

Two octacyanometallate-based Ni(II)W(V) bimetallic assemblies with metamagnetism^{†‡}

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Reactions of the precursors [Ni(macrocylic ligand)]²⁺ with [W(CN)₈]³⁻ afford two octacyanotungstate-based assemblies, (H₂L¹)_{0.5}[Ni(L¹)]₂[W(CN)₈]₂·2DMF·H₂O (L¹ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) (**1**) and [Ni(L²)₃][W(CN)₈]₂·4H₂O (L² = 3,10-dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) (**2**). Single crystal X-ray diffraction shows that **1** consists of anionic one-dimensional (1D) linear chains, while **2** is built of 2D graphite-like layers with (6, 3) topology. Magnetic studies reveal that both complexes exhibit metamagnetic behavior from the spin-canted antiferromagnet to the ferromagnet induced by field.

Introduction

In the field of molecule-based magnets, cyano-bridged bimetal assemblies have been aggressively studied to demonstrate their intriguing topologies¹ and novel functionalities.^{2–6} More recently, a considerable effort on crystal engineering has been devoted to the design and construction of octacyanometallate [M(CN)₈]^{3-/4-} (M = Mo, W)-based magnets.⁷ [M(CN)₈]^{3-/4-} as a versatile class of building blocks can adopt three different spatial configurations depending on their chemical environments, such as the surrounding ligands. Because the diffuse *d* orbitals on 4*d* and 5*d* transition metals enhance the supra-exchange interaction through coordinating ligands, the combination of [M(CN)₈]³⁻ as a carrier of unpaired spin (*d*¹) with transition-metal cations has produced various dimensional molecular structures spanning from zero-dimensional (0D) discrete molecules, 1D chains, 2D layers, to 3D frameworks, and further displayed relatively high Curie temperatures,⁸ photo-induced magnetism⁹ and single-molecule magnetism.¹⁰

In search of new synthetic strategies for 3*d*-4*d*/5*d* cyano-bridged assemblies, we have carried out rationally the reactions of the octacyanometallates with octahedral transition-metal cations in the presence of tetradentate macrocyclic ligands,

in which four equatorial positions are occupied by four N atoms from macrocycles and two axial sites are reserved for incoming bridging ligands.¹¹ We have attempted to seek the correlation between adjusted structural parameters and resulting magnetic characters by varying pendant groups on macrocyclic ligands. In the present contribution, we described the syntheses, crystal structures and magnetic properties of 1D complex (H₂L¹)_{0.5}[Ni(L¹)]₂[W(CN)₈]₂·2DMF·H₂O (L¹ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) (**1**) with linear chain and [Ni(L²)₃][W(CN)₈]₂·4H₂O (L² = 3,10-dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) (**2**) with 2D graphite-like layer, in which tetradentate macrocyclic ligands with diverse pendant groups were chelated. To the best of our knowledge, 1D¹² and 2D¹³ octacyanometallate-based Ni^{II}-M^V (M = Mo, W) assemblies characterized structurally are rare to date.

Experimental

Physical measurements

C, H, N elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. All of the magnetization data were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer. The molar magnetic susceptibilities were corrected for the diamagnetism estimated from Pascal's tables¹⁴ and for the sample holder by a previous calibration.

Syntheses

Starting materials. All of the chemicals were of analytical grade and were used without further purification. The precursors [Ni(L¹)](ClO₄)₂,¹⁵ [Ni(L²)](ClO₄)₂¹⁶ and [HN(*n*-C₄H₉)₃]₃[W(CN)₈]₂·H₂O¹⁷ were prepared according to the published procedures.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in

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small quantities with great care. In addition, the reactions must be carried out under low light conditions because $[\text{W}(\text{CN})_8]^{3-}$ precursor is readily photo-reduced to $[\text{W}(\text{CN})_8]^{4-}$.

$(\text{H}_2\text{L}^1)_{0.5}[\text{Ni}(\text{L}^1)][\text{W}(\text{CN})_8] \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$ (**1**)

Single crystals of **1** were prepared at room temperature in the dark by slow diffusion of a DMF solution (2 mL) containing $[\text{Ni}(\text{L}^1)](\text{ClO}_4)_2$ (0.075 mmol) into a DMF solution (20 mL) of $[\text{HN}(n\text{-C}_4\text{H}_9)_3]_3[\text{W}(\text{CN})_8] \cdot \text{H}_2\text{O}$ (0.05 mmol). After about three weeks, block-shaped yellow crystals were obtained. Elemental analysis: Calcd for $\text{C}_{38}\text{H}_{71}\text{N}_{16}\text{NiO}_3\text{W}$: C 43.78, H 6.86, N 21.49%. Found: C 43.25, H 7.01, N 21.66%.

$[\text{Ni}(\text{L}^2)]_3[\text{W}(\text{CN})_8]_2 \cdot 4\text{H}_2\text{O}$ (**2**)

The same synthesis procedure as **1** was used to prepare **2**, substituting $[\text{Ni}(\text{L}^2)](\text{ClO}_4)_2$ for $[\text{Ni}(\text{L}^1)](\text{ClO}_4)_2$. After about three months, block-shaped yellow crystals were obtained. Elemental analysis: Calcd for $\text{C}_{55}\text{H}_{109}\text{N}_{34}\text{Ni}_3\text{O}_4\text{W}_2$: C 35.62, H 5.92, N 25.68%. Found: C 35.51, H 5.70, N 25.97%.

X-ray data collection and structure determination

Single crystal X-ray diffraction data for **1** and **2** were collected on a Bruker SMART APEX II diffractometer equipped with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. Diffraction data analysis and reduction were performed within *SMART* and *SAINT+*.¹⁸ Correction for Lorentz, polarization, and absorption effects were performed within *SADABS*.¹⁹ Structures were solved using Patterson method within *SHELXL-97* and refined using *SHELXL-97*.²⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms of macrocyclic ligands (L^1 and L^2) were calculated at idealized positions ($\text{C}-\text{H} = 0.97$ or 0.96 Å, $\text{N}-\text{H} = 0.91$ or 0.90 Å, and $\text{O}-\text{H} = 0.96$ Å) and included in the refinement in a riding mode with U_{iso} for H assigned as 1.2 or 1.5 times U_{eq} of the attached atoms. The H atoms of water molecules and DMF molecules were located from difference maps and refined as riding ($\text{O}-\text{H} = 0.85$ Å), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The crystallographic data and experimental details for structural analyses of **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table S1† and Table S2, respectively.

Results and discussion

Single crystal X-ray structures

Single crystal X-ray diffraction analysis (Fig. 1) reveals that the structure of **1** consists of anionic $\{[\text{Ni}^{\text{II}}(\text{L}^1)][\text{W}^{\text{V}}(\text{CN})_8]\}$ 1D chains, isolated counter cation $[\text{H}_2\text{L}^1]^{2+}$, crystallized DMF and water molecules. The W center is coordinated by two bridged and six terminal CN groups in a distorted square antiprism (*SAPR*, D_{4d}) with metric parameters typical for the $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ -based bimetallic complexes.^{11a,12,21} The average W–C and C–N distances are 2.169 and 1.132 Å, respectively, while the M–C–N bond angles are nearly linear with a maximum deviation from linearity of 5.7° . The two Ni centers (Ni(1) and Ni(2)) are both in an axially elongated octahedral geometry, in which four nitrogen atoms from L^1 ligand are located at the equatorial positions with

Table 1 Crystal data and structure refinement of X-ray data collection for **1** and **2**

	1	2
Formula	$\text{C}_{38}\text{H}_{71}\text{N}_{16}\text{NiO}_3\text{W}$	$\text{C}_{55}\text{H}_{109}\text{N}_{34}\text{Ni}_3\text{O}_4\text{W}_2$
$M_r/\text{g mol}^{-1}$	1042.67	1854.59
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
$a/\text{Å}$	9.2611(12)	9.0767(9)
$b/\text{Å}$	17.378(2)	27.661(3)
$c/\text{Å}$	18.191(3)	16.8542(17)
α ($^\circ$)	116.1960(10)	90
β ($^\circ$)	91.363(2)	92.062(2)
γ ($^\circ$)	104.822(3)	90
$V/\text{Å}^3$	2507.8(6)	4228.9(8)
Z	2	2
$D_{\text{calcd}}/\text{g cm}^{-3}$	1.381	1.456
μ/mm^{-1}	2.717	3.424
Total, unique	19568, 9729	32819, 8286
Observed [$I > 2\sigma(I)$]	8162	6180
GOF on F^2	1.078	1.028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0463, 0.1002	0.0490, 0.0992
R_1, wR_2 (all data)	0.0538, 0.1015	0.0660, 0.1023

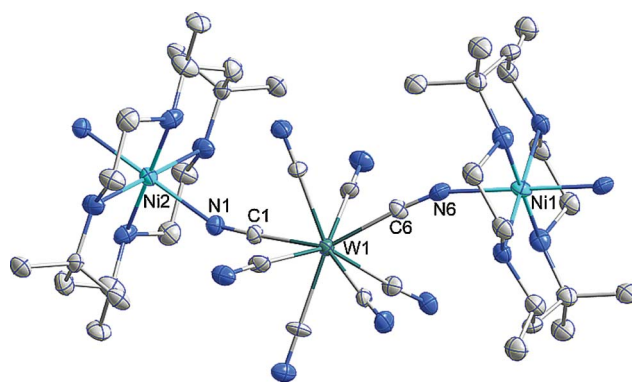


Fig. 1 ORTEP diagram of **1**, showing the 30% probability thermal motion ellipsoid. Hydrogen atoms, isolated $[\text{H}_2\text{L}^1]^{2+}$, crystallized water and DMF molecules have been omitted for clarity.

an average Ni– N_{eq} distance of 2.089 Å, while the axis sites are occupied by two nitrogen atoms from bridging cyanide groups of $[\text{W}(\text{CN})_8]^{3-}$ with the mean Ni–N distance of 2.126 Å. The Ni–N–C bridging units are strongly bent in opposition to the case of the almost linear W–C–N units. These metric parameters $[\text{Ni}(\text{L}^1)]^{2+}$ are reminiscent of those in related complexes containing ligand L^1 .^{11c,11e,22} As a result, $[\text{Ni}(\text{L}^1)]^{2+}$ and $[\text{W}(\text{CN})_8]^{3-}$ moieties are linked in an alternating fashion to form an anionic 1D infinite chain (Fig. 2). The intrachain distances between Ni and W are *ca.* 10.11 and 10.61 Å, respectively, while the intrachain W \cdots W distance is *ca.* 9.26 Å. The neighboring $\{\text{Ni}^{\text{II}}\text{W}^{\text{V}}\}$ chains weakly interact with isolated $[\text{Ni}(\text{L}^1)]^{2+}$ through hydrogen bonding, leading to the formation of a 2D supramolecular layer.

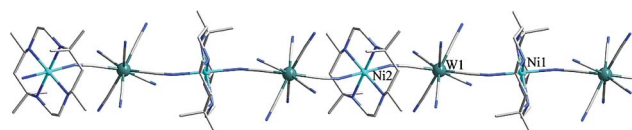


Fig. 2 View of the structure of **1**, showing an anionic 1D chain. Hydrogen atoms, isolated $[\text{H}_2\text{L}^1]^{2+}$, crystallized DMF and water molecules have been omitted for clarity.

The structure of **2** is built of neutral 2D graphite-like layers consisting of W and Ni centers joined by cyano bridges, and crystallized DMF and water molecules located within the layer. It should be mentioned here that the structures are rather different between **1** and **2**, although they were prepared under similar conditions. The noticeable structural disparity may be attributed to the diverse pendant groups on the macrocyclic ligands employed, which cause different steric congestion to the coordination sphere around the metal center. The coordination geometries (Fig. 3) of Ni and W centers are similar to those found in **1**. In the repeating fragment $\{\text{Ni}_3\text{W}_2\}_n$, the W atom is coordinated by three bridged and five terminal CN groups with W–C distances ranging from 2.117(7) to 2.176(5) Å in a distorted square antiprism. The two Ni atoms are both in an axially elongated octahedral geometry, in which the equatorial sites are occupied by four nitrogen atoms from L^2 ligand, and the apical positions are located by two nitrogen atoms from two bridging CN groups. As displayed in Fig. 4, two-connected $[\text{Ni}(\text{L}^2)(\mu\text{-CN})_2]^{2+}$ and three-connected $[\text{W}(\text{CN})_5(\mu\text{-CN})_3]^{3-}$ units are linked *via* cyanides in the *bc* plane, resulting in the formation of 2D graphite-like structure with (6, 3) topology (Fig. 4), in which a 12-metal 36-atom irregular hexagon with the W atoms in the corners and –CN–Ni–NC– linkages on the edges, $\text{Ni}_6\text{W}_6(\text{CN})_{12}$, is the basic building unit. The edge distance between W atoms in a hexagon is *ca.* 10.68 Å, while the separation between adjacent layers is *ca.* 9.08 Å (W···W distance). The 2D layered structure of **2** has also been observed in other octacyanomethylate-based bimetallic assemblies.^{11a,23}

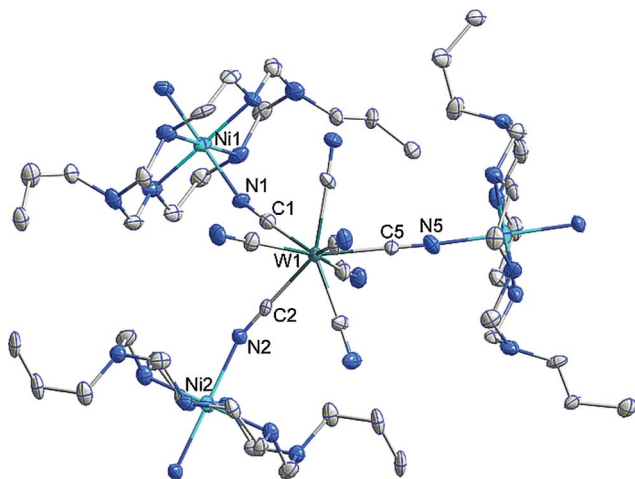


Fig. 3 ORTEP diagram of **2**, showing the 30% probability thermal motion ellipsoid. Hydrogen atoms, crystallized DMF and water molecules have been omitted for clarity.

Magnetic properties

$(\text{H}_2\text{L}^1)_{0.5}[\text{Ni}(\text{L}^1)][\text{W}(\text{CN})_6] \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$ (**1**). The temperature-dependent molar magnetic susceptibilities of **1** were measured in an applied field of 2 kOe (Fig. 5). The $\chi_{\text{M}}T$ value of $1.36 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K is consistent with the spin-only one ($1.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) expected for one Ni(II) ($S_{\text{Ni}} = 1$) and one W(V) ($S_{\text{W}} = 1/2$) center assuming $g = 2$. As the temperature is lowered, the $\chi_{\text{M}}T$ value monotonically increases and then increases abruptly up to a maximum value of $6.07 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 6 K, followed

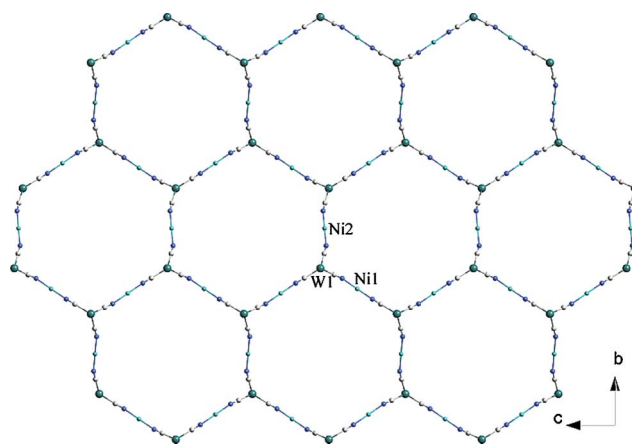


Fig. 4 View of the 2D graphite-like structure with (6, 3) topology of **2**.

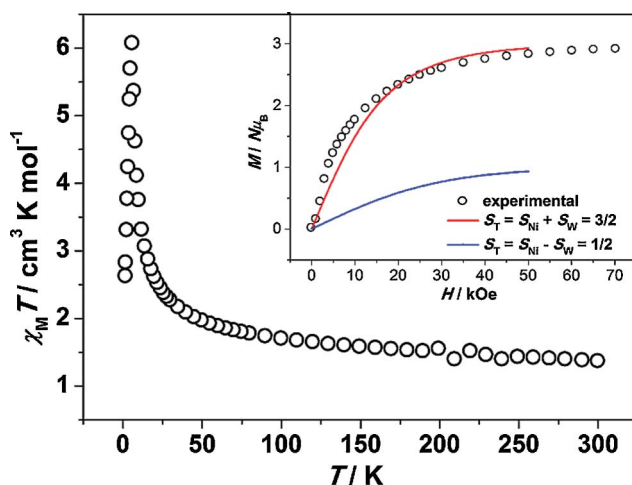


Fig. 5 Temperature dependence of $\chi_{\text{M}}T$ for **1** measured at 2 kOe. Inset: Field dependence of the magnetization performed at 1.8 K for **1**. The Brillouin curve for the independent one Ni(II) and one W(V) ions is given at 1.8 K.

by a drop to 2.62 at 1.8 K. The magnetic susceptibility above 60 K obeys the Curie–Weiss law with a positive Weiss constant, θ , of +24.45 K (Fig. S1†), which indicates that the ferromagnetic coupling between metal ions dominates the magnetic properties of **1**. The decrease of $\chi_{\text{M}}T$ below 6 K results from the saturation of the χ_{M} value, interchain antiferromagnetic interaction and/or the zero-field splitting effect.

The field dependence of the magnetization measured at 1.8 K is shown in Fig. 5 (inset). The magnetization increases very rapidly in low field and almost reaches a saturation of magnetization above *ca.* 50 kOe. The magnetization $M_{\text{s}} = 2.92 N\mu_{\text{B}}$ in 70 kOe is in agreement with the ferromagnetic $\text{Ni}^{\text{II}}\text{W}^{\text{V}}$ system based on $3 N\mu_{\text{B}}$ with $S = 3/2$. The experimental curve at 1.8 K is slightly higher than that derived from the Brillouin function in low fields, confirming further ferromagnetic coupling between the adjacent Ni(II) and W(V) ions.

As shown in Fig. 6, the variable-field magnetization curve reveals an S-shape, indicating that **1** is a metamagnet with a critical field of ± 1.5 kOe. Both sides of ± 1.5 kOe, two regions with loops can be observed. Below ± 1.5 kOe, the loop with remnant magnetization of $0.039 N\mu_{\text{B}}$ and coercive field of ± 150 Oe indicates

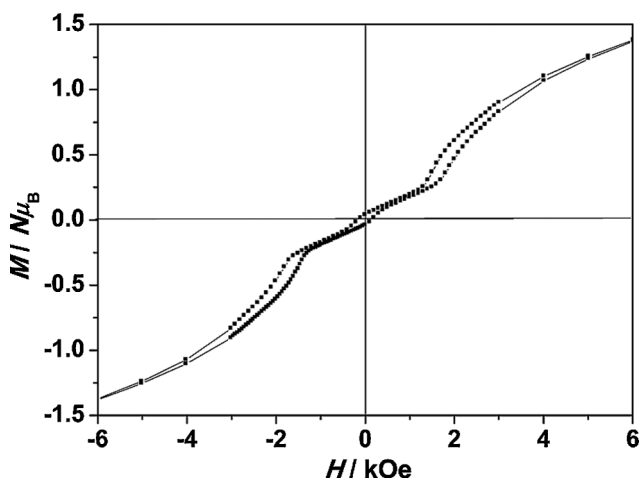


Fig. 6 Field-dependent magnetization and hysteric loops at 1.8 K for **1**.

1 is a spin-canted antiferromagnet. In the range of $\pm(1.5\text{--}6)$ kOe the loop is ascribed to the field-induced ferromagnet rather than the decoupled phenomenon by field. So, **1** is a metamagnet from spin-canted antiferromagnet to ferromagnet induced by field.

The M vs. T curves of **1** measured at 1.0 and 1.5 kOe show a peak at *ca.* 6 K (Fig. 7), implying a long-range antiferromagnetic ordering below this point, due to the antiferromagnetic interaction between the chains according to the structure of **1**. The temperature dependence of the ac susceptibility for its in-phase component (χ'), and out-of-phase component (χ'') performed in a zero applied direct current (*dc*) field at 10 Hz (Fig. S2†) show peaks at 5.0 and 4.0 K, respectively, which indicates the presence of a long-range ferromagnetic ordering. However, the small values of χ'' can be attributed to the small net spin per mole. The ac susceptibility of **1** was measured in the frequency range 1–1.5 kHz at 1.8–20 K to determine that it is a Single-Chain Magnet (SCM) or not, but no frequency-dependent signal was observed (Fig. S3†).

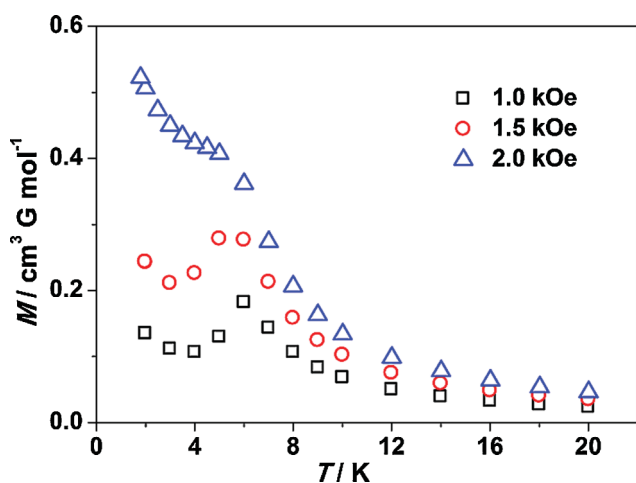


Fig. 7 Temperature dependence of M in an applied field of 1.0, 1.5, and 2.0 kOe for **1**.

$[\text{Ni}(\text{L}^2)]_3[\text{W}(\text{CN})_8]_2 \cdot 4\text{H}_2\text{O}$ (**2**). The ferromagnetic behavior and metamagnetism are also observed in **2**. The $\chi_M T$ value per Ni_3W_2 unit at 300 K ($3.61 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) is close to the expected

value ($3.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) for magnetically isolated three Ni(II) ions and two W(V) ions (Fig. 8). Upon cooling, the changing trend in $\chi_M T$ vs. T curve is similar to that of **1**. The plot of $1/\chi_M$ vs. T above 30 K obeys the Curie–Weiss law with a Weiss constant $\theta = +20.81 \text{ K}$ (Fig. S4†), which also indicates the presence of the ferromagnetic coupling between the adjacent Ni(II)–W(V) magnetic centers within the layer. As shown in Fig. 8 (inset), the saturation magnetization ($7.41 N\mu_B$) in 70 kOe is close to the expected $S = 4$ value of $8 N\mu_B$ for the Ni_3W_2 system.

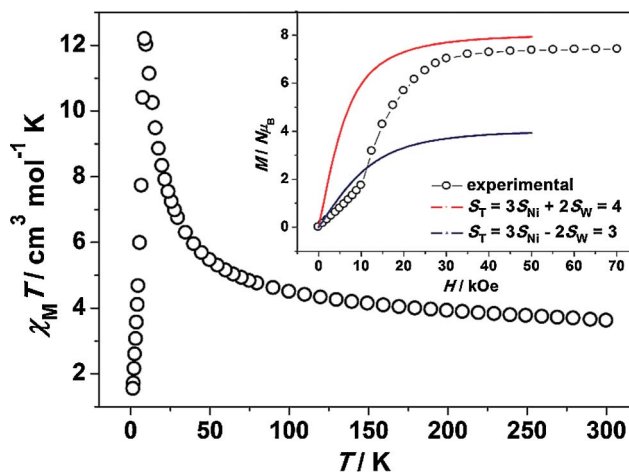


Fig. 8 Temperature dependence of $\chi_M T$ for **2** measured at 2 kOe. Inset: Field dependence of the magnetization performed at 1.8 K for **2**. The Brillouin curve for the independent three Ni(II) and two W(V) ions is given at 1.8 K.

Below 15 kOe, the observation of peaks at *ca.* 7 K in M vs. T plots (Fig. 9) is a signature of the existence of the long-range antiferromagnetic ordering, while the lack of the peak at $H \geq 15$ kOe implies a field-induced magnetic phase transition from antiferromagnet to ferromagnet. The peak at 8.5 for χ' indicates the presence of a long-range ferromagnetic ordering and no peak for χ'' was observed (Fig. S5†).

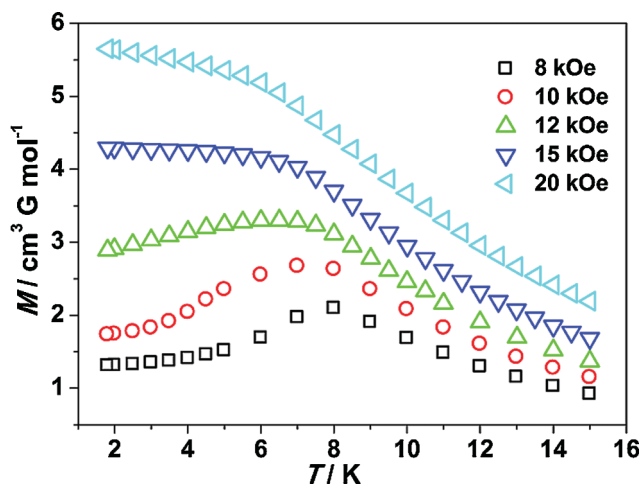


Fig. 9 Temperature dependence of M in an applied field of 8, 10, 12, 15, and 20 kOe for **2**.

Conclusions

Two cyano-bridged bimetallic Ni^{II}–W^V complexes chelated by tetradentate macrocyclic ligands with various pendant groups have been prepared and characterized. Single crystal X-ray diffraction analysis shows that **1** consists of anionic 1D chains linked by [Ni(L¹)]²⁺ and [W(CN)₈]³⁻ moieties in an alternating fashion, while **2** is built of neutral 2D graphite-like structure with (6, 3) topology, in which 12-metal 36-atom hexagon, Ni₆W₆(CN)₁₂, is the basic building unit. Magnetic studies reveal that both complexes exhibit a metamagnetic behavior from the spin-canted antiferromagnet to the ferromagnet induced by field.

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