

2-D soft ferromagnet based on $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ and Cu^{II} with a T_c of 34 K \dagger Robert Podgajny,^a Tomasz Korzeniak,^a Maria Balanda,^b Tadeusz Wasiutynski,^b William Errington,^c Terence J. Kemp,^c Nathaniel W. Alcock^c and Barbara Sieklucka^{*a}^a Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland.

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Self-assembly of $[\text{Cu}(\text{tetren})]^{2+}$ (tetren = tetraethylenepentamine) and $[\text{W}(\text{CN})_8]^{3-}$ in acidic aqueous solution yields the double-layered square grid cyanide-bridged polymer of $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2\text{H}_2\text{O}\}_n$ with $\text{Cu}(\text{II})$ centres of square pyramidal geometry coordinatively saturated solely by CN bridges supplied by five $[\text{W}(\text{CN})_8]^{3-}$ ions; it exhibits soft ferromagnetic behaviour with an ordering temperature T_c of 34 K.

A work on crystal engineering of cyano-bridged coordination networks based on octacyanomethylates(v) ($\text{M} = \text{Mo}, \text{W}$) is stimulated, in part, by widespread interest in the field of molecule-based magnetism.^{1–5} Clusters, chains and polymers have been formed *via* self-assembly of $[\text{M}(\text{CN})_8]^{3-}$ and 3d cationic complex paramagnetic constituent blocks. In each case, the information for the self-assembly of the entire structure is coded into the individual building blocks due to their steric, topological and intermolecular bonding capabilities. Thus $[\text{M}(\text{CN})_8]^{3-}$ in the presence of $[\text{Mn}^{\text{II}}(\text{solvent})_6]^{2+}$ templates self-assembles to give $\text{Mn}^{\text{II}}_6[\text{M}^{\text{V}}(\text{CN})_8]_6^{1,2}$ high-spin clusters as well as the 3-D polymer $\{\text{Mn}^{\text{II}}_6[\text{W}^{\text{V}}(\text{CN})_8]_4\}_n$ with $T_c = 54 \text{ K}$.³ The *cis*-protected $[\text{Mn}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ (*bpy* = 2,2'-bipyridine) units with $[\text{W}(\text{CN})_8]^{3-}$ results in formation of the high-spin molecule $[\text{Mn}^{\text{II}}(\text{bpy})_2]_3[\text{W}^{\text{V}}(\text{CN})_8]_2 \cdot 9\text{H}_2\text{O}$.⁴ The self-assembly of $[\text{Cu}^{\text{II}}(\text{dien})(\text{H}_2\text{O})_2]^{2+}$ (*dien* = diethylenetriamine) and $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ in aqueous solution generates the one-dimensional chain $\{\text{W}^{\text{V}}[\text{CN}-\text{Cu}^{\text{II}}(\text{dien})-\text{NC}]_4^{5+}\}_n$, whose 5+ charge is balanced by isolated $[\text{W}(\text{CN})_8]^{3-}$ and Na^+ counter ions, and which exhibits alternating ferro- and antiferromagnetic interactions between W and Cu centres.⁵

The goal of our study is the construction of magnetic coordination polymers based on bare $\text{Cu}(\text{II})$ centres combined with $[\text{W}(\text{CN})_8]^{3-}$. Here we report the synthetic strategy, structure and magnetism of the system formed by the self-assembly of $[\text{W}(\text{CN})_8]^{3-}$ and the new precursor $[\text{Cu}(\text{tetren})]^{2+}$ **1** \ddagger (tetren = tetraethylenepentamine) in acidic aqueous solution: $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2\text{H}_2\text{O}\}_n$ **2** \ddagger . The $[\text{Cu}(\text{tetren})]^{2+}$ complex ion provides the pre-programmed bare $\text{Cu}(\text{II})$ centres formed by release of fully protonated tetren ligand. The self-assembly of **2** results in the formation of layers of the $\{\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4\}_n$ backbone with tetrenH_5^{5+} counterions 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 $\text{Cu}(\text{II})$ centres of square pyramidal geometry coordinatively saturated solely by CN bridges supplied by five $[\text{W}(\text{CN})_8]^{3-}$ ions.

The crystal structure of the $[\text{Cu}(\text{tetren})](\text{ClO}_4)_2$ precursor **1** \ddagger consists of mononuclear $[\text{Cu}(\text{tetren})]^{2+}$ cations of distorted trigonal bipyramidal geometry and ClO_4^- anions (Fig. S1). The $[\text{Cu}(\text{tetren})]^{2+}$ has significantly longer terminal equatorial Cu–N bonds of 2.124(5) and 2.067(5) Å compared to the remaining Cu–N bonds of 2.041(5), 2.017(5) and 2.009(6) Å. The use of crystallographically characterised $[\text{Cu}(\text{tetren})](\text{ClO}_4)_2$ precur-

sor allows the control of experimental conditions in construction of the supramolecular assembly with $[\text{W}(\text{CN})_8]^{3-}$.

Crystal structure analysis of **2** \ddagger reveals that $\{(\text{tetrenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2\text{H}_2\text{O}\}_n$ consists of anionic double-layers $\{\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4^{4-}\}_n$ aligned in the *ac* plane, the charge of which is balanced by tetrenH_5^{5+} cations (Fig. 1). Each $[\text{W}(\text{CN})_8]^{3-}$ of bicapped trigonal prism geometry links five Cu centres coordinated by (NC) bridges in a square pyramid, with the apical Cu–N rather longer (Cu1–N1 2.115(7) Å) than the equatorial ones (Cu1–N2B 1.992(8) and Cu1–N3B 1.971(8) Å) (Fig. S2). Four slightly bent equatorial cyanide bridges (Cu1–N2B–C2B 169.3(7), Cu1–N3B–C3B 169.4(8)°) give rise to the square-grid pattern of the single layer, while the practically linear axial CN[–] bridge (Cu1–N1–C1 174(2)°) joins two layers and thus forms the double-layer. In consequence the double-layer is realized by the two stacked sheets of edge sharing Cu–(NC–W)₅ square-pyramids of antiparallel orientation. The inter-double-layer W–W and W–Cu distances are 9.96 and 11.22 Å, respectively (Fig. 1). The unit cell contains four Cu–W units and should therefore have 4/5 of a cation. The cation and the inferred water molecules lie in planes between the Cu–W double layers. Because the numbers of cations in each cell is fractional, cation layers are completely disordered. No trace of a superlattice was found despite extensive searching. The remaining three terminal CN ligands of $[\text{W}(\text{CN})_8]^{3-}$, standing out of the layer, are presumably involved in the extensive network of hydrogen bonds linking parallel double-layers through the lattice water molecules and are undoubtedly significant in construction of the system.

The IR spectrum shows three bands at 2204s (br), 2164m and 2148m (sh) cm^{-1} . The bands at 2164 and 2148 cm^{-1} are within the range of terminal $\nu(\text{CN})$ bands of $[\text{W}(\text{CN})_8]^{3-}$.⁶ The highest frequency band at 2204 cm^{-1} we assign to bridging $\nu(\text{CN})$, in agreement with the dominant kinematic effect, which results in constraints on the motion of CN[–] and increase of $\nu(\text{CN})$.^{3,5,7}

The magnetic measurements of crystalline compound **2** were carried out with the 7227 Lake Shore AC Susceptometer /DC

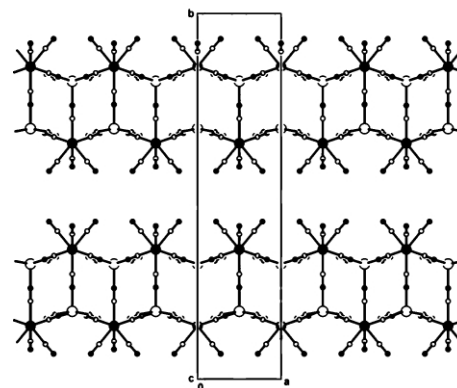


Fig. 1 Projection of double layer on *ab* crystallographic plane (● W, ○ Cu, ● N, ○ C). The disordered tetrenH_5^{5+} cation and H_2O molecules are omitted.

\ddagger Electronic supplementary information (ESI) available: structure of $[\text{Cu}(\text{tetren})]^{2+}$ in **1** and (NC)₇W–CN–Cu(NC)₄ structural motif of **2**; table and figures of IR spectra of **1**, **2**, tetren·5HCl and free tetren. See <http://www.rsc.org/suppdata/cc/b2/b202810g/>

Magnetometer in the temperature range 4.2–200 K. Fig. 2 shows the temperature dependence of $\chi_M T$, per Cu_4W_4 unit, measured in a field of 0.5 T. The $\chi_M T$ value at 200 K tends to ca. 3 emu K mol^{-1} , in agreement with the spin-only value of 3 emu K mol^{-1} , expected for an uncoupled spin system [$4(S_{\text{Cu}} = \frac{1}{2})$, $4(S_{\text{W}} = \frac{1}{2})$]. Upon cooling below 150 K, the $\chi_M T$ curve increases slowly and then sharply starting from 80 K, reaching a maximum value of $140 \text{ emu K mol}^{-1}$ around 30 K and then decreases rapidly as T is lowered further. The magnetic susceptibility above 30 K obeys the Curie–Weiss law; the positive Weiss constant $\theta = 43.5 \pm 3 \text{ K}$ (in the range 70–190 K) depends on the fit range. These features suggest the onset of long-range ferromagnetic ordering. The ac magnetic susceptibility measurements confirm the appearance of magnetic ordering and precisely determine the critical temperature (inset of Fig. 2). The frequency independent maximum in the in-phase signal (χ') at 34 K and an out-of-phase signal (χ'') that starts to appear just below 34 K gives a T_c of 34 K for **2**. The field dependence of magnetization at $T = 4.38 \text{ K}$ reveals a hysteresis loop with a weak coercive field H_c of 80 Oe and a remnant magnetization M_R of $1.04 \mu_B$ per unit, typical of a soft ferromagnet (Fig. 3). The value of magnetization of $7.76 N\beta$ at high field (56 kOe) is very close to the expected $8 N\beta$ (assuming isotropic g factor of 2.0) value for a ferromagnetic Cu_4W_4 system (Fig. 3, inset), which confirms the presence of ferromagnetic interactions. The ferromagnetic coupling in **2** can be rationalized in terms of the interactions of unpaired electrons originating from the mutually orthogonal $3d_{x^2-y^2}$ orbital of Cu(II) and the mixture of $5d_{z^2}$ and $5d_{x^2-y^2}$ ground state orbitals of the W(V) centre of bicapped trigonal prism geometry⁸ along both types of Cu–NC–W bridge.

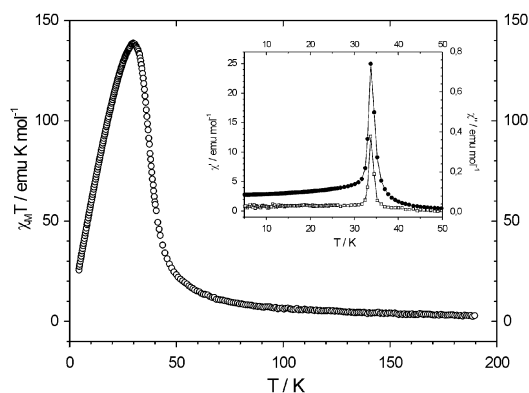


Fig. 2 Product $\chi_M T$ vs. T at a field of 0.5 T; Inset: in phase (χ') and out of phase (χ'') components of ac susceptibility vs. T , field $H_{ac} = 1 \text{ G}$ and frequency $f = 125 \text{ Hz}$.

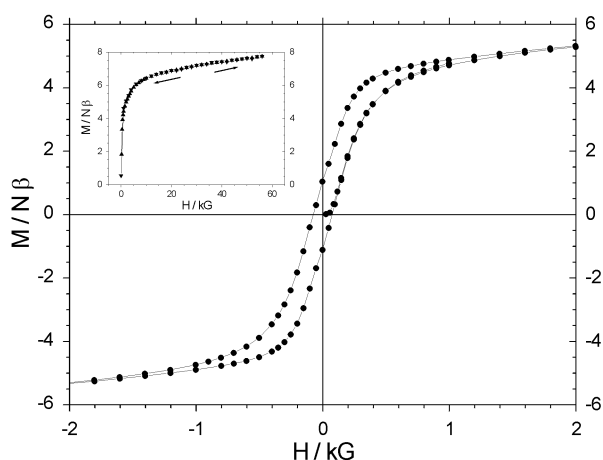


Fig. 3 Magnetic hysteresis loop and magnetization curve up to 56 kG (inset) at $T = 4.38 \text{ K}$.

In summary, a new soft ferromagnetic two-dimensional coordination polymer $\{(\text{trenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2\text{H}_2\text{O}\}_n$ has been synthesised using the synthetic strategy of pre-programmed bare 3d metal centres formed by release of the fully protonated polyamine ligand. Further work on the construction of supramolecular systems along this line is currently in progress.

Notes and references

‡ *Syntheses*: $[\text{Cu}(\text{tren})](\text{ClO}_4)_2$ **1**: A warm aqueous solution of tren-5HCl (4.09 g, 11.0 mmol, 5 ml, pH = 4.5) was mixed with an aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.71 g, 10 mmol, 10 ml). The solution was stirred and heated for 30 min and then aqueous NaClO_4 (2.70 g, 22 mmol, 4 ml) was added. The addition of concentrated aqueous NaOH up to pH = 12.5 gave the light blue polycrystalline $[\text{Cu}(\text{tren})](\text{ClO}_4)_2$. The solid was recrystallized from water. Yield: 3.60 g, 80% (Found: C, 21.4; N, 15.3; H, 5.1. Calc. for $\text{C}_8\text{H}_{23}\text{Cl}_2\text{CuN}_5\text{O}_8$: C, 21.4; N, 15.5; H, 5.1%).

$\{(\text{trenH}_5)_{0.8}\text{Cu}^{\text{II}}_4[\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 7.2\text{H}_2\text{O}\}_n$ **2**: Green crystalline plates of **2** were grown reproducibly by slow diffusion of the precursors (0.28 mmol, 0.150 g of $\text{Na}_3[\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ in 2 ml vs. 0.28 mmol, 0.127 g of $[\text{Cu}(\text{tren})](\text{ClO}_4)_2$ in 2 ml) in acidic aqueous solutions (pH 1.5, HClO_4) in an H-tube over 2 months at 4°C . The crystals were washed with small portions of cooled water and EtOH, then dried in air. Yield: 30 mg, 20% (Found: Cu, 12.1; C, 22.0; H, 1.5; N, 23.8. Calc. for $\text{C}_9.60\text{H}_9.20\text{CuN}_9\text{O}_{1.8}\text{W}$: Cu, 12.1; C, 21.9; H, 1.8; N, 23.9%). Elemental analysis and comparison of IR spectra with those of tren-5HCl and free tren confirm the stoichiometric presence of the fully protonated ligand cation.

§ *Crystal data*: compound **1**: $\text{C}_8\text{H}_{23}\text{Cl}_2\text{CuN}_5\text{O}_8$, $M_w = 451.75$, monoclinic, space group Cc , $a = 8.2510(9)$, $b = 15.2479(14)$, $c = 13.8062(14)$ Å, $\beta = 98.737(3)^\circ$, $V = 1716.8(3)$ Å³, $T = 180(2)$ K, $Z = 4$, $D_c = 1.748 \text{ Mg m}^{-3}$, $\mu = 1.631 \text{ mm}^{-1}$, graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å), Siemens SMART diffractometer. The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. The refinement was performed against all reflections (2720). The goodness-of-fit on F^2 is 1.074. The final refinement gave $R1$ [for 2516 reflections with $I > 2\sigma(I)$] = 0.0407 and $wR2 = 0.1076$.

Compound **2**: $\text{C}_9.60\text{H}_9.20\text{CuN}_9\text{O}_{1.8}\text{W}$, $M_w = 526.7$, orthorhombic, space group $Cmc2(1)$, $a = 7.3792(6)$, $b = 32.096(2)$, $c = 7.0160(6)$ Å, $V = 1661.7(2)$ Å³, $T = 180(2)$ K, $Z = 4$, $D_c = 2.160 \text{ Mg m}^{-3}$, $\mu = 8.22 \text{ mm}^{-1}$, graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å), Siemens SMART diffractometer, 5385 reflections collected, 2073 reflections unique ($R_{int} = 0.0585$). The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) 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 were modelled as 11 carbon atoms, mostly at 0.5 or 0.25 occupancy. Anisotropic displacement parameters were used for all non-H atoms apart from two CN groups and the disordered cation layer. The crystals show perfect racemic twinning. Floating origin constraints were generated automatically. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.100)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. The goodness-of-fit on F^2 is 1.038. The final refinement gave $R1$ [for 1954 reflections with $I > 2\sigma(I)$] = 0.0419 and $wR2 = 0.0990$.

CCDC reference numbers 182458 and 182459. See <http://www.rsc.org/suppdata/cc/b2/b202810g/> for crystallographic data in CIF or other electronic format.

- Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. I. Ohkoshi and K. Hashimoto, *J. Am. Chem. Soc.*, 2000, **122**, 2952.
- J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. Güdel and S. Decurtins, *Angew. Chem., Int. Ed.*, 2000, **39**, 1605.
- Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, M. Verdagner, S. I. Ohkoshi and K. Hashimoto, *Inorg. Chem.*, 2000, **39**, 5095.
- R. Podgajny, C. Desplanches, B. Sieklucka, R. Sessoli, V. Villar, C. Paulsen, W. Wernsdorfer, Y. Dromzee and M. Verdagner, *Inorg. Chem.*, 2002, **41**, 1323.
- R. Podgajny, C. Desplanches, F. Fabrizi de Biani, B. Sieklucka, Y. Dromzee and M. Verdagner, in preparation.
- W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1975, 2489.
- B. S. Lim and R. H. Holm, *Inorg. Chem.*, 1998, **37**, 4898.
- J. K. Burdett, R. Hoffmann and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 2553.