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A new family of magnetic 2D coordination polymers based on $[\text{M}^{\text{V}}(\text{CN})_8]^{3-}$ (M = Mo, W) and pre-programmed Cu^{2+} centres

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Abstract

The self-assembly of $[\text{M}(\text{CN})_8]^{3-}$ (M = Mo, W) anion and polyamine complexes of $\text{Cu}^{\text{II}}[\text{Cu}(\text{tetren})]^{2+}$ and $[\text{Cu}(\text{dien})(\text{H}_2\text{O})_2]^{2+}$ (tetren = tetraethylenepentamine, dien = diethylenetriamine) in acidic aqueous solution gives $(\text{tetrenH}_5)_{0.8}\{\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4\}\cdot 7.2\text{H}_2\text{O}$ **1**, $(\text{tetrenH}_5)_{0.8}\{\text{Cu}^{\text{II}}_4[\text{Mo}^{\text{V}}(\text{CN})_8]_4\}\cdot 7.2\text{H}_2\text{O}$ **2**, $(\text{dienH}_3)\{\text{Cu}^{\text{II}}_3[\text{W}^{\text{V}}(\text{CN})_8]_3\}\cdot 4\text{H}_2\text{O}$ **3** and $(\text{dienH}_3)\{\text{Cu}^{\text{II}}_3[\text{Mo}^{\text{V}}(\text{CN})_8]_3\}\cdot 4\text{H}_2\text{O}$ **4** 2D coordination polymers. All compounds are structure-related: the crystal structures of isomorphous **1**–**2** and **3**–**4**, respectively, consist of double-layered cyano-bridged $\{\text{Cu}^{\text{II}}[\text{W}^{\text{V}}(\text{CN})_8]^{-}\}_n$ square grid backbones and non-coordinated fully protonated polyamine countercations as well as H_2O molecules located between the sheets. The magnetic measurements reveal long range ferromagnetic ordering with sharp phase transitions at T_{C} in range 28–37 K and coercivity in range 30–225 Oe at liquid helium temperature, $T = 4.3$ K.

Keywords: Cyano-bridged coordination compounds; Coordination polymers; Crystal structures; Octacyanometallates; Molecular magnets

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1. Introduction

The construction of discrete heteropolynuclear complexes with high-spin ground states [1–3] as well as extended infinite coordination networks [4–9] based on the paramagnetic (d^1) octacyanometalate(V) (M = Mo, W) and 3d transition metal tectons have attracted intense interest in the last years as a result of their potential application as magnetic materials.

The engineering of cyano-bridged heterometallic coordination networks follows the principal self-assembly approach, in which coordinative bonds M′–NC–M engaged between divergent 3d transition metal tecton and multidimensional non-rigid octacyanometalate 'linker', accompanied by weaker intermolecular forces (hydrogen bonding, π–π interactions, electrostatic interactions), propagate the coordination geometry into infinite architecture of various dimensionality and topology [10–17].

Our previous work had shown that $[\text{W}(\text{CN})_8]^{3-}$ reacts with $[\text{Cu}(\text{tetren})]^{2+}$ (tetren = tetraethylenepentamine) in acidic aqueous solution to generate $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4\cdot 7.2\text{H}_2\text{O}\}_n$ (**1**) [6]. The self-assembly of **1** results in the formation of layers of the $\{\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4^{4-}\}_n$ backbone with tetrenH_5^{5+} countercations and H_2O molecules located between the sheets. The $\{\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4\}_n$ backbone features Cu^{II} centres of square pyramidal geometry coordinatively saturated solely by CN bridges supplied by $[\text{W}(\text{CN})_8]^{3-}$ ions. The $[\text{Cu}(\text{tetren})]^{2+}$ complex ion is the source of pre-programmed divergent Cu^{II} centres formed by dechelation of fully protonated tetren ligand. The compound **1** is characterised by magnetic phase transition at $T_{\text{C}} = 34$ K and reveals the soft ferromagnetic behaviour. Ferromagnetic coupling is assigned to exchange interaction between W^{V} and Cu^{II} centres through the CN^- bridges as well as through possible hydrogen bonding network between the CN-bridged

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layers. Here we explore this approach, based on analogous molecular tectons: pre-programmed divergent Cu^{II} centres, formed by release of fully protonated polyamine ligands from $[Cu(tetren)]^{2+}$ and $[Cu(dien)(H_2O)_2]^{2+}$, and $[M(CN)_8]^{3-}$ ions. This synthetic strategy offers the opportunity to generate molecular networks with predictable structural motifs and predictable magnetic properties.

Our first results presented here concern the preparation and crystal structure of $(tetrenH_5)_{0.8}\{Cu^{II}_4[Mo^V(CN)_8]_4\}\cdot 7.2H_2O$ (**2**), $(dienH_3)\{Cu^{II}_3[W^V(CN)_8]_3\}\cdot 4H_2O$ (**3**) and $(dienH_3)\{Cu^{II}_3[Mo^V(CN)_8]_3\}\cdot 4H_2O$ (**4**) and the investigation of the magnetic properties of **2**–**4**.

2. Experimental

2.1. Materials

The $K_4[W(CN)_8]\cdot 2H_2O$ [18], $K_4[Mo(CN)_8]\cdot 2H_2O$ [19], $Na_3[W(CN)_8]\cdot 4H_2O$ [20], $Na_3[Mo(CN)_8]$ [20], $[Cu(tetren)](ClO_4)_2$ [6] and $[Cu(dien)Cl]ClO_4$ [21] were prepared by the literature methods. Tetren ligand in tetren·5HCl form and liquid dien ligand were purchased from Aldrich and used without further purifications. The $Na_3[Mo(CN)_8]$ solution was protected from light by means of aluminium-covered container and kept in a refrigerator. All manipulations and measurements were carried out in red light due to photosensitivity of the octacyanometallates(V) ions [22,23].

2.2. Synthesis

2.2.1. $(tetrenH_5)_{0.8}\{Cu^{II}_4[Mo^V(CN)_8]_4\}\cdot 7.2H_2O$ (2)

To an ice-cooled solution of $Na_3[Mo^V(CN)_8]$ (0.2 mmol, 0.083 mol l^{-1}, 2.4 ml) diluted to 15 ml a cold solution of $[Cu(tetren)](ClO_4)_2$ (0.3 mmol, 0.15 g) in 2 ml of concentrated $HClO_4$ was added dropwise upon cooling. The light green precipitate formed immediately. The mixture was filtrated and the precipitate was washed several times with cold water until the acid was removed. The green solid was dried under P_4O_{10}. Yield: 55%. Found: C, 26.1; H, 1.9; N, 28.5%. Calc. for $C_{9.60}H_{9.20}CuMoN_9O_{1.8}$: C, 26.3; H, 2.1; N, 28.7%. Green single crystals of **2** were obtained by slow diffusion in a H-tube after 2 months. IR: 2161s $\nu(CN)_t$, 2204m $\nu(CN)_b$ (t, terminal; b, bridging). The compound **2** was found to be isomorphous with its tungsten analogue **1** with unit cell parameters: $a = 7.3307$, $b = 31.9989$ and $c = 7.0196$ Å (orthorhombic crystal system).

2.2.2. $(dienH_3)\{Cu^{II}_3[W^V(CN)_8]_3\}\cdot 4H_2O$ (3)

The procedure was analogous to that of compound **1**, but $[Cu(dien)Cl]ClO_4$ (0.3 mmol, 0.0904 g) was used. The light green precipitate formed immediately. The mixture was filtrated and the precipitate was washed several times with cold water until the acid was removed. The green solid was dried under P_4O_{10}. Yield: 68%. Found: C, 21.9; H, 1.3; N, 24.3%, Calc. for $C_{9.32}H_{8.32}CuN_9O_{1.33}W$: C, 21.8; H, 1.6; N, 24.5%. IR: 2162s $\nu(CN)_t$, 2205m $\nu(CN)_b$. Green single crystals of **3** were obtained by slow diffusion in a H-tube after 2 months.

2.2.3. $(dienH_3)\{Cu^{II}_3[Mo^V(CN)_8]_3\}\cdot 4H_2O$ (4)

The procedure was analogous to that of compound **2**, but $[Cu(dien)Cl]ClO_4$ (0.3 mmol, 0.0904 g) was taken. The light green precipitate formed immediately. The mixture was filtrated and the precipitate was washed several times with cold water until the acid was removed. The green solid was dried under P_4O_{10}. Yield: 45%. Elemental analysis: Found: C, 25.9; H, 1.6; N, 29.3%, Calc. for $C_{9.33}H_{8.32}CuMoN_9O_{1.33}$: C, 26.2; H, 1.9 N, 29.5%. IR: 2159s $\nu(CN)_t$, 2201m $\nu(CN)_b$. Green single crystals of **4** were obtained by slow diffusion in a H-tube after 2 months. The compound **4** was found to be isomorphous with its tungsten analogue **3** with unit cell parameters: $a = 7.340$, $b = 31.667$ and $c = 7.030$ Å (orthorhombic crystal system).

2.3. Physical measurements

IR spectra of the assemblies were recorded between 4000–400 cm^{-1} on Bruker IFS 47 spectrometer on KBr pellets. The magnetic measurements of crystalline compounds **1**, **2**, **3** and **4** were carried out with the 7227 Lake Shore AC Susceptometer /DC Magnetometer in the temperature range 4.2–200 K.

2.4. Crystallography

X-ray diffraction experiment for compound **3** was performed on Siemens SMART [24] three-circle system with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and with CCD area detector. The crystal was held at 180(2) K with the Oxford Cryosystem Cryostream Cooler [25]. Intensity data were collected using ω scan mode. Unit cell was determined from 4478 reflections in the range 3–20°. Systematic absences indicated either space group $Cmc2_1$ or $Cmcm$. The former was chosen on the basis of intensity statistics and shown to be correct by successful refinement. The structure was solved by direct methods using SHELXS (Sheldrick) (TREF) [26] with additional light atoms found by Fourier methods. The cation and the water molecules inferred from the chemical analysis were highly disordered and it was not possible to identify specific molecules nor the full number of atoms expected from the stoichiometry. No hydrogen atoms were included. The cation and lattice water molecules were modelled as seven carbon atoms, one at full occupancy (C005), the others at 0.5 or 0.25 occupancy; no identification was possible of N or O atoms in the cation layer. Anisotropic displacement parameters were used for all non-H atoms apart from the atoms in the disordered cation layer. The absolute structure of the individual crystal chosen was checked by refinement of a racemic twinning parameter, which refined to a value of 0.5. Floating origin constraints were generated automatically. The only largest residual peaks were close to the W atom. The refinement was performed using SHELXTL (Sheldrick) [27]. Details of crystal structure solution and refinement are presented in Table 1.

3. Results and discussion

3.1. Syntheses

Self-assembly of [Cu(tetren)]ClO$_4$ or [Cu(dien)Cl]ClO$_4$ with octacyanometalates(V) in HClO$_4$ solution at pH 1.5 generates four coordination compounds of general formula $\{(LH_x)Cu^{II}_x[M^V(CN)_8]_x \cdot yH_2O\}_n$ (L = tetren, dien). The compounds were obtained according to two-step synthetic strategy: (i) dechelation of coordinated polyamine ligand by its complete protonation in acidic aqueous solution and followed by (ii) formation of Cu–N–C–M linkages leading to the saturation of coordination sphere at Cu(II) centres. The synthetic procedure was designed to generate pre-programmed Cu(II) centres and to ensure the stabilization of M(V) oxidation state in octacyanometalate(V) moiety, which at higher pH undergo the redox reactions to diamagnetic $[M(CN)_8]^{4-}$ [28]. By slow diffusion, crystals of good enough quality were grown for $(tetrenH_5)_{0.8}\{Cu^{II}_4[Mo^V(CN)_8]_4\} \cdot 7.2H_2O$ (**2**), $(dienH_3)\{Cu^{II}_3[W^V(CN)_8]_3\} \cdot 4H_2O$ (**3**) and $(dienH_3)\{Cu^{II}_3[Mo^V(CN)_8]_3\} \cdot 4H_2O$ (**4**).

Table 1
Crystal data for $\{(dienH_3)Cu^{II}_3[W^V(CN)_8]_3 \cdot 4H_2O\}_n$ (**3**)

Formula	$C_{9.32}H_{8.32}CuN_9O_{1.33}W$
Fw	515.18
Crystal system	orthorhombic, space group
Space group	$Cmc2_1$
Unit cell dimensions	
a (Å)	7.3707(15)
b (Å)	31.725(5)
c (Å)	7.0119(15)
V (Å^3)	1639.6(5)
T (K)	180(2)
Z	4
D_{calc} (Mg m^{-3})	2.087
μ/Mo Kα (mm^{-1})	8.322
F(0 0 0)	964
Crystal size (mm)	0.08 × 0.08 × 0.01, green plates
Reflections collected/unique	5332/1767
Max./min. transmission factors	0.68/0.89
Goodness-of-fit on F^2	0.993
R_1 [for 1563 reflections with $I > 2\sigma(I)$], wR_2	0.0249, 0.0585
Largest difference Fourier peak and hole (e Å^{-3})	1.134 and −1.223

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0340P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

3.2. Crystal structures

All compounds $(tetrenH_5)_{0.8}\{Cu^{II}_4[W^V(CN)_8]_4\} \cdot 7.2H_2O$ (**1**), $(tetrenH_5)_{0.8}\{Cu^{II}_4[Mo^V(CN)_8]_4\} \cdot 7.2H_2O$ (**2**), $(dienH_3)\{Cu^{II}_3[W^V(CN)_8]_3\} \cdot 4H_2O$ (**3**) and $(dienH_3)\{Cu^{II}_3[Mo^V(CN)_8]_3\} \cdot 4H_2O$ (**4**) are structure-related. The crystal structures of isomorphous **1**–**2** and **3**–**4** consist of double-layered cyano-bridged $\{Cu^{II}[W^V(CN)_8]^-\}_n$ square grid backbones and non-coordinated fully protonated polyamine countercations as well as H$_2$O molecules located between the sheets.

The crystal structure of **3** consists of $\{Cu^{II}[M^V(CN)_8]^-\}_n$ backbones aligned in the *ac* plane and $dienH_3^{3+}$ countercations as well as H$_2$O molecules located between the sheets (Fig. 1). The compound **3** crystallizes in the orthorhombic crystallographic system, space group $Cmc2_1$, similarly to the compound **1** [6], but with slightly different unit cell parameter ($a = 7.3707(15)$, $b = 31.725(5)$, $c = 7.0119(15)$ Å for (**3**) and $a = 7.3792(6)$, $b = 32.096(2)$, $c = 7.0160(6)$ Å for (**1**)]. Selected bond lengths and angles for **3** are presented in Table 2.

Within the double-layers, $\{Cu^{II}[W^V(CN)_8]^-\}_n$ backbones of **3** W(V) and Cu(II) centres are joined by the

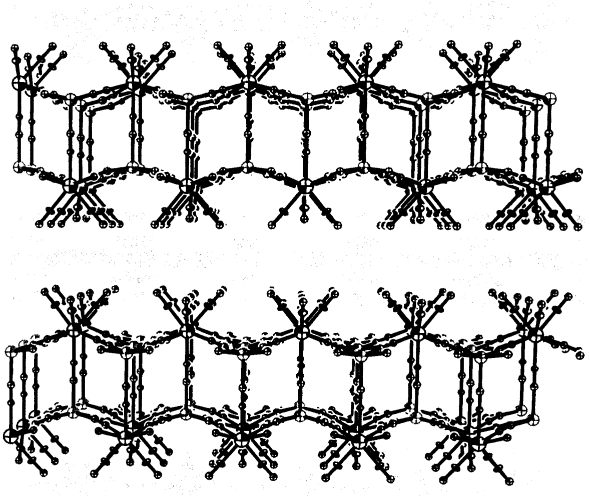


Fig. 1. Crystal structure of $\{(LH_x)Cu^{II}_x[M^V(CN)_8]_x \cdot yH_2O\}_n$ (**1**–**4**): projection showing alternatively stacked layers of $\{Cu^{II}[M^V(CN)_8]^-\}_n$ polymeric backbones (black lines) and disordered fully protonated LH_x^{x+} polyamine cations and H$_2$O molecules (light grey small spheres).

Table 2
Selected bond lengths and angles for $(dienH_3)\{Cu_3^{II}[W^V(CN)_8]_3\} \cdot 4H_2O$ (**3**)

W(1)					
W1–C1	2.192(7)	N1–C1	1.118(10)	N1–C1–W1	173(3)
W1–C2	2.086(18)	N2–C2	1.191(17)	N2–C2–W1	170.2(15)
W1–C3	2.216(18)	N3–C3	1.12(2)	N3–C3–W1	166.9(17)
W1–C4	2.148(12)	N4–C4	1.176(15)	N4–C4–W1	180.0(14)
W1–C5	2.153(7)	N5–C5	1.125(11)	N5–C5–W1	179.4(9)
C1–W1–C2	73.9(7)	C2–W1–C3	81.8(4)	C3–W1–C5	84.3(6)
C1–W1–C3	73.2(8)	C2–W1–C4	133.5(5)	C4–W1–C5	74.8(4)
C1–W1–C4	122.0(8)	C2–W1–C5	69.8(6)	C3–W1–C5a	139.5(6)
C1–W1–C5	139.4(3)	C3–W1–C4	65.5(6)	C3–W1–C3a	86.1(12)
Cu(1)					
Cu1–N1	2.135(7)	Cu1–N1–C1	177(3)	N3c–Cu1–N3b	81.8(10)
Cu1–N2b	2.005(13)	Cu1–N2b–C2b	169.7(15)	N3b–Cu1–N2b	88.7(4)
Cu1–N3b	1.927(15)	Cu1–N3b–C3b	162.5(16)	N2–Cu1–N1	98.8(8)
				N2c–Cu1–N2b	93.8(10)
				N3b–Cu1–N1	101.4(9)
				N3c–Cu1–N2b	159.0(3)

Symmetry operations: (a)$-x, y, z$; (b)$-x+1/2, -y+1/2, z+1/2$; (c) $x-1/2, -y+1/2, z+1/2$.

network of cyano-bridges. Each copper centre coordinates five neighbouring $[W(CN)_8]^{3-}$ units in a slightly distorted square pyramidal arrangement $Cu(-NC-W)_5$ (Fig. 2). The axial Cu–N–C–W linkage is characterised by slightly longer Cu–N distance (Cu1–N1 = 2.135(6) Å) than the equatorial ones (Cu1–N2b = 2.005(13) and Cu1–N3b = 1.927(15) Å). Four slightly bent equatorial cyanide bridges (Cu1–N2b–C2b = 169.7(15), Cu1–N3b–C3b = 162.5(16)°) give rise to the square grid pattern of the single layer (Fig. 3), while the almost linear axial CN^- bridges (Cu1–N1–C1 = 177(3)°) join two layers and thus form the double-layer. In consequence the double-layer is formed by two planes of edge sharing $Cu-(NC-W)_5$ square-pyramids of antiparallel orientation (Fig. 4). Within the one sheet the pyramids

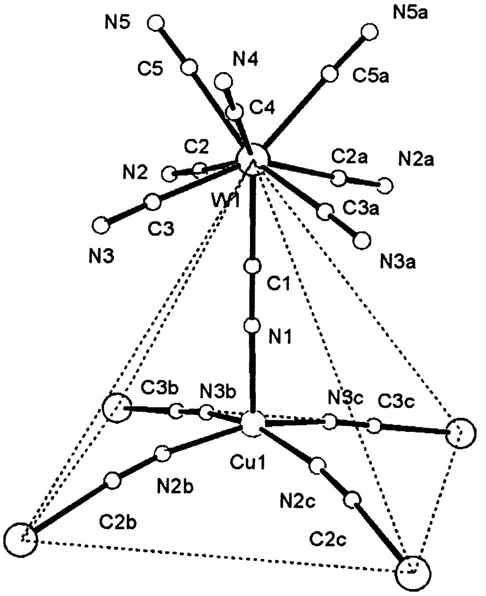


Fig. 2. Atom numbering scheme of structural motif of square pyramidal arrangement $Cu(-NC-W)_5$ in polymeric double-layer in **1**–**4**.

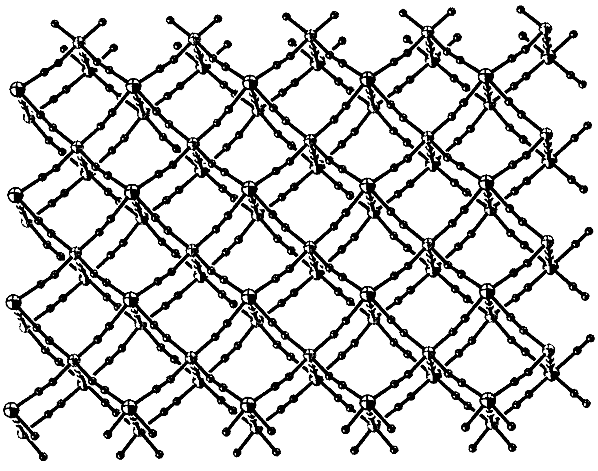


Fig. 3. Structure of cyano-bridged $\{Cu^{II}[W^V(CN)_8]^-\}_n$ double-layer in **1**–**4** (W, dark grey big spheres; Cu, light grey big spheres; C, N, dark grey small spheres (terminal cyano ligands are omitted for clarity).

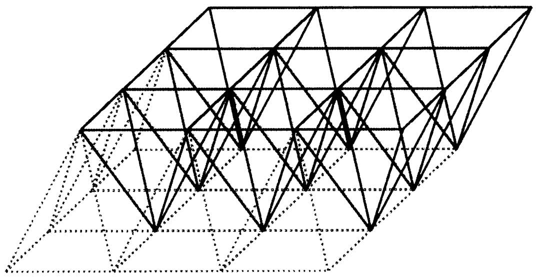


Fig. 4. Two planes of $Cu-(NC-W)_5$ square-pyramids of antiparallel orientation forming the double-layer.

share the basal edges and between the adjacent antiparallel sheets they share the side edges.

Each $[W(CN)_8]^{3-}$ anion of distorted bicapped trigonal prism (BTP) geometry, coordinates five copper centres by N ends of four (CN2b, CN2c, CN3b, CN3c) cyano-bridges arranged in square and the N atom of the fifth one (CN1) capping this square. The remaining three neighbouring cyano ligands stand out of the layer and are not involved in its construction. Almost identical mutual arrangement of bridging and terminal CN^- ligands were observed for $Mn_9^{II}[M^V(CN)_8]_6$ (M = W, Mo) supermolecules [1,2]. The average values of W–C and C–N bond lengths of 2.156 and 1.146 Å and W–C–N angle of 173.25 in **3** are slightly different from those found for compound **1** [6].

The fully protonated dienH_3^{3+} cations and lattice H_2O molecules are completely disordered to form the clouds of positive charge between the negatively charged double-layers. Two neighbouring bi-layers are characterised by the closest inter-layer W···W, W···Cu and $_{WCN}$N···N$_{NCW}$ distances of 9.96, 11.22 and 5.23 Å, respectively. The latter value indicate that the N atoms of terminal CN ligands are presumably involved in the extensive network of hydrogen bonds linking double-layers through the lattice water molecules.

3.3. Magnetic properties

We have shown recently that the magnetic properties of **1** revealed long range ferromagnetic ordering between Cu(II) and W(V) [6]. The value of magnetization of 1.94 Nβ at $T = 4.3$ K and $H = 56$ kOe (where Nβ is Bohr magneton per mole) was very close to the expected 2 Nβ per $Cu^{II}W^V$ unit. The magnetic susceptibility above 30 K obeyed Curie–Weiss law with $\theta = 44 \pm 3$ K. The frequency independent maxima in the in-phase and the out-of-phase AC susceptibility signals point to the magnetic transition at $T_C = 34$ K. The ferromagnetic coupling was assigned to the interactions of unpaired electrons originating from the orthogonal $3d_{x^2-y^2}$ orbitals of Cu(II) and the mixture of $5d_{z^2}$:$5d_{x^2-y^2}$ ground state orbitals of W(V) along both types of Cu–NC–W bridges.

The magnetic susceptibility behaviour of compounds **1**–**4** are essentially similar. All members obey the Curie–Weiss law above $T = 30$ K with positive Weiss constants. Magnetic data for compounds **1**–**4** are summarized in Table 3 and in Figs. 5–7.

The values of magnetization at $T = 4.3$ K and $H = 56$ kOe of 1.84 Nβ (**2**) and 1.88 Nβ (**3**), very close to the expected 2 Nβ (assuming isotropic g factor of 2.0), are in agreement with the result for (**1**) (Fig. 5) indicating ferromagnetic interactions between neighbouring Cu(II) and M(V) centres. To confirm the appearance of magnetic ordering and to determine the critical temperatures precisely, AC magnetic susceptibility measurements were performed. The in-phase signal χ' measured at $H_{ac} = 5$ Oe and $H_{dc} = O$ in the frequency range 5–650 Hz has the maximum at $T_C = 37$ K (**2**), 33 K (**3**) and 28 K (**4**) (Fig. 6). The χ' signal is always accompanied by the out-of-phase χ'' component with the maximum appearing just below the maximum of χ'. AC susceptibility hardly depends on the frequency of the driving field for compounds **2**–**4**.

The magnetic hysteresis loops of these compounds at $T = 4.3$ K show coercive fields H_c of 40 Oe (**2**), 225 Oe (**3**) and 30 Oe (**4**) and remnant magnetization M_R of 0.46 Nβ (**2**) and 0.93 Nβ (**3**), which indicate that these compounds can be referred to as soft ferromagnets (Fig. 7). The non-regular shape of $\chi''(T)$ curves may suggest the presence of additional phase transitions, which generally are possible in the systems with a high crystal anisotropy [1,29,30]. This hypothesis conforms to the presence of two completely different directions in 3D supramolecular architecture of **1**–**4**, suggesting the presence of non-negligible anisotropy of the lattice. The apparent domination of ferromagnetic coupling in coordination compounds **1**–**4** can be rationalized in terms of orthogonality of Cu(II) $(3d_{x^2-y^2})^1$ and M(V) $(5d_{z^2}{:}5d_{x^2-y^2})^1$ magnetic orbitals. The qualitative picture of exchange interactions through the equatorial (a) and the axial (b) Cu–N–C–M linkages is presented in Scheme 1. In the 2D networks of **1**–**4**, the distorted BTP coordination geometry of the $[M(CN)_8]^{3-}$ anion has lowest energy a_1 orbital of the mixture of d_{z^2} and $d_{x^2-y^2}$ orbitals. In the equatorial and the axial Cu–N–C–M linkages, the $(5d_{z^2}{:}5d_{x^2-y^2})$ magnetic orbital of M(V) centre can overlap with the empty π^*_{CN} orbitals, while the $Cu(3d_{x^2-y^2})^1$ magnetic orbital may not be effectively delocalised on the π^*_{CN} orbitals of the bridge. We cannot also exclude small antiferromagnetic contribution corresponding to the interaction of $Cu(3d_{x^2-y^2})$ single magnetic orbital with occupied orbitals of cyano-bridge, giving the non-zero J_{AF} contribution to total value of spin–spin coupling constant J. The experimental results of magnetic measurements suggest that antiferromagnetic contribution is negligible. The work on theoretical explanation of magnetic properties of compounds **1**–**4** is in progress.

3.4. Conclusion

Four heterometallic 2D coordination networks have been assembled by capping Cu(II) centres of square pyramidal geometry by octacyanometalate(V) moieties. Due to electrostatic interactions between negatively charged $\{Cu^{II}[W^V(CN)_8]^-\}_n$ layers (A^-) and protonated polyamine molecules (B^+), which are stacked alternatively in $\cdots A^-/B^+/A^-/B^+/A^-/B^+\cdots$ arrangement, the double-layered $\{Cu^{II}[W^V(CN)_8]^-\}_n$ backbones in **1**–**4** form supramolecular 3D architecture.

Table 3
Magnetic data for **1**–**4**

Compound	θ/K	T_C/K	M [a]/Nβ	H_c/Oe	M_R/Nβ	Ref.
1	44	34	1.94	80	0.27	[6]
2	41	37	1.88	40	0.46	This work
3	37	33	1.84	225	0.93	This work
4	35	28		30		This work

[a] At $T = 4.3$ K and $H = 56$ kOe.

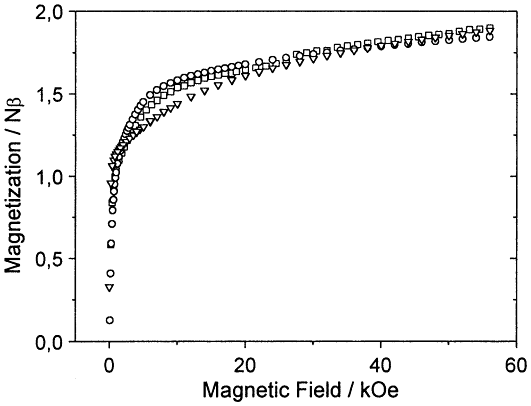


Fig. 5. Magnetization M per $Cu^{II}M^{V}$ unit vs magnetic field H at $T = 4.3$ K: (□) **1**, (▽) **2**, (○) **3**.

The general magnetic features of all these compounds are similar. We observe close T_C critical temperatures and the coercive fields without significant variations. The magnetic measurements indicate that the nature of polyamine cations in the network and electronic nature of the metal centre in $[M(CN)_8]^{3-}$ (Mo or W) building unit in $\{Cu^{II}[M^{V}(CN)_8]^{-}\}_n$ layers is not a relevant factor in soft ferromagnetic $\{(LH_x)Cu^{II}_x\,[M^{V}(CN)_8]_x \cdot xH_2O\}_n$ systems.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 195781. Copies of this information may be obtained free of charge from The

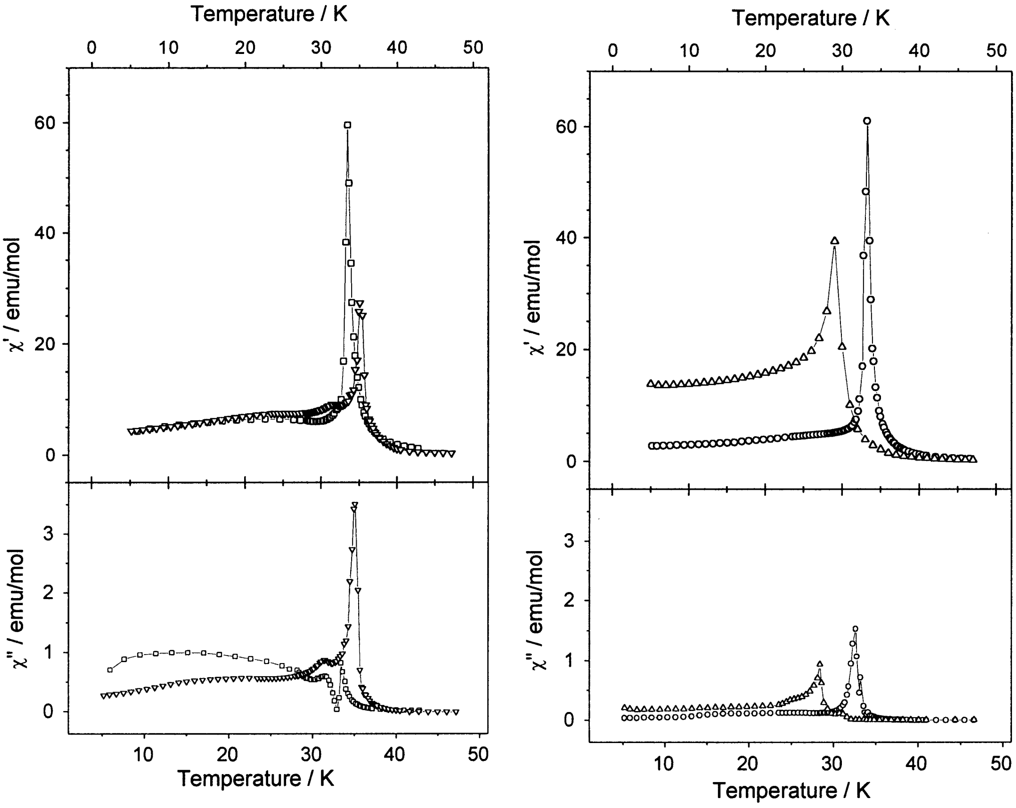


Fig. 6. In-phase χ' and out-of phase χ'' components of AC susceptibility vs T ($f = 140$ Hz, $H_{ac} = 5$ Oe, $H_{dc} = 0$): (□) **1**, (▽) **2** (left), (○) **3**, (△) **4** (right).

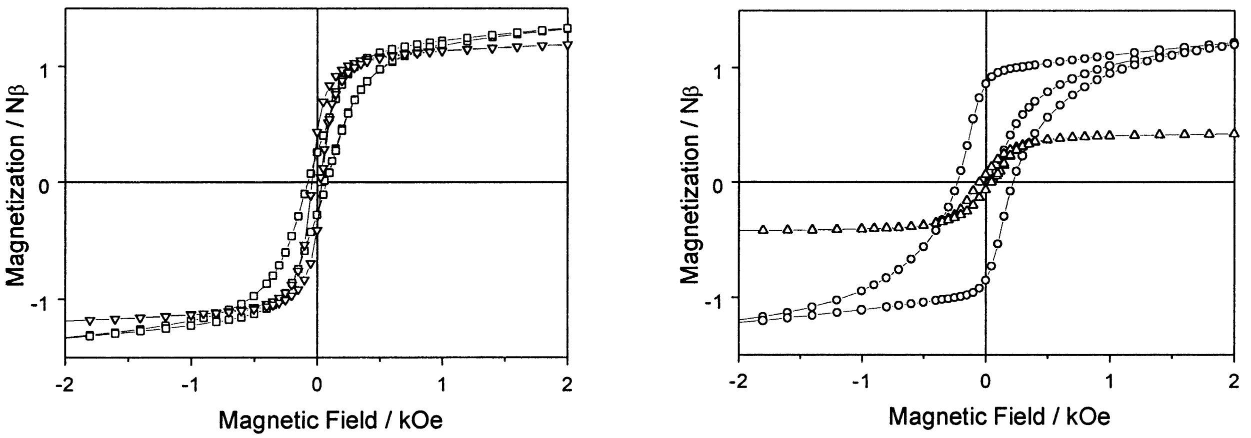
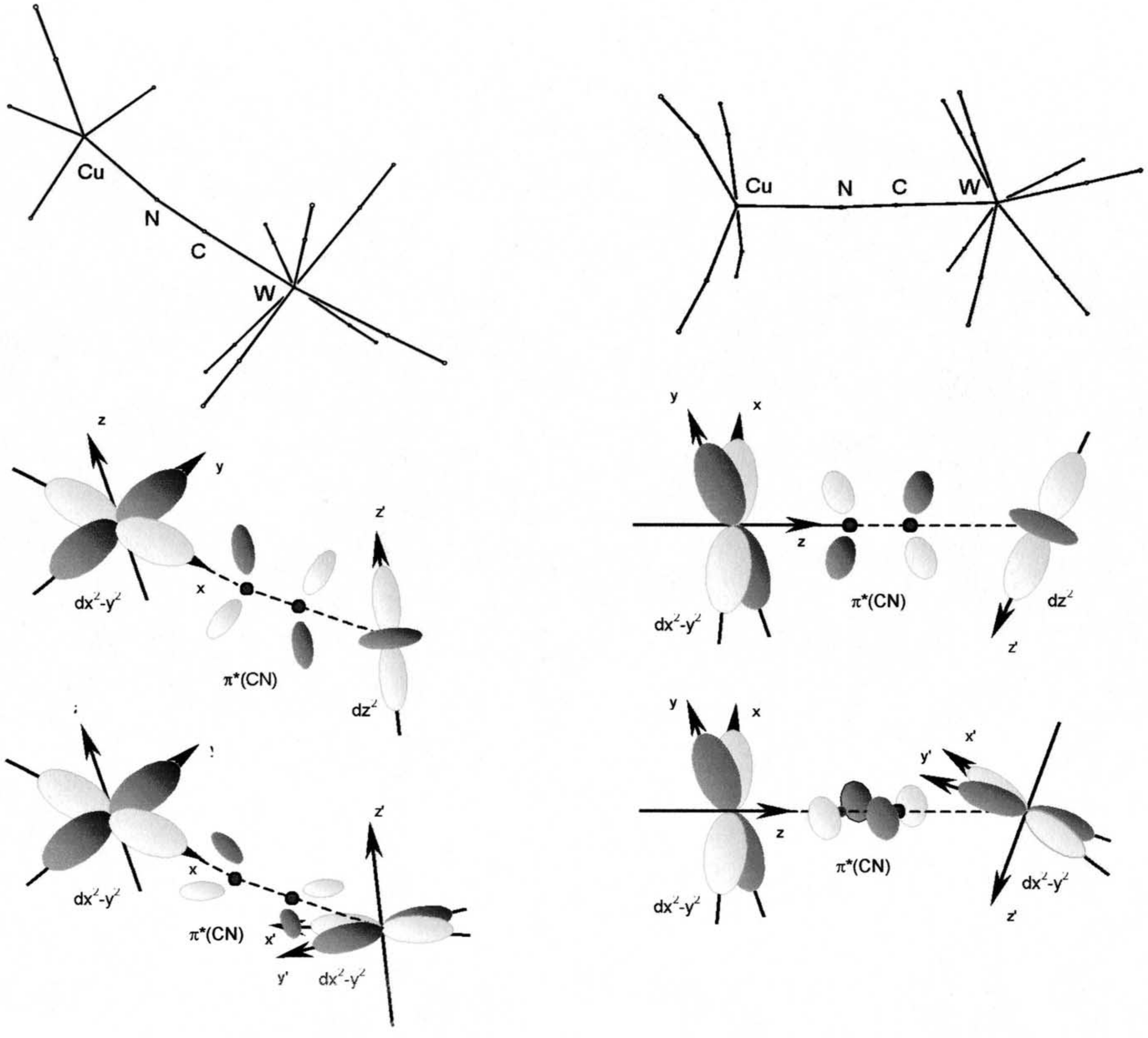


Fig. 7. Magnetic hysteresis loops for $Cu^{II}M^{V}$ unit at $T = 4.38$ K: (□) **1**, (▽) **2** (left), (○) **3**, (△) **4** (right).



(a) (b)

Scheme 1.

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