-temperature phase (HT) and $Co^{III}(S = 0)W^{IV}(S = 0)$ (low spin, LS) low-temperature phase (LT) with a wide thermal hysteresis loop in the range 167–216 K. Furthermore, irradiation within the MMCT band of low-temperature phase induces *light-induced excited spin state trapping* (LIESST) of the metastable HS $Co^{II}(S = 3/2)W^V(S = 1/2)$ phase vanishing under heating to about 30 K.

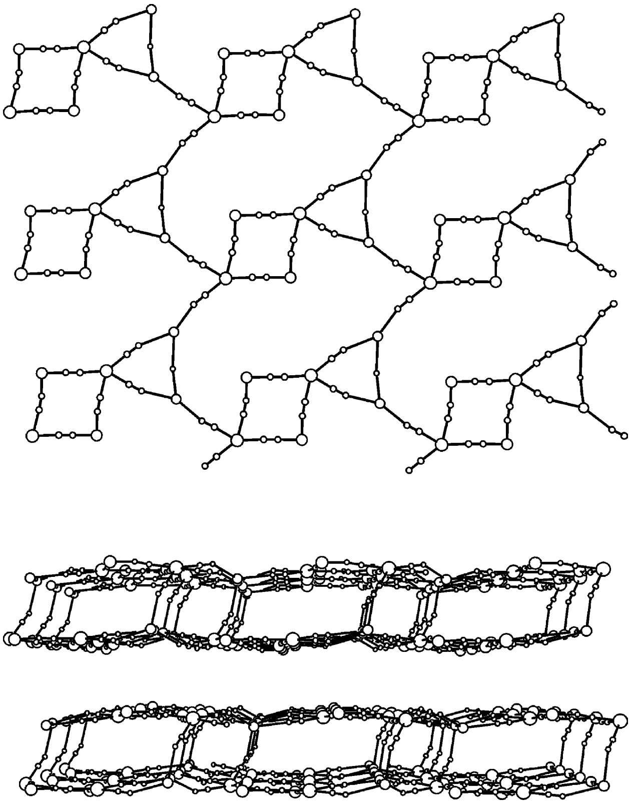


Fig. 8. View of the monolayer in $K_2\{[Co^{III}(tren)]_2[W^{IV}(CN)_8]_2\}\cdot 9H_2O$ (**5**). View along the *bc* plane (top) and the *b* direction (bottom) (adapted from Ref. [27]).

We were particularly interested in construction of Co^{III}–octacyanometallate(IV) discrete clusters, characterised by MMCT transition and acting as photomagnetic switches. We have prepared $K_2\{[Co^{III}(tren)]_2[W^{IV}(CN)_8]_2\}\cdot 9H_2O$ (**5**) [tren = tris(2-aminoethyl)amine] and $K_2\{[Co^{III}(trien)]_2[W^{IV}(CN)_8]_2\}\cdot 8H_2O\cdot EtOH$ (**6**) [trine = triethylenetetramine] [27]. Compound **5** contains $\{[Co(tren)]_2[W(CN)_8]_2\}^{2-}$ square units bridged by potassium ions into two-dimensional bilayered array of MMCT characteristics. The $\{[Co(tren)]_2[W(CN)_8]_2\}^{2-}$ consists of the alternating $[Co^{III}(NC)_2(tren)]$ and $[W^{IV}(CN)_8]$ corners joined by bent cyano-bridges (Fig. 7). Each W(IV) centre has two bridging and six terminal cyano ligands arranged in a slightly distorted square antiprismatic geometry. The cyano-bridges are formed by the two neighbouring ligands with the angles C_{br}–W–C_{br} of 72.9 and 73.3°. The hexacoordinate $[Co(tren)(NC)_2]^+$ units present a distorted octahedral geometry with two CN^- ligands arranged in *cis* positions. The $\{[Co(tren)]_2[W(CN)_8]_2\}^{2-}$ squares are linked by potassium cations involving two terminal cyano ligands of each W centre to form a two-dimensional layer structure (Fig. 8, top). Formation of the layered structure by –CN–K–NC– linkage conforms to the analogous phenomena in some cyano-bridged networks based on hexacyanometalates [65,66]. The K^+ centres bind additionally solvent water to give seven and six coordinate K^+ ions. One of the water molecules forms the bridge between potassium ions leading to additional triangular WK_2 motif of the bridged layer. The neighbouring layers related by $(-x, -y+1$ and $-z+1)$ 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 K^+ and one of $[W(CN)_8]^{4-}$ corners of $\{[Co(tren)]_2[W(CN)_8]_2\}^{2-}$ square (Fig. 8, bottom). Layers are also linked through extensive network of hydrogen bonds involving interactions between cyano ligands, tren 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 counter-cation and solvent can be used to control the dimensionality of the lattice. The ESI MS spectra of **6** revealed the presence of $\{[Co^{III}(trien)]_2[W^{IV}(CN)_8]\}^{2-}$ molecular square in aqueous solution.

Compounds **5** and **6** exhibit metal-to-metal charge-transfer (MMCT) transitions at 519 and 512 nm in aqueous solution, respectively. MMCT irradiation of **5** does not lead to photoinduced modification of ground spin state of metal centres due to very low energy barrier for back electron transfer to the ground state. However, they present very elegant examples of 0-D bimetallic discrete $Co_2{}^{II}Mn_2{}^{IV}$ squares being the starting point for crystal engineering of Co–octacyanometalate systems of potential photomagnetic properties.

2.3. Coordination networks based on manganese(III) Schiff-base complexes

It has been already shown that quadridentate Mn(III) Schiff-base complexes are potentially interesting precursors of the polynuclear cyano-bridged magnetic systems due to magnetic anisotropy related to Mn(III) centre and high-spin ground state ($S = 4/2$) [67]. They display slightly oxidizing properties and usually, in solution, exist in equilibrium between mononuclear $[Mn^{III}(SB)(S)]^{n+}$ (SB = quadridentate Schiff-base ligand and S = solvent) and dinuclear phenolate-bridged $[Mn_2{}^{III}(SB)_2(S)_2]^{2n+}$ complex.

The self-assembly reaction between $[Mn^{III}(salen)(H_2O)]ClO_4$ and $K_4[W^{IV}(CN)_8]$ leads to formation of tetranuclear $[Mn^{III}(salen)(H_2O)]_3[W^{V}(CN)_8]\cdot H_2O$ (**7**) molecules [28]. Regardless of the substrates molar ratio, the resulting product presents Mn/W 3:1 stoichiometry due to the electroneutrality of the system.

In slightly distorted V-shaped molecules of **7**, metallic centres are linked through the two cyano bridges and one single phenolate bridge (Fig. 9). The hexacoordinated Mn(III) moieties [Mn (**1**) and Mn (**2**) centres] have equatorial positions occupied by quadridentate salen ligand and axially coordinated aqua ligand and nitrogen bonded bridging cyanides. In case of Mn (**3**), centre one of the axial positions is occupied by the oxygen phenolate atom from the neighbouring Mn (**2**) moiety. The distance between Mn (**3**) and $O_{phenolate}$ is 2.979(3) Å and lies in the middle of the range of phenolate bridges typical for the quadridentate Mn(III) Schiff-base complexes. The $[W^{V}(CN)_8]^{3-}$ unit displays a distorted square antiprism geometry (D_{4d}). It has two bridging and six terminal cyano ligands. In the crystal lattice, the neighbouring molecules of **7** are linked through the hydrogen bonds between aqua ligands and phenolate oxygen as well as by the face-to-face π–π stacking interactions of the salen rings. The tetranuclear molecules are arranged in columns along the *a* direction and stabilized by the hydrogen bonds network (Fig. 10).

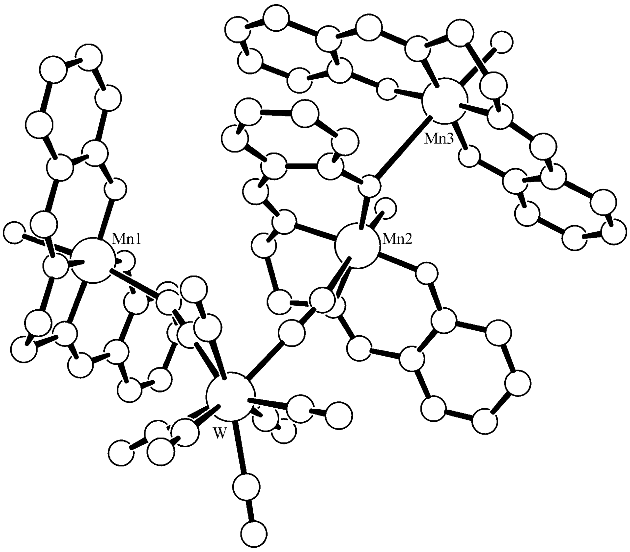


Fig. 9. Asymmetric unit of $[Mn^{III}(salen)(H_2O)]_3[W^{V}(CN)_8]\cdot H_2O$ (**7**) (adapted from Ref. [28]).

The magnetic studies of **7** reveal the antiferromagnetic intramolecular interactions through the CN and phenolate bridges and an antiferromagnetic lon-range ordering below $T_N = 4.6$ K with planar anisotropy and the *spin-flop* transition from the antiferromagnetic ground state of $S_T = 3/2$ to the state of $S_T = 5/2$ in the external magnetic field.

The self-assembly of $[Mn^{III}(salen)(H_2O)]^+$ and $[Mo^{IV}(CN)_8]^{4-}$ in aqueous solution leads to the formation of one-dimensional $[Mn^{III}(salen)(H_2O)_2]_2\{[Mn^{III}(salen)(H_2O)][Mn^{III}(salen)]_2[Mo^{IV}(CN)_8]\}\cdot 0.5ClO_4\cdot 0.5OH\cdot 4.5H_2O$ (**8**) [28]. The crystal structure of **8** consists of the $\{[Mn(salen)(H_2O)][Mn(salen)]_2[Mo(CN)_8]\}_n{}^-$ zigzag chains, isolated $[Mn(salen)(H_2O)_2]^+$ cations, $ClO_4{}^-$ counter-anions and water molecules. In the $\{Mn_3Mo\}^-$ repeating

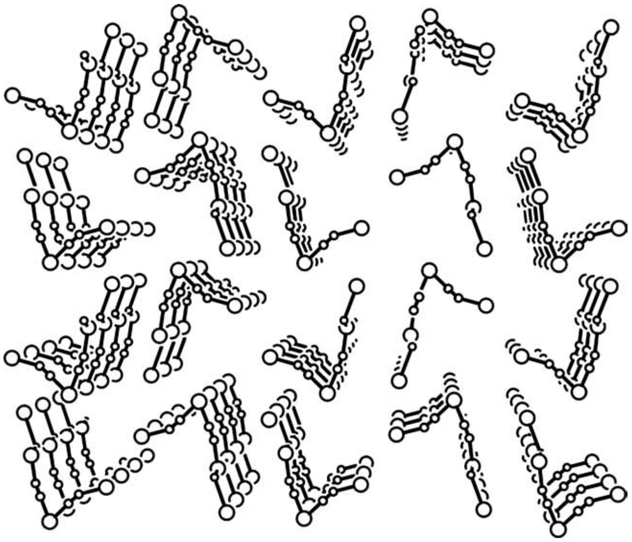


Fig. 10. Packing diagram of $[Mn^{III}(salen)(H_2O)]_3[W^{V}(CN)_8]\cdot H_2O$ (**7**) along the *a* axis. Ligands are omitted for clarity (adapted from Ref. [28]).

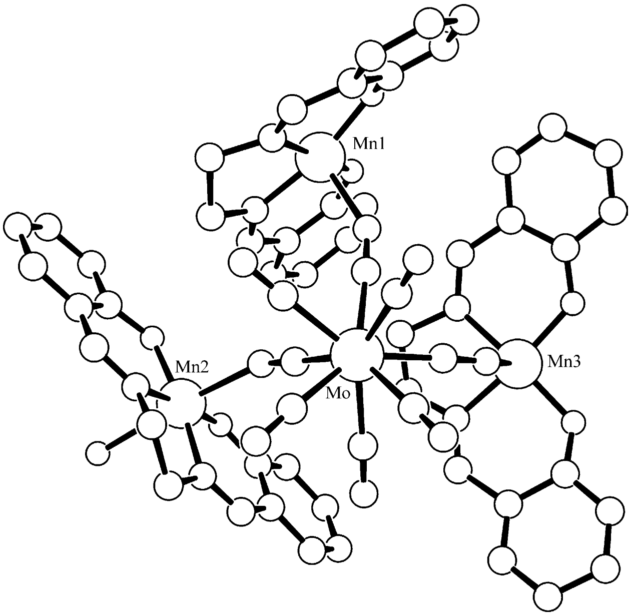


Fig. 11. $\{Mn^{III}{}_3Mo^{IV}\}^-$ repeating unit of $[Mn^{III}(salen)(H_2O)_2]_2\{[Mn^{III}(salen)(H_2O)][Mn^{III}(salen)]_2[Mo^{IV}(CN)_8]\}\cdot 0.5ClO_4\cdot 0.5OH\cdot 4.5H_2O$ (**8**) (adapted from Ref. [28]).

unit each Mn(III) moiety is hexacoordinated having the aqua and nitrogen bonded cyano ligands arranged in *trans* positions (Fig. 11). The $[Mo^{IV}(CN)_8]^{4-}$ unit displays a square antiprism geometry (D_{4d}) where three neighbouring cyano ligands are coordinated to the Mn(III) centres.

The 1-D chains are arranged along the *b* direction (Fig. 12). The neighbouring repeating units are linked through the double phenolate bridges at Mn (**1**) or Mn (**3**) centres which is typical for the Mn(III) Schiff-base complexes. In the Mn (**2**) moiety the axial position is occupied by an aqua ligand preventing from the phenolate bridging. The neighbouring zigzag chains of **8** are linked through the hydrogen bonds between aqua ligands and phenolate oxygen as well as by the face-to-face π–π stacking contacts of the salen rings of Mn (**2**) moieties. The supramolecular interactions provide the linking of 1-D chains into layers parallel to the $(1\,0\,\bar{1})$ plane (Fig. 12).

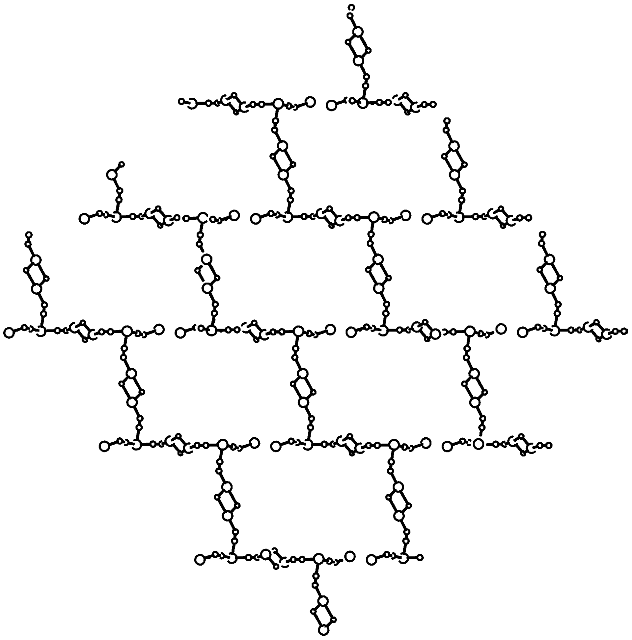


Fig. 12. Packing diagram of 1-D chains of $[Mn^{III}(salen)(H_2O)_2]_2\{[Mn^{III}(salen)(H_2O)][Mn^{III}(salen)]_2[Mo^{IV}(CN)_8]\}\cdot 0.5ClO_4\cdot 0.5OH\cdot 4.5H_2O$ (**8**) along the *a* axis. Ligands and counter-ions omitted for clarity (adapted from Ref. [28]).

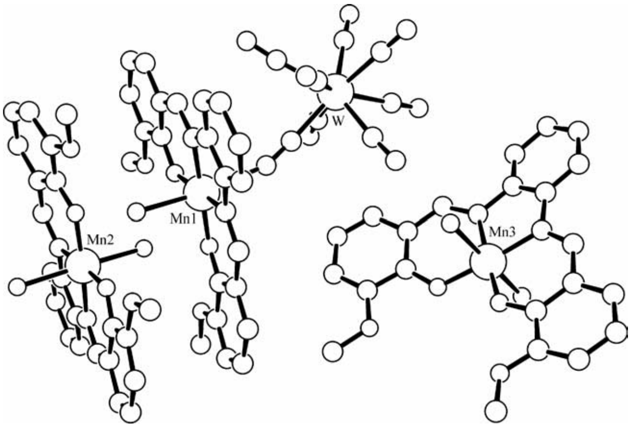


Fig. 13. Asymmetric unit of $[Mn^{III}(3\text{-OMesalophen})(H_2O)_2]_2[Mn^{III}(3\text{-OMesalophen})(H_2O)][W^V(CN)_8]\cdot 2H_2O$ (**9**) (adapted from Ref. [29]).

In consequence of the separation of the Mn(III) centres by the diamagnetic Mo(IV) spacer, the magnetic behaviour of **8** is nearly paramagnetic with a very weak antiferromagnetic coupling of Mn(III) centres through the phenolate bridges.

The Mn(III) Schiff-base complexes are likely to form single or double phenolate bridges leading to antiferromagnetic or ferromagnetic coupling [68a]. Indeed, the compound **7** has the antiferromagnetic ground state of $S_T = 3/2$ due to formation of the phenolate bridges.

In an effort to raise the ground state total spin, we decided to use of more bulky and less flexible 3-OMesalophen ligand at Mn(III) centre. The $[Mn^{III}(3\text{-OMesalophen})(H_2O)_2]^+$ complex contains the 3-OMe substituents as well as axially coordinated aqua ligands which should prevent from the formation of the phenolate bridges [68b] and form only cyano-bridged molecule. The self-assembly reaction of $[Mn^{III}(3\text{-OMesalophen})(H_2O)_2]^+$ with $[W^V(CN)_8]^{3-}$ leads to the zero-dimensional $[Mn^{III}(3\text{-OMesalophen})(H_2O)_2]_2[Mn^{III}(3\text{-OMesalophen})(H_2O)][W^V(CN)_8]\cdot 2H_2O$ (**9**) compound [29].

In the crystal, the asymmetric unit of **9** consists of anionic $\{[Mn^{III}(3\text{-OMesalophen})(H_2O)][W^V(CN)_8]\}^{2-}$ dimers, $[Mn^{III}(3\text{-OMesalophen})(H_2O)_2]^+$ countercations and H_2O molecules (Fig. 13). In the dimeric unit, the Mn(III) moiety is linked to the W(V) centre of slightly distorted square antiprism geometry (D_{4d}) through the one single cyano bridge. The cationic Mn(III) moieties are hexacoordinated having H_2O molecules arranged in *trans* positions.

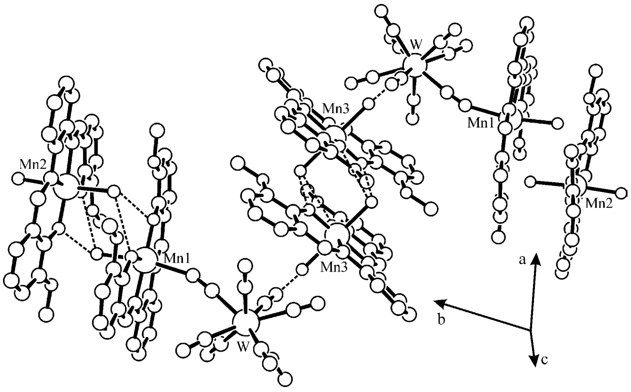


Fig. 14. H-bonded supramolecular unit of $[Mn^{III}(3\text{-}OMesalophen)(H_2O)_2]_2[Mn^{III}(3\text{-}OMesalophen)(H_2O)][W^{V}(CN)_8]\cdot 2H_2O$ (**9**) (adapted from Ref. [29]). Hydrogen bonds between axially coordinated H_2O molecules and phenolate oxygen atoms generated by symmetry are omitted for clarity.

The axially coordinated aqua ligands form the hydrogen bonds with the phenolate oxygen atoms and nitrogen atoms from the terminal cyano ligands. In consequence, two neighbouring asymmetric units of **9** are arranged into H-bonded supramolecular unit (Fig. 14). The donor–acceptor distances in the range of 2.903–2.997 Å for O_{water}–$O_{phenolate}$ and O_{water}–$N_{cyanide}$ bonds suggest the medium strength of the H-bonds. Along with hydrogen bonds the face-to-face π–π stacking of the 3-OMesalophen aromatic rings provide the formation of the supramolecular units.

The cyano and H-bonds linkages in **9** results in antiferromagnetic behaviour with $T_N = 4.3$ K.

The most characteristic for the $[Mn^{III}(SB)(S)]^{n+}$-$[M(CN)_8]^{3-/4-}$-based polynuclear systems are single and double phenolate bridges and H-bonds between axially coordinated solvent and phenolate oxygen atoms. The formation of μ-$O_{phenolate}$ linkage or H-bonds depends on the nature of the Schiff-base ligand. The extended aromatic parts of Schiff-base ligands are favourable for the π–π stacking interactions. The formation of the cyano bridges is usually limited by the Jahn–Teller effect at Mn(III) centre.

2.4. *Coordination networks based on Cu(II) complexes*

Copper(II) complexes characterised by the electronic spin $S = 1/2$ along with the different coordination geometries were widely used as building blocks in construction of magnetic polynuclear networks [69]. They are also very effective in design and synthesis of magnetic and photomagnetic cyano-bridged octacyanometalate-based assemblies [30–48]. The bare Cu(II) centres in aqueous solution coordinate $[Mo^{V}(CN)_8]^{3-}$ to give the 3-D polymeric network $\{Co_{1.5}{}^{II}[Mo^{V}(CN)_8]\cdot 3H_2O\}_n$ characterised by $T_C = 35$ K [30]. The incorporation of 3- and 4-CNpy blocking ligands results in formation of two original 2-D networks $\{[Cu^{II}(3\text{-}CNpy)_2(H_2O)_2]_2[Cu^{II}(3\text{-}CNpy)_2(H_2O)_2][W^{V}(CN)_8]_2\}_n$ and $\{[Cu^{II}(4\text{-}CNpy)_2]_2[Cu^{II}(4\text{-}CNpy)_2(H_2O)_2][W^{V}(CN)_8]_2\cdot 6H_2O\}_n$, revealing T_N of 8 and 4.4 K, respectively, and metamagnetic behaviour in low temperature [31]. The use of polyamine blocked Cu(II) complexes leads to the series of further unique architectures. Three-dimensional $\{[Cu^{II}(en)_2]_3[W^{V}(CN)_8]\cdot H_2O\}_\infty$ (en = ethylenediamine) network is constructed of adjacent cube-like W_8Cu_{12} motifs with isolated $[W(CN)_8]^{3-}$ as a molecular template [32]. Two-dimensional assemblies $[Cu^{II}(L)]_3[W^{V}(CN)_8]_2\cdot 3H_2O$ (L = tn: 1,3 diaminopropane, pn: 1,2-diaminopropane) provide another example of networks characterised by metamagnetism [33]. Application of $[O_3N]$-donor $TeaH_3$ tripodal ligand ($TeaH_3$ = triethanolamine) affords the $Cu_2{}^{II}(TeaH_2)_2$ O-bridged dimers coordinating $[W(CN)_8]^{3-}$ as well as reduced $[W(CN)_8]^{4-}$ into a 3-D open network containing the layers of brick-wall topology [34].

The coordination networks built of diamagnetic $[M^{IV}(CN)_8]^{4-}$ (d^2) building blocks are employed in the synthesis of potentially photomagnetic materials. The light-induced modifications of magnetic properties consisting in photo-oxidation of $[M^{IV}(CN)_8]^{4-}$ to $[M^{V}(CN)_8]^{3-}$ were observed in 3-D $\{Cu_2{}^{IV}[Mo^{IV}(CN)_8]\}\cdot xH_2O$ [30,35,36] as well as 0-D $[Cu^{II}(bpy)_2]_2[Mo^{IV}(CN)_8]\cdot 5H_2O\cdot CH_3OH$ [35] or $\{Mo^{IV}(CN)_2[CN\text{-}Cu^{II}(tren)]_6\}(ClO_4)_8$ [37]. The further octacyanotungstate(IV)-based compounds provide further examples of original cyano-bridged architectures: 3-D $\{[Cu(en)_2][Cu(en)][W^{IV}(CN)_8]\cdot H_2O\}_n$ [38], 2-D $\{[Cu(cyclam)]_2[Mo^{IV}(CN)_8]\cdot 10.5H_2O\}_n$ [39] or 1-D $\{Cu_2{}^{II}(NH_3)_8[Mo^{IV}(CN)_8]\}_n$ [40].

We have investigated the role of coordination geometry along with the degree of chelation in cationic Cu(II)-polyamine complexes in self-assembly with octacyanometalates precursors [44–48]. Our strategy is based on the pH-dependent coordination of polyamine ligand in $[Cu(tetren)]^{2+}$ (tetren = tetraethylenepentaamine). The stepwise protonation of $[Cu(tetren)]^{2+}$ results in subsequent dechelation of the N atoms of tetren ligand and generates three complex forms: (i) $[Cu(tetren)]^{2+}$ at pH > 6 ($[N_5]$ coordination of tetren), (ii) $[Cu^{II}(tetrenH_2)(H_2O)_2]^{4+}$ and/or $[Cu^{II}(tetrenH)(H_2O)_2]^{3+}$ at pH range 3–5 ($[N_3]$ coordination of tetren) and (iii) $[Cu(H_2O)_6]^{2+}$ at pH < 2 (release of $tetrenH_5{}^{5+}$) [44].

Setting the initial pH to 7.0, the self-assembly of coordinatively saturated $[Cu(tetren)]^{2+}$ units together with $[W(CN)_8]^{3-}$ affords $[Cu^{II}(tetrenH_2)]_2[W^{IV}(CN)_8]_2\cdot 8H_2O$ (**10**) [44]. The formation of **10** is preceded by the reduction of $[W^{V}(CN)_8]^{3-}$ to $[W^{IV}(CN)_8]^{4-}$. The crystal structure of **10** is built of 1-D chains formed by Cu_2W_2 molecular squares joined alternately by cyano bridges (Fig. 15). The copper(II) moieties presents square pyramidal (Cu1) or axially distorted *mer*-octahedral (Cu2) geometry. Coordination sites of copper centres are occupied by the three second order amine N donor atoms originating from tetren ligand and aligned in the equatorial (Cu1) or the meridional (Cu2) plane, respectively. The coordination is completed by two (Cu1) or three (Cu2) CN^- bridging ligands, respectively. Octacyanotungstate building blocks exhibit distorted dodecahe-

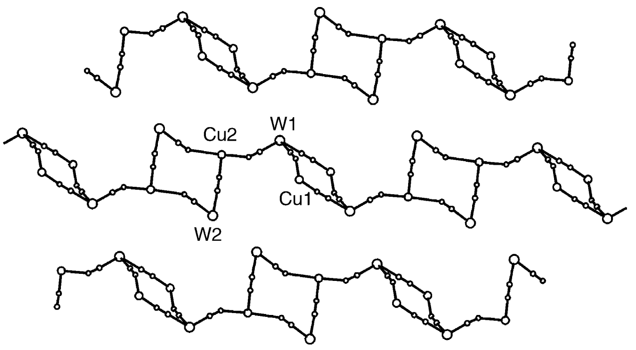


Fig. 15. View of the chain of $[Cu^{II}(tetrenH_2)]_2[W^{IV}(CN)_8]_2 \cdot 5H_2O$ (**10**). Atoms not involved in bridging have been omitted for clarity (adapted from Ref. [44]).

dral geometry, forming three CN^- bridges with C–W1–C–W angles of 72.2°, 73.9° and 124.3° or two CN^- bridges with C–W2–C angle of 75.0°, respectively. Hydrogen bonds between the terminal amino groups of $tetrenH_2$, terminal cyano ligands and water molecules join the chains together, forming a 3-D architecture. The formation of **10** is the result of breaking of two terminal nitrogen Cu–N bonds in $[Cu(tetren)]^{2+}$ and reduction of W(V) to W(IV). This has been confirmed by the direct synthesis of 10 from $[Cu^{II}(tetrenH_2)(H_2O)_2]^{4+}$ and $[W^{IV}(CN)_8]^{4-}$.

Setting the initial pH to 3.5, $[Cu^{II}(tetrenH_2)(H_2O)_2]^{4+}$ assembles with $[W^{V}(CN)_8]^{3-}$ to give the 1-D $[Cu^{II}(tetrenH_2)]$ $[Cu^{II}(tetrenH)]$ $[W^{V}(CN)_8][W^{IV}(CN)_8] \cdot 13H_2O$ (**11**) [44]. The formation of **11** is preceded by the partial reduction of $[W^{V}(CN)_8]^{3-}$ to $[W^{IV}(CN)_8]^{4-}$ and a simultaneous increase of pH to 4.5 resulting in the presence of $[Cu^{II}(tetrenH_2)(H_2O)_2]^{4+}$ and $[Cu^{II}(tetrenH)(H_2O)_2]^{3+}$. The product **11** reveals a 1-D polymeric structure of a three-row pattern (Fig. 16). The central row is built from Cu_2W_2 square units, while the two side rows consist of rectangular six-membered Cu_3W_3 units. Both copper(II) centres have the distorted octahedral geometry with three N donors of tetren ligand and three N ends of bridging CN^- ligands aligned in meridional planes of the complexes. Octacyanotungstate moieties feature distorted square antiprism geometry. The $[W(CN)_8]^{n-}$ ions reveal two different types of connectivity: the W1 centres located in the central row bridge four Cu centers with C–W1–C angles of 73.9°, 76.4°, 79.6°, 116.1°, 142.2° and 142.9°, whereas W2 centres in the side rows bind two Cu centers with the C–W2–C angle of 119.9°. Hydrogen bonds between the terminal amino groups of $tetrenH_2$, terminal cyano ligands and water molecules join the chains together, forming a 3-D architecture.

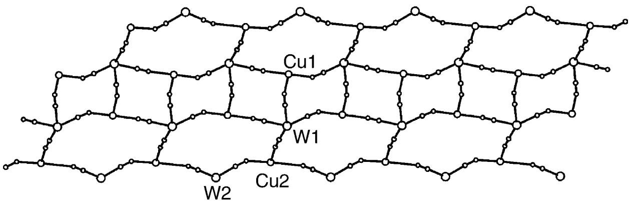


Fig. 16. The polymeric chain structure of $[Cu^{II}(tetrenH_2)][Cu^{II}(tetrenH)][W^{V}(CN)_8][W^{IV}(CN)_8] \cdot 2.5H_2O$ (**11**). Non-bridging atoms have been omitted (adapted from Ref. [44]).

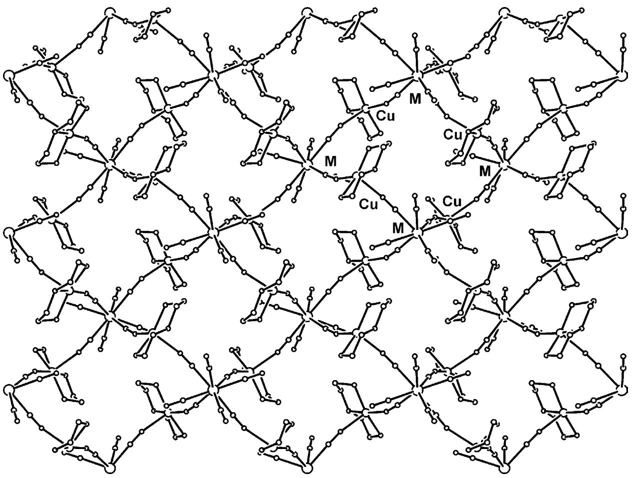


Fig. 17. View on the 2-D square grid structure of $[Cu^{II}(dien)]_2[M^{IV}(CN)_8] \cdot 4H_2O$ (**12**, **13**) (adapted from Ref. [44]).

The $[Cu(dien)(H_2O)_2]^{2+}$ (dien = diethylenetriamine) tecton analogous to the previous case $[N_3O_2]$ coordination set reacts with $[M(CN)_8]^{4-}$ generating two isomorphic $[Cu^{II}(dien)]_2[M^{IV}(CN)_8] \cdot 4H_2O$ [M = Mo (**12**) and W (**13**)] 2-D coordination polymers [44]. The crystal structure of **12** and **13** contains strongly waved cyano-bridged grid-type layers. The layer is built of edge sharing Cu_4M_4 squares with $[M(CN)_8]^{4-}$ at the corners and $[Cu(dien)]^{2+}$ in the middle of the edges (Fig. 17). $[M(CN)_8]^{4-}$ features square antiprism geometry and forms four cyano bridges with C–M–C angles of 73.5°, 77.5°, 77.1° and 142.0°. The copper centres retain the square pyramidal geometry coordinating three N donor atoms of dien ligand aligned in the equatorial plane and two bridging CN^- ligands. The 2-D layers are stabilized into 3-D superstructure by an extensive pattern of hydrogen bonds.

In acidic aqueous solution (pH < 2) $[Cu(dien)(H_2O)_2]^{2+}$ and $[Cu(tetren)]^{2+}$ release protonated $dienH_3{}^{3+}$ (or $tetrenH_5{}^{5+}$) ligand generating $[Cu(H_2O)_6]^{2+}$ labile ions. The combination of the resulting systems with $[M^{V}(CN)_8]^{3-}$ produced four structure related 2-D coordination networks: $\{(dienH_3)Cu_3{}^{II}[Mo^{V}(CN)_8]_3 \cdot 4H_2O\}_n$ (**14**), $\{(dienH_3)Cu_3{}^{II}[W^{V}(CN)_8]_3 \cdot 4H_2O\}_n$ (**15**), $\{(tetrenH_5)Cu_5{}^{II}[Mo^{V}(CN)_8]_5 \cdot 9H_2O\}_n$ (**16**) and $\{(tetrenH_5)Cu_5{}^{II}[W^{V}(CN)_8]_5 \cdot 9H_2O\}_n$ (**17**) of the general formula $\{(LH_n)Cu_n{}^{II}[M^{V}(CN)_8]_n \cdot xH_2O\}_\infty$ [45–47]. The polymers contains Cu^{II} centres of square pyramidal geometry coordinatively saturated solely by CN bridges supplied by five $[W(CN)_8]^{3-}$ ions. The compounds **14–17** are constructed of the alternatively stacked 2-D anionic double layers $\{Cu^{II}[W^{V}(CN)_8]^-\}_n$ and cationic layers of fully protonated $LH_n{}^{n+}$ ligands and crystallization water molecules (Fig. 18). The double layers are formed by two grid-like Cu and W knotted mono-layers joined by perpendicular CN^- bridges (Fig. 19). The $[M(CN)_8]^{3-}$ unit adopts a distorted bicapped

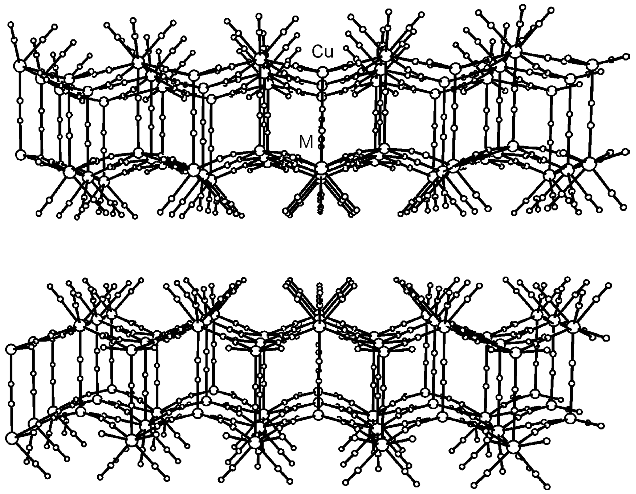


Fig. 18. The 2-D bilayered structure of $\{(LH_y)Cu_y{}^{II}[M^V(CN)_8]_y \cdot zH_2O\}_n$ (**14–17**) (adapted from Ref. [45,46]).

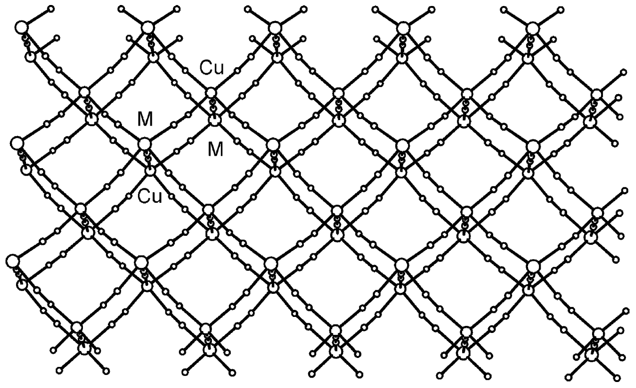
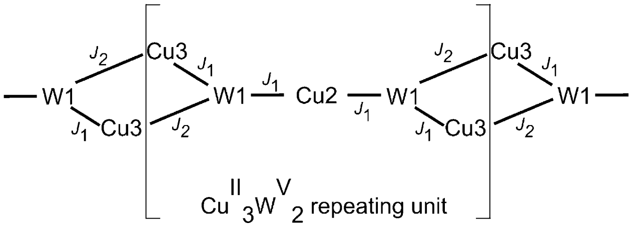


Fig. 19. Double layers of $\{(LH_y)Cu_y{}^{II}[M^V(CN)_8]_y \cdot zH_2O\}_n$ (**14–17**) (adapted from Ref. [45,46]).

trigonal prism geometry with five bridging ligands. The full connectivity of paramagnetic Cu(II) and W(V) centres with CN^- bridge results in short range W–Cu ferromagnetic coupling and long-range magnetic ordering to ferromagnetic state with T_C in range of 28–34 K (Fig. 20). The compounds **14–17** are characterised by magnetic hysteresis loop of the coercive field H_c in 30–220 Oe and remnant magnetisation M_r of 15–50% of magnetisation at saturation M_s, which indicates a soft ferromagnetic behaviour.

A logical extension of the building block approach is to combine the pre-organized multinuclear supramolecular coordination compound formed by Cu(II) metal centre bridged by organic *spacer* ligands with an octacyanometalate moiety. We have chosen the predictable coordination polymer network of 1-D chains that is generated from the metal ions coordinated to linear bi-functional ligands such as 4,4′-bipyridine (4,4′-bpy) [70]. These polymeric strands are usually cross-linked by hydrogen-bonded bridging 4,4′-bpy ligands. The new strategy consisting in the cross-linking of $\{[Cu^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ chains [71] by $[M(CN)_8]^{3-/4-}$ *spacers* resulted in $[Cu(\mu\text{-}4,4'\text{-bpy})(DMF)_2][Cu(\mu\text{-}4,4'\text{-bpy})(DMF)]_2[W^V(CN)_8]_2 \cdot 2DMF \cdot 2H_2O$ (**18**), the first representative of new class of magnetic multinuclear metal complexes [48].



Scheme 1. Magnetic interactions in $[Cu(\mu\text{-}4,4'\text{-bpy})(DMF)_2][Cu(\mu\text{-}4,4'\text{-bpy})(DMF)]_2[W^V(CN)_8]_2 \cdot 2DMF \cdot 2H_2O$ (**18**) (adapted from Ref. [48]).

The structure of **18** consists of the expected two-dimensional sheet structure which is built of infinite $\{[Cu^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ chains cross-linked by octacyanotungstate units (Fig. 21). The Cu^{II}–NC–W^V–CN–Cu^{II} linkage thus formed exhibits the topology of 3,2-chain assured by electroneutrality of **18**. In the 3,2 chain $[W(CN)_8]^{3-}$ moiety connects three Cu centres whereas each Cu centre is bonded to two W centres (Scheme 1). The W^V site exhibits a distorted square antiprism coordination geometry forming three cyano-bridges with C–W–C angles of 77.6°, 122.8° and 141.1°. [Cu(**3**)(μ-4,4′-bpy)(DMF)$(NC)_2$] moieties of compressed square pyramidal geometry occupy the alternate corners of $Cu_2{}^{II}W_2{}^V$ squares, whereas [Cu(2)(μ-4,4′-bpy)$(DMF)_2(NC)_2$] of elongated octahedral geometry acts as a linker between the two squares in the chain. The structure of the layer is additionally stabilized by a hydrogen bond network formed by terminal cyano ligands of $[W(CN)_8]^{3-}$ moiety and water molecules. The distance between the adjacent $Cu_3{}^{II}W_2{}^V$ chains within the layer is 11.12 Å along the *a* axis. The layers are connected by H-bonds of N_{CN}–N_{DMF}–N_{CN} linkages into 3-D supramolecular architecture.

The magnetic system of **18** (Fig. 22) can be treated as alternating $Cu_3{}^{II}W_2{}^V$ pentamers with identical $Cu^{II} \cdots W^V$ ferromagnetic intra-pentamer interactions defined by the parameter J_1 and much weaker AF inter-unit coupling (J_2) (Scheme 1).

2.5. Coordination networks based on Pt(II) complexes

The construction of *trans*-hexacyanometalate-based $[(CN)_5M^{II}\text{-}CN\text{-}Pt^{IV}L_4\text{-}NC\text{-}M^{II}(CN)_5]^{4-}$ (M^{II} = Fe, Ru, Os; L = NH_3 or 1/2 en) trinuclear species requires the inner-sphere two-electron redox reaction between Pt(II) and $[M(CN)_6]^{3-}$ [72]. These compounds reveal MMCT transition in visible region and have been studied due to the collective properties related to photoinduced multielectron charge transfer between metallic centres within the cyano-bridged polymeric framework [72g].

To study the metal–metal interactions through *trans*-cyano bridges in trinuclear compounds based on octacoordinate $[M(CN)_8]^{3-/4-}$ precursors we have chosen the $[M(CN)_8]^{3-}$ (M = Mo and W) and $[PtL_4]^{2+}$

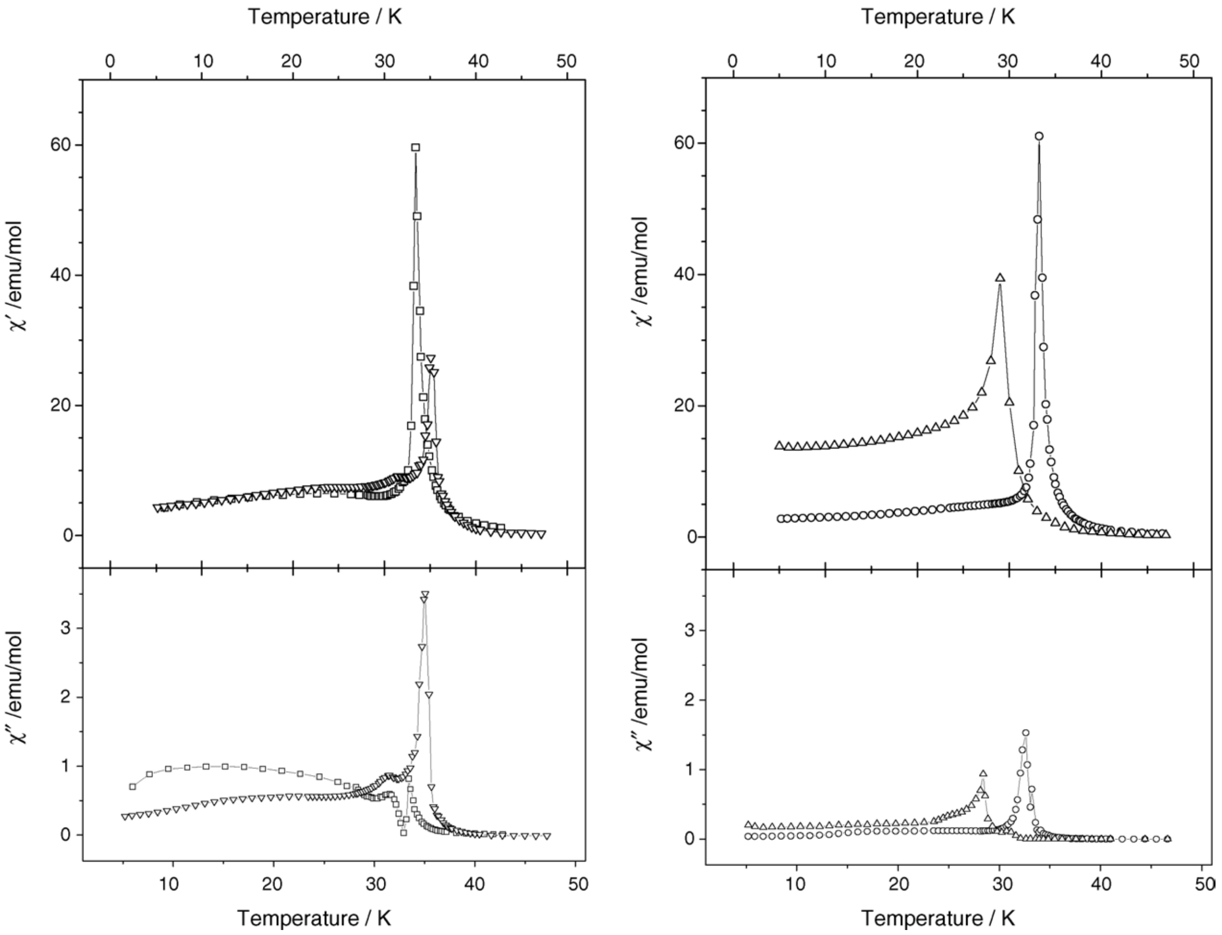


Fig. 20. Long-range magnetic ordering in $\{(LH_n)Cu_n^{II}[M^V(CN)_8]_n\cdot xH_2O\}_\infty$ compounds: in-phase χ' and out-of-phase χ'' components of ac susceptibility vs. T ($f = 140$ Hz, $H_{ac} = 5$ Oe, $H_{dc} = 0$): (□ and ▽) tetren analogues (left); (○ and △) dien analogues (right) (adapted from Ref. [46]).

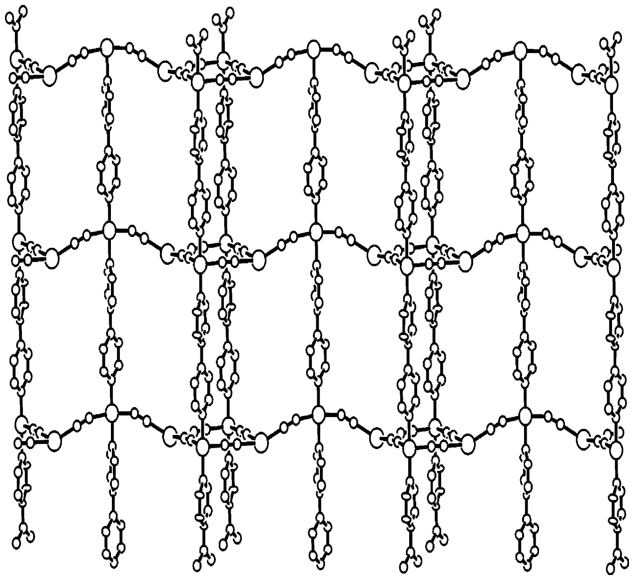


Fig. 21. The crystal structure of $[Cu(\mu\text{-}4,4'\text{-}bpy)(DMF)_2][Cu(\mu\text{-}4,4'\text{-}bpy)(DMF)]_2[W^V(CN)_8]_2\cdot 2DMF\cdot 2H_2O$ (**18**). Atoms not involved in bridging have been omitted for clarity (adapted from Ref. [48]).

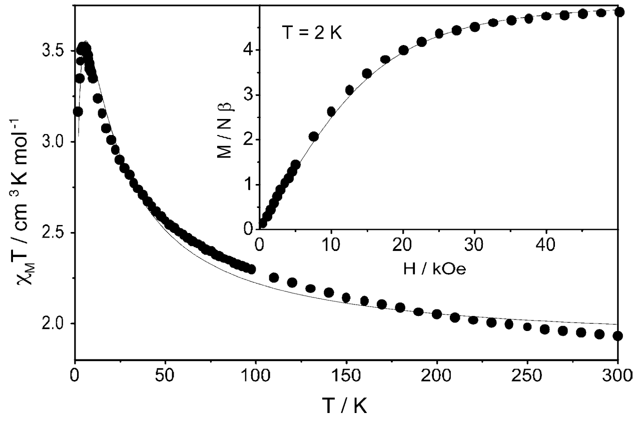


Fig. 22. Magnetic properties of $[Cu(\mu\text{-}4,4'\text{-}bpy)(DMF)_2][Cu(\mu\text{-}4,4'\text{-}bpy)(DMF)]_2[W^V(CN)_8]_2\cdot 2DMF\cdot 2H_2O$ (**18**) (adapted from Ref. [48]).

($L = NH_3$, 1/2en) substrates. The inner-sphere redox reaction of $[Mo(CN)_8]^{3-}$ with Pt(II) in aqueous solution resulted in the formation of $[(CN)_7Mo^{IV}\text{-}CN\text{-}Pt^{IV}L_4\text{-}NC\text{-}Mo^{IV}(CN)_7]^{4-}$ in aqueous solution and $[Pt^{II}(NH_3)_4]_2\{$*trans*-$Pt^{IV}(NH_3)_4[(\mu\text{-}NC)\text{-}Mo^{IV}(CN)_7]_2\}\cdot 6H_2O\cdot EtOH$ (**19**) and $Cs_2[Pt^{IV}(en)_2Cl_2]\{$*trans*-$Pt^{IV}(en)_2[(\mu\text{-}NC)\text{-}Mo^{IV}(CN)_7]_2\}\cdot$

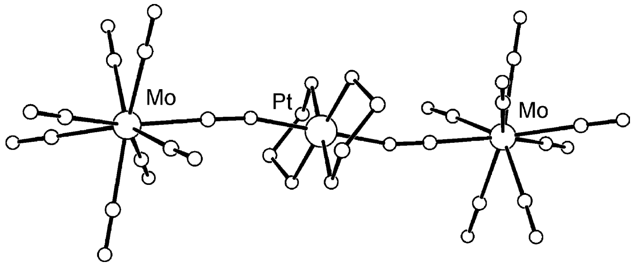


Fig. 23. Trinuclear $\{trans\text{-}Pt^{IV}(en)_2[(\mu\text{-NC})\text{-}Mo^{IV}(CN)_7]_2\}^{4-}$ species in $Cs_2[Pt^{IV}(en)_2Cl_2]\{trans\text{-}Pt^{IV}(en)_2[(\mu\text{-NC})\text{-}Mo^{IV}(CN)_7]_2\}\cdot 10H_2O$ (**20**) (adapted from Ref. [73]).

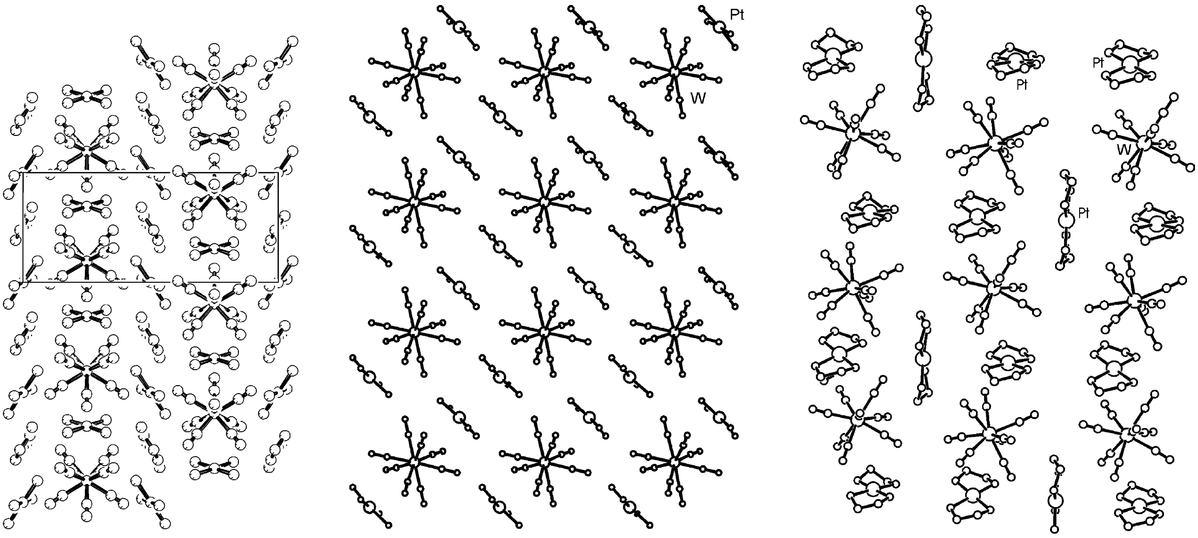
$10H_2O$ (**20**) of 0-D topology in solid state [73]. The crystal structure of **20** contains almost linear trimeric $[(CN)_7Mo^{IV}\text{-CN-}Pt^{IV}L_4\text{-NC-}Mo^{IV}(CN)_7]^{4-}$ anions. Octacyanomolybdate(IV) units of distorted antiprismatic geometry are coordinated through bent cyano-bridges at *trans* position in the $[Pt^{IV}(en)_2]$ moiety (Fig. 23). The network reveals alternating columns of trimers and isolated $[Pt(en)_2Cl_2]^{2+}$ cations. The important feature of the network is the presence of Cs^+ cations trapped within the "cage" formed by Cl, N and O atoms of $[Pt(en)_2Cl_2]^{2+}$, terminal CN ligands and water molecules, indicating a crucial role of Cs^+ in stabilization of the structure. Spectroscopic and cyclic voltammetry studies provide evidence of weak-to-moderate metal-to-metal Mo(IV)–Pt(IV) interaction and good electronic contact between remote Mo(IV) centres in solution as well as ground state electronic isomerism in solid state.

The inner-sphere two-electron oxidation of Pt(II) by $[W(CN)_8]^{3-}$ towards trimeric $W^{IV}Pt^{IV}W^{IV}$ cyano-bridged analogue species has been unsuccessful. The reactions resulted in the formation of mixed-valence ion-pair or ternary adduct in the solution and $[Pt^{II}(NH_3)_4]_2[W^V(CN)_8](NO_3)\cdot 2H_2O$(**21**) [74,75], $[Pt^{II}(NH_3)_4]_2[W^{IV}(CN)_8]$ (**22**) [accompanied by the $[Pt^{IV}(NH_3)_4Cl_2]Cl_2$ (**22a**)] [76] and $[Pt^{II}(en)]_3[W^V(CN)_8]_2\cdot 4H_2O$ (**23**) [77] ionic salts in solid state. The common characteristic feature of crystal structure of **21**, **22** and **23** are hydrogen bonded 1-D arrays formed by alternating antiprismatic $[W(CN)_8]^{n-}$ anions and square planar Pt(II) cations. The squares of Pt(II) moieties are parallel to the square or triangle planes of octacyanotungstate, with Pt···W contact distance within the range of 4.5–5.1 Å (Fig. 24). This mutual orientation hinders the perpendicular alignment of cyano-ligands towards Pt complex plane required for *trans*-cyano bridging. The salts **21** and **23** have been classified as localized-to-delocalized mixed-valence species with weak-to-moderate coupling between Pt(II) and W(V) centres. In appropriate experimental conditions (presence of Cl^- anions), the rare outer-sphere pathway of the oxidation of Pt(II) by $[W(CN)_8]^{3-}$ produced **22** and **22a**.

The formation of M^{IV}–CN–Pt^{IV} linkages in the inner-sphere two-electron oxidation reaction of $[Pt^{II}L_4]^{2+}$ by $[M^V(CN)_8]^{3-}$ in aqueous solution is controlled not only by the redox potentials of the substrates, but also by their geometries and resulting stereochemical barrier.

3. IR cyanide stretching frequencies

The cyanide stretching frequencies are used as the diagnostic tool in structure determination of octacyanometalate-based coordination networks. They are the most sensitive and informative markers of structural differences. The position, intensity and number of ν(CN) bands are very sensitive to oxidation state of the metal centre, geometry of $M(CN)_8{}^{3-/4-}$ moiety, bridging pattern of the ligands, counter-ions, hydro-



21 **22** **23**

Fig. 24. Topologies of hydrogen bonded {W, ..., Pt, ..., W} arrays in $[Pt^{II}(NH_3)_4]_2[W^V(CN)_8](NO_3)\cdot 2H_2O$ (**21**), $[Pt^{II}(NH_3)_4]_2[W^{IV}(CN)_8]$ (**22**) and $[Pt^{II}(en)]_3[W^V(CN)_8]_2\cdot 4H_2O$ (**23**) (adapted from Ref. [75-77]).

gen bonding and solvent molecules present in the crystal lattice [78]. The values of cyanide stretching frequencies relative to the free cyanide ion are governed by three main factors: (i) electron donation from the filled 5σ^* molecular orbital of CN^- to the metal centre strengthens the C–N bond and hence increases the value of ν(CN); an effect that increases with increasing oxidation state of metal centre, (ii) the back-donation of electrons from metal orbitals to unoccupied 2π^* orbitals of CN^- which lowers the cyanide stretching frequencies and (iii) kinematic coupling in the M–CN–M′ fragment, which restricts the vibrations of cyanide ligand, and hence increases the ν(CN) values. The ν(CN) bands of bridging cyano ligands are usually less intense than the terminal M–CN ones and overlap due to lowering of symmetry, which leads to band splitting.

The experimental ν(CN) frequencies for ionic and cyano bridged $[M(CN)_8]^{3-/4-}$ assemblies are presented in Table 1. Terminal cyano ligands in $[M(CN)_8]^{4-}$ ions generally exhibit sharp, very intense bands in the region 2070–2130 cm^{-1} which shift to 2130–2170 cm^{-1} region with substantial decrease in intensity for $[M(CN)_8]^{3-}$ complexes [78a]. The formation of M–CN–M′ cyano bridge extends the range of stretching frequencies to 2166 cm^{-1} for compounds containing the $[M(CN)_8]^{4-}$ moiety and to 2236 cm^{-1} for assemblies based on $[M(CN)_8]^{3-}$ ion. Exceptions from this general rule are observed for cyano-bridged compounds with Mn(II,III) complexes bearing electron withdrawing ligands, such as bpy or Schiff base ligands [21,28,29]. The ν(CN) bands of these compounds are in the range of those of isolated octacyanometalates. This demonstrates that the kinematic coupling [increasing of ν(CN)] is compensated by the electronic effect. The latter consists in the electron-withdrawal by M′ units, which causes enhanced π-back-donation from M centre to the π^* MO's of cyanide with consequences opposite to those of kinematic coupling. In such cases there is no possibility to distinguish between the terminal and bridging ν(CN) bands.

4. Magnetic properties

The summary of magnetic characteristics of cyano-bridged assemblies built by paramagnetic 3d metal centres and octacyanometalates discussed above is presented in Table 2. For the description of the magnetic properties of low-dimensional architectures we assumed the model of dominating intramolecular interaction within isolated polynuclear molecules with J_i ($i = 1, 2, 3, \ldots$) coupling constant (or constants) and less pronounced intermolecular interactions with J' coupling constant. This model is represented by the phenomenological Hamiltonian (Eq. (1)):

$$\boldsymbol{H} = -\Sigma_J J \Sigma_{\mathrm{M,M'}} \cdot \boldsymbol{S}_{\mathrm{M}} \boldsymbol{S}_{\mathrm{M'}} + \beta g H \mathbf{S}_{\mathrm{T}z} - zJ' \langle \mathbf{S}_{\mathrm{T}z} \rangle \mathbf{S}_{\mathrm{T}z}, \tag{1}$$

where the magnetic field (H) is assumed to be along the z direction, $\mathbf{S}_{\mathrm{M}}$ and $\mathbf{S}_{\mathrm{M'}}$ the spin operators of paramagnetic centres, g the effective Landé factor, $\mathbf{S}_{\mathrm{T}}$ the total spin operator of the polynuclear molecule, $\mathbf{S}_{\mathrm{Tz}}$ the z component of $\mathbf{S}_{\mathrm{T}}$ operator, and z is the number of nearest neighbours of the molecule in the crystal lattice. The magnetic susceptibility in the form of $\chi_{\mathrm{M}}T$ is expressed then with the following formula (2):

$$\chi_{\mathrm{M}}T = \frac{\chi_{\mathrm{mol}}T}{(1 - \chi_{\mathrm{mol}} zJ'/Ng^2\beta^2)} \tag{2}$$

where χ_{mol} denote the magnetic susceptibility of the isolated polynuclear molecules being a function of intramolecular J coupling constants.

Using this model intra- and intermolecular coupling constants have been calculated for three 0-D compounds $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2$ $[W^V(CN)_8]_2 \cdot 7H_2O$ (**3**), $[Mn^{III}(salen)H_2O]_3[W^V(CN)_8] \cdot H_2O$ (**7**) and $[Mn^{III}$(3-OMesalophen)$(H_2O)_2]_2[Mn^{III}$(3-OMesalophen)$(H_2O)][W^V(CN)_8] \cdot 2H_2O$ (**9**) as well as for 2-D architecture $[Cu^{II}$(μ-4,4′-bpy)$]_3[W^V(CN)_8]_2 \cdot 6DMF \cdot 2H_2O$ (**18**). In the latter case we have not observed long-range magnetic ordering, which is normally plausible for 2-D networks. On the basis of a qualititative consideration, the magnetic system of **18** is treated as $Cu_3{}^{II}W_2{}^{V}$ pentameric units with identical ferromagnetic intra-unit interaction defined by parameter J and much weaker effective inter-unit coupling J', including both intra- and inter-3,2-chain interaction between pentamers.

The bilayered 2-D coordination networks (tetrenH$_5$) $Cu_5{}^{II}W^V(CN)_8]_5 \cdot 9H_2O\}_n$ (**14**, **16**) and (dienH$_3$)$\{Cu^{II}$ $[M^V(CN)_8]\}_3 \cdot 4H_2O$ (M = Mo, W) (**15**, **17**) reveal long-range ferromagnetic ordering with sharp phase transitions at T_C in the range 28–37 K and coercivity in range 30–225 Oe at 4.3 K. We have also noticed that even above T_C the short range ferromagnetic interaction is significant.

Compounds based on manganese(II,III) and $[M(CN)_8]^{3-}$ moieties: **3**, **7** and **9** exhibit the short range Mn(II)–M(V) and Mn(III)–M(V) antiferromagnetic interaction with the variety of coupling constants J values, similarly to all other compounds of this type [6–19]. In the architectures **11** and **14–18** built from Cu(II) centres Cu(II)–W(V) ferromagnetic interaction dominates over much weaker antiferromagnetic interaction. These results are related to the axial and equatorial Cu–NC–M bridges at Cu(II) centres of square-pyramidal or axially elongated octahedral geometry [30–43]. The cobalt(II)–octacyanometalate(V) assemblies are characterised by the effective Co(II)–M(V) ferromagnetic interactions [18,24,26]. The magnetic interactions in these particular cases are controlled mainly by the geometry and electronic configuration of cationic building block and the M′–NC–M bridge geometry. The type of $[M(CN)_8]^{3-}$ polyhedra and their bridging functionality seems to be of secondary importance in the competition between ferro- (J_F) and antiferromagnetic (J_{AF}) coupling pathways and resulting orthogonality or overlapping of magnetic orbitals, respectively.

Table 1
Cyanide stretching frequencies of the relevant assemblies and reference compounds

Ionic compound	ν_{CN} (cm^{-1})	References
$K_4[W^{IV}(CN)_8]\cdot 2H_2O$	2138w, 2130vs, 2128vw, 2125vs, 2114vw, 2110vw, 2101m(sh), 2095vs	[79]
$Tl_4[W^{IV}(CN)_8]$	2134w, 2123w, 2118sh, 2115m, 2104s, 2100vs, 2098s,sh, 2088s, 2079s,sh, 2075vs	[79a]
$(4,4'-bpyH_2)_2[W^{IV}(CN)_8]$	2105vs, 2117sh	[80]
$Na_3[W^V(CN)_8]\cdot 4H_2O$	2170m, 2164m, 2160vs, 2154vs, 2146m, 2144m	[78a]
$K_3[W^V(CN)_8]\cdot 1.5H_2O$	2162w, 2159m, 2151vs, 2148vs	[78a]
$(Bu_4N)_3[W^V(CN)_8]\cdot H_2O$	2140s, 2130vs	[78a]
Bridged assemblies		
$[Mn^{II}(bpy)_2]_4[Mo^{IV}(CN)_8]_2\cdot 8H_2O$	2150m, 2138vs, 2119vs, 2110vs, 2069w	[20]
$[Mn^{II}(bpy)_2]_4[W^{IV}(CN)_8]_2\cdot 14H_2O$	2147m, 2124(sh), 2108vs	[20]
$[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^V(CN)_8]_2\cdot 7H_2O$	2169m, 2143w, 2121w	[21]
$[\{[Mn^{II}(bpy)_2(DMF)_2]_2[W^V(CN)_8]_2[Mn^{II}(DMF)_4]\}_n$	2178m, 2158m	[17,18]
$[\{[Mn^{II}(bpy)_2(DMF)_2]_2[Mo^V(CN)_8]_2[Mn^{II}(DMF)_4]\}_n$	2178m, 2158m	[17,18]
$[\{Mn_6{}^{II}(H_2O)_9[W^V(CN)_8]_4\cdot 13H_2O\}_n$	2196, 2172, 2160sh, 2140sh	[9]
$[\{[Mn_2{}^{II}(H_2O)_2(CH_3CO_2)][W^V(CN)_8]\cdot 2H_2O]\}_n$	2176	[11]
$[\{Mn_2{}^{II}Cs_{0.5}[W^V(CN)_8](CH_3CO_2)_{1.5}(H_2O)\}_n$	2181, 2156(sh), 2150.5, 21118.2(sh), 2109.5	[11]
$[\{Mn^{II}(pym)(H_2O)\}_2\{Mn^{II}(H_2O)_2\}\{W^V(CN)_8\}_2](pym)_2\cdot 2H_2O$	2183, 2176, 2172, 2168, 2164, 2160, 2153	[12]
$[\{\mu-(bpym)[Mn^{II}(H_2O)]_2-\mu-(NC)_6Mo^{IV}(CN)_2\}$	2161m, 2118s	[14]
$[\{\mu-(bpym)[Mn^{II}(H_2O)]_2-\mu-(NC)_6W^{IV}(CN)_2\}$	2160m, 2112s	[14]
$[Cs[Mn^{II}(3-CNpy)_2\{W^V(CN)_8\}]\cdot H_2O$	2182, 2177, 2161, 2155, 2150, 2145, 2140	[13]
$[Mn_2{}^{II}(H_2O)_4\{W^V(CN)_8\}(OH)2H_2O]_n$	2154	[19]
$[\{Mn^{II}L\}_2\{Nb^{IV}(CN)_8\}(H_2O)\cdot 5H_2O]_n$	2122, 2113	[15,16]
$[Fe_2{}^{II}(H_2O)_4][Mo^{IV}(CN)_8]\cdot 4H_2O$	2134	[81]
$[K_2\{[Co^{III}(tren)]_2[W^{IV}(CN)_8]_2\}\cdot 9H_2O$	2150, 2113	[27]
$[\{[W^V(CN)_2]_2[(\mu-CN)_4-Co^{II}(H_2O)_2]_3\cdot 4H_2O\}_n$	2201, 2178, 2162	[24]
$[\{[Co_3(DMF)_{12}][W(CN)_8]_2\}_n$	2194m, 2180m, 2170m, 2144w	[18]
$[Cs\{[Co^{II}(3-CNpy)_2][W^V(CN)_8]\}\cdot H_2O$	2187, 2179, 2166, 2157, 2141	[26]
$[\{Co_2{}^{II}(H_2O)_4[W^{IV}(CN)_8]\cdot 4H_2O\}_n$	2151(sh), 2134	[24]
$[Ni^{II}L]_{12}[Nb^{IV}(CN)_8]_6(H_2O)_6]\cdot 100H_2O$	2153w, 2129(sh), 2111m	[15]
$[Mo^{IV}(CN)_8Ni_2{}^{II}(pn)_4]_n\cdot 4nH_2O$	2154w, 2142(sh), 2130vs, 2120vs, 2110vs	[49]
$[Mo^{IV}(CN)_8Ni^{II}(en)_2(H_2O)][Ni^{II}(en)_3]\cdot 2H_2O$	2144s, 2129(sh), 2112vs, 2102vs	[49]
$[Ni^{II}(cyclam)]_2[Mo^{IV}(CN)_8]\cdot 3H_2O$	2122s, 2111vs, 2085s	[50]
$[Ni^{II}(cyclam)]_2[W^{IV}(CN)_8]\cdot 3H_2O$	2124s, 2113vs, 2086s	[50]
$[Cu^{II}(tetrenH_2)]_2[W^{IV}(CN)_8]_2\cdot 8H_2O$	2160w, 2151w, 2128m, 2107s, 2101s, 2095s	[44]
$[Cu^{II}(tetrenH_2)][Cu^{II}(tetrenH)][W^V(CN)_8][W^{IV}(CN)_8]_4\cdot 13H_2O$	2156m, 2143w(sh), 2115m	[44]
$[Cu^{II}(dien)]_2[W^{IV}(CN)_8]\cdot 4H_2O$	2157s, 2131s(sh), 2112m	[44]
$[Cu^{II}(dien)]_2[Mo^{IV}(CN)_8]\cdot 4H_2O$	2157s, 2132s(sh), 2112m	[44]
$[(tetrenH_5)Cu_5W^V(CN)_8]_5\cdot 9H_2O\}_n$	2201m, 2164s	[45]
$[Cu^{II}(\mu-4,4,'-bpy)(DMF)_2][Cu^{II}(\mu-4,4,'-bpy)(DMF)]_2[W^V(CN)_8]_2\cdot 2DMF\cdot 2H_2O$	2188s, 2171s, 2143sh	[48]
$[Cu_2[Mo^{IV}(CN)_8]\cdot xH_2O$	2166s(br)	[30]
$[Cu(bpy)_2]_2[Mo^{IV}(CN)_8]\cdot 5H_2O\cdot MeOH$	2124, 2112	[35]
$[\{Cu_{1.5}{}^{II}[Mo^V(CN)_8]\cdot 3H_2O\}_n$	2236, 2201	[30]
$[Cu^{II}(tn)_3][W^V(CN)_8]_2\cdot 3H_2O$	2189m, 2150s	[33]
$[Cu^{II}(pn)_3][W^V(CN)_8]_2\cdot 3H_2O$	2203s, 2188s, 2156s	[33]
$[\{[Cu^{II}(en)_2]_3[W^V(CN)_8]_2\cdot H_2O\}_n$	2144	[32]
$[\{[Cu^{II}(cyclam)]_2[Mo^{IV}(CN)_8]\cdot 10.5H_2O\}_n$	2134m, 2123m, 2101s	[39]
$[\{[Cu_2{}^{II}(H_2Tea)_2]_5[W^V(CN)_8]_2[W^{IV}(CN)_8]\cdot xH_2O\}_\infty$	2184w, 2164s, 2135(sh), 2125(sh)	[34]
$[\{[Cu^{II}(3-CNpy)_2(H_2O)]_2[Cu^{II}(3-CNpy)_2(H_2O)_2][W^V(CN)_8]_2\}_n$	2213, 2196, 2190, 2169, 2162, 2152	[31]
$[\{[Cu^{II}(4-CNpy)_2]_2[Cu^{II}(4-CNpy)_2(H_2O)_2][W^V(CN)_8]_2\cdot 6H_2O\}_n$	2205, 2199, 2192, 2161, 2159, 2151, 2140, 2136	[31]
$[Mn(salen)(H_2O)]_3[W^V(CN)_8]\cdot H_2O$	2165m, 2157s, 2150s, 2138m	[28]
$[Mn_3{}^{III}(salen)(H_2O)_2]_2[Mn^{III}(salen)(H_2O)][Mn^{III}(salen)]_2[Mo^{IV}(CN)_8]_2 0.5ClO_4\cdot 0.5OH\cdot 4.5H_2O$	2103(br)	[28]
$[Mn^{III}(3-OMesalophen)(H_2O)_2]_2[Mn^{III}(3-OMesalophen)(H_2O)][W^V(CN)_8]\cdot 2H_2O$	2144	[29]
$[Cs_2[Pt(en)_2Cl_2]\{Pt(en)_2[Mo^{IV}(CN)_8]_2\cdot 10H_2O$	2151s, 2133s, 2124s, 2114s, 2107s	[73]
$[Sm^{III}(H_2O)_5[W^V(CN)_8$	2178, 2164	[82]
$[(UO_2)_2[Mo^{IV}(CN)_8]\cdot nH_2O$	2140(br)	[83]

Table 2
Magnetic properties of selected cyano-bridged octacyanometalate-based compounds

Compound	Topology	Magnetic properties	References
$[Mn^{II}(bpy)_2]_4[M^{IV}(CN)_8]_2\cdot 8H_2O$ [M = Mo (**1**), W (**2**)]	0-D	Paramagnetic, the irradiation within the π–π* band of bpy (336–356 nm) at 5 K causes the conversion of paramagnetic $Mn_4^{II}M_2^{IV}$ clusters into the $Mn_2^{II}Mn_2^{I}M_2^{V}$ clusters characterized by Mn–M antiferromagnetic coupling of ground state spin $S = 8$	[20]
$[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\cdot 7H_2O$ (**3**)	0-D	Intramolecular antiferromagnetic coupling: W(V)–Mn(II) interaction through cyano-bridges with $J = -12\ cm^{-1}$ ($g = 2.00$) leading to ground state spin $S = 13/2$, intermolecular ferromagnetic coupling $zJ' = 0.05\ cm^{-1}$ leading to $T_C = 0.66\ K$	[21]
$[Mn^{III}(salen)H_2O]_3[W^{V}(CN)_8]\cdot H_2O$ (**7**)	0-D	Intramolecular antiferromagnetic coupling W(V)–Mn(III) through cyano bridges with $J_1 = -1.5\ cm^{-1}$ and Mn(III)–Mn(III) through phenolate bridges with $J_2 = -3.9\ cm^{-1}$ leading to ground state spin $S = 3/2$ ($g = 1.99$) and intermolecular antiferromagnetic coupling $zJ' = -0.7\ cm^{-1}$ leading to long-range magnetic ordering below $T_N = 4.6\ K$, the presence of magnetic anisotropy, at $T = 1.8$ the *spin-flop* transition in $H = 18$ k Oe || easy *bc* plane, metamagnetic behaviour from antiferromagnetic ground state $S_T = 3/2$ to ferromagnetic state $S_T = 5/2$	[28]
$[Mn^{III}(3\text{-}OMesalophen)(H_2O)_2]_2[Mn^{III}(3\text{-}OMesalophen)(H_2O)][W^{V}(CN)_8]\cdot 2H_2O$ (**9**)	0-D	Intramolecular antiferromagnetic coupling W(V)–Mn(III) through cyano-bridges with $J_1 = 20\ cm^{-1}$, very weak antiferromagnetic coupling Mn(III)–Mn(III) through hydrogen bonds with $J_2 = -0.46\ cm^{-1}$, the axial anisotropy parameter $D = -4.0\ cm^{-1}$ related to the zero-field splitting term of Mn(III) centres ($g = 1.94$)	[29]
$[Mn_3^{III}(salen)(H_2O)_2]_2[Mn^{III}(salen)(H_2O)][Mn^{III}(salen)]_2[Mo^{IV}(CN)_8]_2\cdot 0.5ClO_4\cdot 0.5OH\cdot 4.5H_2O$ (**8**)	1-D	Weak antiferromagnetic coupling Mn(III)–Mn(III) in double phenolate bridged $[Mn^{III}(salen)]_2$ subunits with $J_1 = -0.81\ cm^{-1}$ and very weak intermolecular ferromagnetic interaction between these subunits through diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ spacer with $J_2 = 0.04\ cm^{-1}$ ($g = 2.27$)	[28]
$[Cu^{II}(tetrenH_2)]_2[W^{IV}(CN)_8]_2\cdot 8H_2O$ (**10**)	1-D	Paramagnetic	[44]
$[Cu^{II}(tetrenH_2)][Cu^{II}(tetrenH)][W^{V}(CN)_8][W^{IV}(CN)_8]\cdot 12.5H_2O$ (**11**)	1-D	Weak short range ferromagnetic interaction within $W^{V}Cu^{II}$ subunit isolated by diamagnetic $[W^{IV}(CN)_8]^{4-}$ spacer and very weak antiferromagnetic interaction between $Cu_2^{II}W^{V}W^{IV}$ units at 4 K, ESR spectra confirm geometrically identical distorted octahedral Cu(II) complex units	[44]
$[Cu^{II}(dien)]_2[M^{IV}(CN)_8]_2\cdot 4H_2O$ (**12**, **13**)	2-D	Paramagnetic	[44]
$\{(tetrenH_5)Cu_5^{II}W^{V}(CN)_8]_5\cdot 9H_2O\}_n$ [M = Mo (**16**), W (**14**)] $\{(dienH_3)\{Cu_3^{II}[M^{V}(CN)_8]\}_3 4H_2O$ (M = Mo (**17**), W (**15**))]	2-D	Short-range dominating W(V)–Cu(II) ferromagnetic interaction, long-range magnetic phase transition in the 28–37 K temperature range, soft ferromagnetic behaviour at 4 K with H_c in the 30–225 Oe field range and R_M of 15–50% vs. M_s, the dipolar interaction through the hydrogen-bonded cationic $tetrenH_5^{5+}$; H_2O layer seems to be significant	[45–47]
$[Cu(\mu\text{-}4,4'\text{-}bpy)(DMF)_2][Cu(\mu\text{-}4,4'\text{-}bpy)(DMF)]_2[W^{V}(CN)_8]_2 2DMF\ 2H_2O$ (**18**)	2-D	Short-range W(V)–Cu(II) ferromagnetic interaction through CN^--bridges within $Cu_3^{II}W_2^{V}$ units with $J = 35\ cm^{-1}$ and very weak inter-unit antiferromagnetic interactions through CN^- and 4,4′bpy with average $J' = -0.05\ cm^{-1}$ ($g = 2.00$), no observation of long-range ordering	[48]

5. Conclusions and outlook

Prior to this research program, only three examples of structural proof of cyano-bridge formation by octacyanometalates had been reported [40,84]. Here we have presented the synthesis, structure and magnetic properties of low-dimensional coordination networks derived from $[M(CN)_8]^{3-/4-}$ (M = W, Mo) and $[M'(L)]^{n+}$ building blocks possessing labile coordination sites. The investigation of $[M(CN)_8]^{3-/4-}$-based supramolecular coordination chemistry has uncovered a wide variety of novel structural patterns and given rise to interesting magnetic and photomagnetic properties. As a preparation method for them, coordination-driven self-assembly proved to be very successful. The major challenge affecting the crystal engineering of octacyanometalate-based coordination networks is related to the coordination versatility of $[M(CN)_8]^{3-/4-}$ building blocks. The possible elements towards the understanding and design of molecular aggregation are the appropriate angles between the binding sites of cationic building block and between the cyano ligands of $[M(CN)_8]^{3-/4-}$ connector [85]. X-ray structure determinations revealed that the molecular square structural motif in their coordination networks is most commonly observed. A molecular square subunit can be assembled either by combining a metal complex having two vacant *cis*-coordination sites with an angular cyano building block or by combining linear *trans*-protected complexes with angular cyano building blocks. Generally, the $[M(CN)_8]^{3-/4-}$ polyhedra have three accessible groups of C–M–C angles: about 75°, 115° and 142°. Indeed, a molecular square structural motif has been realized in low-dimensional architectures, when the C–M–C angle of about 75° was chosen. There are only few examples where the cationic precursor fits a C–M–C angle greater than 110° then leading to the 1-D chains [15–18]. The cyano-bridged polynuclear systems based on Mn(III) Schiff-base complexes establish the special case, where the competition between formation of cyano and phenolate bridges determines the structures partially controlled by octacyanometalate and Mn(III) moieties. In many cases the cationic tecton:octacyanometalate ratio observed in the product coordination network is independent of the reaction stoichiometry.

We have shown, that the assemblies based on manganese(II,III) and $[M(CN)_8]^{3-}$ moieties exhibit the short range Mn(II)–M(V) and Mn(III)–M(V) antiferromagnetic interaction with a variety of J coupling constant values. In the architectures built from Cu(II) centres, Cu(II)–W(V) ferromagnetic interactions dominates the much weaker antiferromagnetic interaction, related to the axial and equatorial Cu–NC–M bridges at the Cu(II) centres, respectively. The magnetic interactions in these particular cases are controlled mainly by the geometry and electronic configuration of the cationic building block and the M′–NC–M bridge geometry.

The flexibility of the $[M(CN)_8]^{3-/4-}$-based coordination networks makes these systems particularly attractive in terms of their future development as functional materials and molecular devices: as magnetic and photomagnetic [6–23,30–48], spin-transition [10,18,24–29] and porous materials [30–48]. Due to the photo- and electrochemical activities of metal centres and chromophoric ligands, the square-grid networks [48,86] also possess considerable potential for applications in supramolecular spintronics [87]. Future work will focus on the design of novel multifunctional materials combining magnetic, optical, and electrochemical properties and attempts to introduce the new structural types into nanoscale applications.

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