Iron(II)-octacyanonitobate(IV) ferromagnet with T_c 43 K†

Dawid Pinkowicz,^a Robert Podgajny,^{*a} Robert Pelka,^b Wojciech Nitek,^a Maria Balanda,^b Magdalena Makarewicz,^b Mariusz Czapla,^b Jan Żukrowski,^c Czesław Kapusta,^c Dariusz Zajączak^{b,d} and Barbara Sieklucka^a

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We have synthesized the octacyanonitobate-based cyano-bridged 3D ferromagnet $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2][\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$ **1** and characterized structurally, spectroscopically (XANES/EXAFS, IR, UV-Vis, Resonance Raman, ^{57}Fe Mössbauer spectroscopy) and magnetically. **1** crystallizes in the tetragonal system, space group $I4/m$, $a = 11.989(5)$ Å, $c = 13.237(5)$ Å, $V = 1902.6(13)$ Å³. 3D coordination architecture comprises two types of $\text{Nb}^{\text{IV}}\text{--C--N--Fe}^{\text{II}}_{\text{HS}}$ (HS = high spin) linkages with Fe--N--C angles of 154.5° and 167.5° . The XANES/EXAFS spectra at Fe:K and Nb:K lines confirm the presence of $\text{Nb}^{\text{IV}}\text{--C--N--Fe}^{\text{II}}$ linkages. Magnetic measurements reveal ferromagnetic ordering below $T_c = 43$ K with some non-collinearity of Nb^{IV} ($S = 1/2$) and Fe^{II} ($S = 2$) magnetic moments. The molecular field model simulation reproduces well the $M(T)$ curve and T_c value with one average exchange coupling constant $J_{\text{FeNb}} = +8.1$ cm^{−1}.

Introduction

The rational design and targeted synthesis of coordination frameworks are currently of great interest in the search for materials with either solvent inclusion or gas adsorption characteristics or with electronic or nonlinear optical properties.^{1–3} Among them the magnetic materials draw particular attention due to potential future application as molecular switches and recording/storage memory devices.^{4–9} Using the building-block methodology, a range of magnetic frameworks has been prepared incorporating cationic paramagnetic centres with paramagnetic octacyanomolybdates(V) and -tungstates(V).^{10–16} We have introduced the inorganic–organic hybrid octacyanonitobate(IV)-based networks offering relatively high T_c (up to 62 K) together with the opportunity of its tuning on the molecular level.^{17–19} Parallel to our research, Ohkoshi and co-workers initiated research on the iron(II) SCO (spin-crossover) in $\text{Fe}^{\text{II}}\text{--}[\text{Nb}^{\text{IV}}(\text{CN})_8]^{4-}$ networks.²⁰ 3D $\text{Fe}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8](3\text{-py-CH}_2\text{OH})\cdot 4.6\text{H}_2\text{O}$ revealed the slow continuous reversible transition between $\text{Fe}^{\text{II}}_{\text{HS}}\text{--Nb}^{\text{IV}}\text{--Fe}^{\text{II}}_{\text{HS}}$ (HT phase) and $\text{Fe}^{\text{II}}_{\text{HS}}\text{--Nb}^{\text{IV}}\text{--Fe}^{\text{II}}_{\text{LS}}$ (LT phase) between 325–150 K, the latter providing the ferrimagnetically ordered phase below $T_c = 12$ K. Incorporation of the 3-py-CH₂OH ligand reduces the number of coordination sites at the Fe centre available for cyano-bridging and thus reduces the overall cyano-connectivity, resulting in the T_c value lying far beyond the reach of spin-crossover phenomena.

Thus, the design of a $\text{Fe}^{\text{II}}\text{--Nb}^{\text{IV}}$ multifunctional framework should not be solely dependent on the ligand field strength, dictating SCO transition, and cyano-bridged connectivity needs to be taken into account, as it controls the critical temperature of ferrimagnetic ordering. Therefore, we report herein the crystal structure and properties of a purely inorganic 3D coordination network $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2][\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$ **1**, representing the foundation in the engineering of FeNb cyano-bridged materials with diverse topologies and required multifunctionality.

Experimental

Materials

All chemicals and solvents of analytical grade were purchased from Sigma-Aldrich Co. and used as received. $\text{K}_4\text{Nb}(\text{CN})_8\cdot 2\text{H}_2\text{O}$ was synthesized as described.²¹

Synthesis of $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2][\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$ **1**

All operations were carried out under an Ar atmosphere. Degassed water solutions of Mohr's salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ (40 ml, 0.20 g, 0.50 mmol) and $\text{K}_4[\text{Nb}(\text{CN})_8]\cdot 2\text{H}_2\text{O}$ (40 ml, 0.13 g, 0.26 mmol) were mixed and the resulting orange solution was left to stand in the dark for 10 h. Small, dark red crystals of **1** (0.04 g, 29%) were isolated from amorphous by-products by repeated decantation with ethanol (95%), dried and stored under argon (Found C, 17.3; H, 2.6; N, 20.35. $\text{C}_8\text{H}_{16}\text{Fe}_2\text{N}_8\text{NbO}_8$ requires C, 17.3; H, 2.9; N, 20.1%). $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3555vs and 3412br $\nu(\text{O--H})$, 2151 m and 2134 s $\nu(\text{C}\equiv\text{N})$, 1611 s $\delta(\text{OH})$, 593br and 473 s $\nu(\text{Nb--C})$, $\nu(\text{MnN})$. TGA/DTG/QMS measurements were performed on a freshly prepared sample and show one peak in the temperature regions: 60–120 °C and one peak above 160 °C, both assigned to the collective loss of H_2O and CN^- . The first region is dominated by the loss of crystallization and coordination water

^aFaculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060, Kraków, Poland. E-mail: podgajny@chemia.uj.edu.pl

^bH. Niewodniczański Institute of Nuclear Physics PAN, Radzikowskiego 152, 31-342, Kraków, Poland

^cAGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Mickiewicza 30, 30-059, Kraków, Poland

^dHasylab, DESY, Notkestrasse 85, 22607, Hamburg, Germany

† Electronic supplementary information (ESI) available: Structure model in CIF format, overall 3D projections of the crystal structure, IR spectra and Resonance Raman spectrum, for **1**. CCDC reference number 717898. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b908486j

molecules, while the second one is dominated by the loss of CN[−] ions.

Physical techniques

Elemental analyses were performed on the EuroEA EuroVector Elemental Analyzer. IR spectra were measured in KBr pellets between 4000 and 400 cm^{−1} using the Bruker EQUINOX 55 FTIR spectrometer. Thermogravimetric data in the temperature range 25–400 °C were collected on a Mettler Toledo TGA/SDTA 851e microthermogravimeter equipped with QMS Thermostat GSD 300 T Balzers at a heating rate of 5 °C min^{−1} in an Ar atmosphere. Reflectance UV-Vis-NIR spectra of the solid phases were recorded on a Perkin-Elmer Lambda 35 spectrophotometer equipped with a 50 mm integrating sphere in the 190–1000 nm wavelength range. Resonance Raman spectroscopy was performed using a Renishaw inVia Raman Microscope equipped with a Spectrophysics Ar⁺ ion-laser. Magnetic measurements were performed at Lake Shore 7225 AC susceptometer/DC magnetometer. The χ_{DC} temperature dependence in the range 4.3 K–200 K was measured in the field 2 kOe. AC susceptibility was measured with the frequency of the oscillating field set to 10 Hz, 80 Hz and 625 Hz and the amplitude of 3 Oe. Both real χ' and imaginary χ'' components were detected. XAS experiments have been performed at the beamline CEMO at DORIS III, in HASYLAB, DESY in Hamburg, Germany. EXAFS spectra were collected in transmission mode at 77 K for Nb:K edge and Fe:K edge, using appropriate gas and pressure in ionisation chambers. Double crystal monochromator, Si(311) for Nb:K edge and Si(111) for Fe:K edge with an energy resolution of 0.4 eV and 1 eV, respectively, has been used. The energy has been calibrated to the spectra of the reference sample, measured simultaneously with the sample. XANES spectra of both samples, K₄[Nb(CN)₈] $\cdot$ 2H₂O and **1**, at the Nb:K edge, have the same edge energy, shifted to 6.6(1) eV and 16.8(5) eV, taken as the first and second maximum of the first derivative and 12.8(1) eV taken as the half of the edge jump, corresponding to the metallic Nb foil (0.0(1) eV, 12.5(1) eV and 5.7(1) eV, respectively). The shape of both lines is also identical in the XANES energy range. Fe:K edge XANES spectrum of the sample of **1** is shifted to 7.3(1) eV, 13.6(1) eV (taken as the first and second maximum of the first derivative) and 10.6(1) eV (taken as the half of the edge jump), corresponding to the metallic Fe foil (0.0(1) eV, 9.4(1) eV and 8.9(1) eV, respectively). The EXAFS spectra have been analyzed using Athena (Ifeffit package).²² The $\chi(k)$ spectra has been analyzed and plotted, amplified by k^3 . EXAFS spectra in the R space has been phase corrected.

Structure solution and refinement

The single crystal diffraction data were collected on a Nonius Kappa CCD equipped with a Mo K α radiation source and graphite monochromator. The space group was determined using ABSSEN.²³ The structure of **1** was solved by direct methods using SIR-97.²⁴ Refinement and further calculations were carried out using SHELXL-97.²⁵ The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2 . All reachable H atoms in water molecules were found from the difference Fourier map and then refined using a riding model (AFIX 3) with $U_{iso}(H)$ fixed at 1.5 $U_{eq}(O)$. Structural diagrams were prepared using Mercury 1.4.2, Ortep32,²⁶ POV-Ray²⁷ and

Table 1 Crystal solution and refinement parameters for **1**

Empirical formulae	C ₃₂ H ₆₄ Fe ₈ N ₃₂ Nb ₄ O ₃₂
Moiety formulae	{[Fe ^{II} (H ₂ O) ₂] ₂ [Nb ^{IV} (CN) ₈] $\cdot$ 4H ₂ O} ₄
M (g mol ^{−1})	2227.08
Crystal dimension (mm ³)	0.7 $\times$ 0.7 $\times$ 0.7
Crystal system	tetragonal
Space group	$I 4/m$
a (Å)	11.989(5)
c (Å)	13.237(5)
V (Å ³)	1902.6(13)
Z	1
ρ (g cm ^{−3})	1.944
T (K)	293
$F(000)$	1108
μ (mm ^{−1})	2.15
Reflections collected	6916
Unique reflections	1140
R_{int}	3.98%
GOF on F^2	1.108
R_1 [$I > 2\sigma(I)$]	0.0275
wR_2 (all data)	0.0618

VESTA²⁸ software. Crystal solution and refinement parameters are presented in Table 1.

Calculations

Continuous Shape Measure Analysis for coordination sphere of Nb^{IV} was performed with use of SHAPE v. 1.1b software. Shape measure relative to the square antiprism S_{SAPR} of 0.17 and shape measure relative to the dodecahedron S_{DD} of 2.29 together with values of generalized interconversion coordinates $\phi_{(SAPR \rightarrow DD)} = 24.4\%$ and $\phi_{(DD \rightarrow SAPR)} = 89.5\%$ and low value of the $\Delta_{(SAPR,DD)} = 0.14$ which represents the deviation from the DD $\leftrightarrow$ SAPR interconversion path show the dominating character of SAPR geometry of [Nb(CN)₈]^{4−} moiety in **1**. The sum ($\phi_{(SAPR \rightarrow DD)} + \phi_{(DD \rightarrow SAPR)}$) is greater than 100% because of the non-zero value of $\Delta_{(SAPR,DD)}$.²⁹

Results and discussion

Crystal structure

Single crystal X-Ray diffraction of **1** revealed a highly symmetrical 3D structure (Fig. S1†), where each [Nb^{IV}(CN)₈]^{4−} of almost ideal square antiprism (SAPR-8) geometry is connected to eight pseudooctahedral *trans*-[Fe^{II}(NC)₄(H₂O)₂]^{2−} moieties through eight cyano-bridges (Fig. 1 left). Each *trans*-[Fe^{II}(NC)₄(H₂O)₂]^{2−} unit is connected to four neighbouring Nb^{IV} centres with four cyano-bridges oriented in the equatorial plane (Fig. 1 right). The most important metric parameters of Nb^{IV}–CN–Fe^{II} linkages are presented in Table 2. 3D architecture comprises vertex-sharing octahedrons Fe₄Nb₂ (Fig. 2). The apical vertexes of each octahedron

Table 2 Metric parameters of Nb^{IV}–CN–Fe^{II} linkages

	Nb1–C1–N1–Fe2		Nb1–C3–N3–Fe2	
Bond length (Å)	Nb–C	2.251(3)	Nb–C	2.257(3)
	C–N	1.145(3)	C–N	1.146(3)
	N–Fe	2.144(2)	N–Fe	2.175(2)
Angle [deg]	Nb–C–N	176.7(2)	Nb–C–N	174.6(2)
	Fe–N–C	167.5(2)	Fe–N–C	154.5(2)
Nb $\cdots$ Fe distance (Å)	5.508		5.409

Fig. 1 Connectivity and geometry of the coordination spheres of $[\text{Nb}(\text{CN})_8]^{4-}$ (left) and $\text{trans-}[\text{Fe}^{\text{II}}(\text{NC})_4(\text{H}_2\text{O})_2]^{2-}$ (right) in **1** with atom labeling scheme.

Fig. 2 Fragment of the structure of **1**; the projection showing two types of octahedral-like vertex-sharing Fe_4Nb_2 units. H_2O molecules are omitted for clarity.

are occupied by Nb^{IV} centers, whereas the equatorial corners are occupied by Fe^{II} ions. Two types of Fe_4Nb_2 units are distinguished: those with longer and less bent cyano-bridges (Nb1-C1-N1-Fe2 , 5.508 Å, 167.5°, pale gray octahedra) and those with shorter and more bent cyano-bridges (Nb-C3-N3-Fe , 5.409 Å, 154.5°, dark gray octahedra). The different Fe_4Nb_2 units are aligned in an alternate manner along [001], [110] and [1-10] crystallographic directions giving rise to a layered-like character of **1**. The 3D coordination framework of **1** (Fig. S1†) is topologically identical to that of $\{[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2][\text{M}^{\text{IV}}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Nb, Mo, W}$)^{30,31} and $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2][\text{M}^{\text{IV}}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Mo, W}$).^{32,33}

XAS studies

Results of XAS studies of **1** in comparison to $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ are presented in Fig. 3 and Table 3. EXAFS spectrum of **1**

Table 3 EXAFS path for induced elements, taken from fits of EXAFS spectra presented in Fig. 3. Fe–N, C–N and Nb–C bond distances are calculated as a difference of corresponding paths, assuming the linear arrangement of Nb–C–N–Fe bonding

Distances [Å]:			
(1)	Fe–N/O	Fe–C	Fe–Nb
Fe:K	1.98 ± 0.17	3.00 ± 0.19	5.25 ± 0.28
(1)	Nb–C	Nb–N	Nb–Fe
Nb:K	2.06 ± 0.19	3.16 ± 0.19	5.16 ± 0.28
$\text{K}_4[\text{Nb}(\text{CN})_8]$	Nb–C	Nb–N	—
Nb:K	2.06 ± 0.19	3.17 ± 0.19	—

Fig. 3 Phase corrected EXAFS spectra, EXAFS signal $\chi(k)k^3$ (upper inset) and normalized XANES spectra (lower inset) for **1** at the Fe:K edge (blue solid line), Nb:K edge (green solid line) and for $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ at Nb:K edge (pink dotted line).

obtained from Fe:K edge exhibits one dominant peak at ~ 2.0 Å corresponding to the nitrogen and oxygen atoms of the first coordination sphere and two minor peaks at ~ 3.0 Å and ~ 5.2 Å corresponding to the carbon and niobium atoms, respectively. Due to the difference of ionic radius of N and O smaller than the $\Delta v_{1/2}$ of the EXAFS peak, the respective peaks are overlapped. EXAFS spectra of **1** and $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ from the Nb:K edge exhibits two strong peaks close to 2.1 Å and 3.2 Å, corresponding to 8 carbon and 8 nitrogen atoms. The additional peak located slightly above 5.1 Å, exists only in the case of **1** and is attributed to the Fe ions. Results of the EXAFS studies are in good agreement with the bond lengths taken from single crystal X-Ray diffraction data. XANES studies show the identical valence state 4+ of Nb in **1** and $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ and Fe is in a 2+ oxidation state.

Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectrum (Fig. 4) of **1** at 300 K shows one quadrupole doublet with $\delta = 1.03 \text{ mm s}^{-1}$ (relative to α -iron) and $\Delta E_Q = 2.48 \text{ mm s}^{-1}$, which are characteristic of Fe^{II} in the HS state. As the temperature is decreased to 80 K there is still one HS iron(II) doublet ($\delta = 1.14 \text{ mm s}^{-1}$ and $\Delta E_Q = 3.34 \text{ mm s}^{-1}$) present. Further decrease in temperature to 4.2 K results in a complicated spectrum, where both magnetic dipole and electric quadrupole interactions are coupled. Preliminary analysis of the spectrum below magnetic transition suggests the presence of two non-equivalent HS iron(II) sites and an interesting magnetic structure of **1**. The presence of the LS iron(II) site at this temperature and the possibility of the spin transition can be ruled out.

Fig. 4 ^{57}Fe Mössbauer spectra of $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$ **1** at $T_1 = 300$ K, $T_2 = 80$ K, $T_3 = 4.2$ K with isomer shift IS and quadrupole splitting QS values.

IR spectroscopy

IR spectrum of **1** in the range of $\nu(\text{CN})$ exhibits two strong bands at 2151 and 2134 cm^{-1} characteristic for the bridging mode of the CN^- ligands (Fig. S2†). There are also peaks connected to the presence of both crystallisation and coordination water molecules: 3555, 3413 cm^{-1} $\nu(\text{OH})$ and 1611 cm^{-1} $\delta(\text{OH})$.

UV-Vis solid state spectroscopy

Solid state UV-Vis spectra of **1** (Fig. 5) and its Mo^{IV} analogue $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Mo}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$ present the contributions from: a very intense signal of LMCT (Nb^{IV}) or MLCT (Mo^{IV}) transitions in the range of 190 to ~ 370 nm, a weaker signal of LF (Nb^{IV} , Mo^{IV}) transitions in ~ 350 – 470 nm^{21,34} and a very broad weak signal of LF (HS Fe^{II}) transitions in visible and NIR region. In addition, **1** exhibits a very intense broad band at 505 nm assigned to the MMCT transition: $\text{Fe}^{\text{III}}\text{--NC--Nb}^{\text{IV}} \rightarrow \text{Fe}^{\text{III}}\text{--NC--Nb}^{\text{III}}$.

Fig. 5 UV-Vis-NIR spectrum of **1** (red) and $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Mo}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$ (black) in the range 190–1100 nm.

Resonance Raman spectroscopy

The resonance Raman spectrum of **1** measured with 532 nm laser line at $T = 300$ K (Fig. S3†) exhibits two very strong $\nu(\text{C}\equiv\text{N})$

bands: narrow at 2139 cm^{-1} characteristic of bridged $[\text{Nb}^{\text{IV}}(\text{CN})_8]^{4-}$ and broad at 2095 cm^{-1} assigned to $[\text{Nb}^{\text{III}}(\text{CN})_8]^{5-}$.²¹ Therefore, RR spectrum support the interpretation of the band at 505 nm in **1** as a MMCT transition.

Magnetic properties

Magnetic properties of **1** are presented in Fig. 6. For temperatures above 100 K $\chi_{\text{DC}}(T)$ obeys the Curie–Weiss law with the positive $\theta_{\text{CW}} = (47 \pm 1)$ K and the Curie constant $C = (7.7 \pm 0.2) \text{ cm}^3 \text{ K mol}^{-1}$, close to the value 7.635 emu K mol^{-1} expected for two high-spin Fe^{II} assuming $g_{\text{Fe}} = 2.2$ ²⁰ and one Nb^{IV} assuming $g_{\text{Nb}} = 2.0$.²¹ The transition to the long-range ordered magnetic state is

Fig. 6 Magnetic characteristics of **1**: (a) $\chi T(T)$ dependence in DC mode and $\chi(T)$ dependence in AC mode (inset); (b) $M(H)$ dependence and hysteresis loop (inset); (c) polynomial regression of $M(H^{-1})$ for $M > 7.5 \text{ N}\beta$ (details in the inset) and the resulting M_s value of 9.61 $\text{N}\beta$ as a limit of the $M(H^{-1})$ function for $H^{-1} \rightarrow 0$.

manifested by the $\chi_{\text{DC}}T$ maximum of 422 emu K mol⁻¹ at 33 K and the strong peak in the AC susceptibility (Fig. 6a). Critical temperature determined from the minimum of the χ' derivative is $T_c = 43.3$ K. The relative variation of the temperature T_p of the χ' peak per decade of frequency f , $\alpha = (\Delta T_p/T_p)/\Delta(\log_{10}f)$ equal to 0.006, is at the lower limit observed for canonical spin glasses. This weak frequency dependence comes probably from the positional disorder of crystallisation water molecules. The magnetization curve measured at 4.3 K shows a fast rise—up to the value of *ca.* 7 N β at the field of 9 kOe, followed by a further increase up to almost 9 N β at 56 kOe (Fig. 6b). Magnetization of saturation obtained as a limit of the $M(H^{-1})$ function for $H^{-1} \rightarrow 0$ is 9.6 N β (Fig. 6c), close to 9.8 N β expected for two high-spin Fe^{II} ($g = 2.2$) and one Nb^{IV} ($g = 2.0$). The compound is a soft magnet with the coercive field $H_c = 130$ Oe and the remanence $M_R = 1.24$ N β (Fig. 6b inset).

Taking into account two different Fe–N–C angles in Nb^{IV}–CN–Fe^{II} linkages (see Fig. 1): Fe–N1–C1 of 167.5° and Fe–N3–C3 of 154.5° one can expect two coupling constants $J_1 \neq J_2$. The magnitude of $J_{\text{M}^{\text{II}}\text{M}^{\text{IV}}}$ (M'–divalent 3d metal ion, M''–Mo^V, W^V or Nb^{IV} in [M''(CN)₈]⁴⁻) depends generally on the M'–N–C angle, valence configuration of the M'' centre and bridging geometry on the M'' centre,^{35–37} while their sign is rather an individual case:¹⁰ *negative* for Mn^{II}, *positive* or *negative* for Co^{II}, Ni^{II} and Cu^{II}, and *negative* for the only one known cyano-bridged Fe–Nb network.²⁰ The DFT estimated trends of J vs M'–N–C angle for M'–NC–M'' (M' = Mn^{II}, Ni^{II}) linkages over the angle range 140–180° reveals the increase in ferromagnetic contribution J_F along with the increasing M'–N–C angle.³⁶ The resulting J values are between –16 and –4 cm⁻¹ for Mn^{II}–N–C–Mo^V, between –22 and –8 cm⁻¹ for Mn^{II}–N–C–W^V, between –7 and +13 cm⁻¹ for Ni^{II}–N–C–Mo^V and between 0–16 cm⁻¹ for Ni^{II}–N–C–W^V. Therefore, taking into account the position of Fe between Mn and Ni in the 3d row, the local magnetic interactions in **1** may be interpreted in terms of two different exchange coupling constants: J_1 assignable to the more bent bridge (154.5°) and J_2 assignable to the less bent one (167.5°), where $J_2 > J_1$. The proximity of the M_s value to 9.8 N β indicates the domination of *ferromagnetic* Nb^{IV}–Fe^{II} coupling. However, the shape of the $M(H)$ curve (Fig. 6b) indicates the ordering of the magnetic moments is most probably non-collinear.

To estimate the values of the exchange coupling constants J_1 and J_2 we analyzed the spontaneous magnetization *vs.* temperature curve for {[Fe^{II}(H₂O)₂]₂[Nb^{IV}(CN)₈]₄·4H₂O}_{*n*} based on the molecular field model.³⁸ We assume that the exchange interactions mediated through both the non-equivalent CN bridges are ferromagnetic, so the mean field model will consist of two types of sublattice sites: one sublattice for the Nb centers and the other formed by the Fe ions. Next, only the superexchange coupling between the nearest-neighbour sites are taken into account. We also take on the simplifying assumption that $J_1 = J_2 = J_{\text{FeNb}}$. This is because there is only one crucial parameter of the mean field $M(T)$ curve, namely the transition temperature T_c . In that case keeping the coupling constants different may lead to a rather arbitrary result. The molecular fields H_{Fe} and H_{Nb} acting on the two sublattice sites are given by the following formulae

$$H_{\text{Fe}} = H_0 + n_{\text{FeNb}}M_{\text{Nb}},$$

$$H_{\text{Nb}} = H_0 + n_{\text{NbFe}}M_{\text{Fe}},$$

where H_0 is the external magnetic field, n_{ij} are the molecular field coefficients, and M_{Fe} and M_{Nb} are the sublattice magnetizations per unit volume for the Fe and Nb sites, respectively. The molecular field coefficients are related to the exchange coefficient by

$$n_{\text{FeNb}} = \frac{Z_{\text{FeNb}}}{\mu N g_{\text{Fe}} g_{\text{Nb}} \mu_B^2} J_{\text{FeNb}},$$

$$n_{\text{NbFe}} = \frac{Z_{\text{NbFe}}}{\lambda N g_{\text{Fe}} g_{\text{Nb}} \mu_B^2} J_{\text{FeNb}},$$

where μ_B is the Bohr magneton, Z_{ij} are the numbers of the nearest-neighbor j -site ions surrounding an i -site ion, N is the total number of formula units per unit volume, and μ and λ represent the mole fractions for the Nb^{IV} ions and Fe^{II} ions, respectively. Let us designate the thermally averaged values of the spins of the Fe and Nb ions in their respective sites by $\langle S_{\text{Fe}} \rangle$ and $\langle S_{\text{Nb}} \rangle$. Then the sublattice magnetizations can be expressed as follows

$$M_{\text{Fe}} = \lambda N g_{\text{Fe}} \mu_B \langle S_{\text{Fe}} \rangle,$$

$$M_{\text{Nb}} = \mu N g_{\text{Nb}} \mu_B \langle S_{\text{Nb}} \rangle,$$

Using the above relations we obtain the following set of coupled equations for the thermally averaged values of the sublattice spins

$$\langle S_{\text{Fe}} \rangle = S_{\text{Fe}0} B_{S_{\text{Fe}0}} \left(\frac{g_{\text{Fe}} \mu_B S_{\text{Fe}0} H_0}{k_B T} + \frac{Z_{\text{FeNb}} J_{\text{FeNb}} S_{\text{Fe}0} \langle S_{\text{Nb}} \rangle}{k_B T} \right),$$

$$\langle S_{\text{Nb}} \rangle = S_{\text{Nb}0} B_{S_{\text{Nb}0}} \left(\frac{g_{\text{Nb}} \mu_B S_{\text{Nb}0} H_0}{k_B T} + \frac{Z_{\text{NbFe}} J_{\text{FeNb}} S_{\text{Nb}0} \langle S_{\text{Fe}} \rangle}{k_B T} \right),$$

where B_S is the Brillouin function, $S_{\text{Fe}0}$ and $S_{\text{Nb}0}$ are the values of $\langle S_{\text{Fe}} \rangle$ and $\langle S_{\text{Nb}} \rangle$ at $T = 0$ K, and k_B is the Boltzmann constant. The means $\langle S_{\text{Fe}} \rangle$ and $\langle S_{\text{Nb}} \rangle$ can be calculated numerically. The total molar magnetization can then be obtained as

$$M_{\text{total}} = N_A \mu_B [\lambda g_{\text{Fe}} \langle S_{\text{Fe}} \rangle + \mu g_{\text{Nb}} \langle S_{\text{Nb}} \rangle]$$

For {[Fe^{II}(H₂O)₂]₂[Nb^{IV}(CN)₈]₄·4H₂O}_{*n*} the numbers of nearest neighbours Z_{ij} are $Z_{\text{FeNb}} = 4$, $Z_{\text{NbFe}} = 8$. Other quantities are as follows: $\lambda = 2$, $\mu = 1$, $S_{\text{Fe}0} = 2$, $S_{\text{Nb}0} = 1/2$, $g_{\text{Fe}} = 2.2$, $g_{\text{Nb}} = 2.0$, $H_0 = 2$ kOe. The value of the averaged coupling constant J_{FeNb} , which is the only free parameter in the model, was chosen to reproduce the value of the transition temperature T_c . It was found that $J_{\text{FeNb}} = +8.1$ cm⁻¹, which falls in the range of coupling constants $J_{\text{M}^{\text{II}}\text{M}^{\text{IV}}}$ found or/and calculated for known octacyanometalate-based bimetallic assemblies.^{10,35–37,39–41} Fig. 7 shows the experimental $M(T)$ curve together with the mean-field prediction. The mean-field curve displays higher values for the spontaneous magnetization at low temperatures. This is due to the fact that the calculated magnetizations are essentially the saturated values, because the molecular-field theory does not incorporate the magnetization process.

For the sake of argument for the character of the coupling between the Fe^{II} and Nb^{IV} ions the magnetization curves for the trinuclear Fe₂Nb were simulated (Fig. 8).⁴² Although such a simple model system lacks the full three dimensional structure of our compound it can be seen that the case of both ferromagnetic couplings is the closest to the experimental curve. The general

Fig. 7 Magnetization vs. temperature curve as obtained in the external field $H_{DC} = 2$ kOe. The red line depicts the result yielded by the mean-field theory for two types of sites occupied by the ferromagnetically coupled Fe and Nb ions.

Fig. 8 Isothermal magnetization at $T = 4.3$ and 15 K. Solid lines show the magnetization for the simple trinuclear model Fe_2Nb for different configurations of the coupling constants $J_1 = J_2 = J_{\text{FeNb}}$. The curve corresponding to both ferromagnetic couplings is the closest to the experimental values.

ferromagnetic character of **1** is in agreement with the earlier theoretical prediction made by means of the Anderson superexchange theory,⁴³ whereas it is in contrast to the ferrimagnetic character of its manganese(II) (d^5) $\{[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Nb}^{\text{IV}}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$ isomorphous analogue.^{30,31}

The above consideration does not include the zero-field splitting effect, which generally decreases the magnetic response at lowest temperatures. The complete description of magnetism of **1** below T_c including the advanced analysis of Mössbauer spectra at $T = 4.3$ K as well as DFT calculations and neutron diffraction experiments is underway.

Conclusions

To conclude, in the design of a series of high connectivity functional $\text{Fe}^{\text{II}}\text{Nb}^{\text{IV}}$ materials, **1** is a strategic framework exhibiting a T_c of 43.3 K and a hysteresis loop with $H_c = 130$ Oe. Contrary to its paramagnetic $\{[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Mo}^{\text{IV}}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$ ³² analogue with a very weak antiferromagnetic interaction between remote (HS)Fe(II) centres through the diamagnetic $[\text{Mo}(\text{CN})_8]^{4-}$ linker and ferrimagnetic $\{[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Nb}^{\text{IV}}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$ isomorph, **1** reveals non-trivial ferromagnetic character.

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