

A single chain magnet involving hexacyanoosmate[†]

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The first single chain magnet (SCM) based on orbitally degenerate hexacyanoosmate(III) was prepared. The high values of energy barriers for the [Mn(acacen)Os(CN)₆]²⁻ complex of 81 and 48.4 K are the result of interplay of three axes anisotropic coupling of [Os(CN)₆]³⁻ with zero field splitted Mn³⁺.

Low-dimensional molecular magnetic materials exhibiting slow magnetic relaxation are important from the viewpoint of fundamental and applied science, since they may find applications in such areas as information storage and quantum computing.¹ Their magnetic behaviour is determined by an energy barrier *U* that has to be surmounted to reverse the magnetization. The *U* value for a single-molecule magnet (SMM) depends on the uniaxial anisotropy energy of a molecule. For a 1D polymer appearance of slow magnetization relaxation was predicted by Glauber.² Reported in 2001 the Co^{II}-radical complex was the first 1D compound displaying slow magnetic relaxation.^{3a} The next experimentally studied SCMs were a series of bimetallic coordination assemblies, involving Fe^{III}-CN-Co^{II}-NC^{-3b} or a Mn^{III} Schiff base (SB) complex as an anisotropic unit, and [Mn₂(SB)₂Ni(pao)₂]²⁺,^{3c-e} one of which having been the first SCMs described by the Glauber model. Since that time study of SCMs has become an especially active field of research, disseminated by the efforts of chemists and physicists. Contrary to SMMs, the energy barrier in SCMs depends not only on the magnetic anisotropy strength but also on the magnitude of intrachain magnetic coupling.^{1b,4} Hence, it should be easier to increase the *U* value for SCMs than for SMMs.

After the theoreticians' proposition to use the orbitally-degenerate 4d/5d cyanometallates with strong spin-orbit coupling as highly anisotropic synthons in the design of molecular nanomagnets,⁵ a variety of SMMs with such building blocks was obtained,⁶ as well as several SCMs.⁷ However, to the best of our knowledge, there are no reports of SCMs based on anisotropic [M(CN)₆]³⁻, M = Ru and Os building units introducing non-Ising type of spin coupling.

A recent report by Miyasaka *et al.* describing 1D polymers based on paramagnetic [M^{3d}(CN)₆]³⁻ units and a Mn^{III} Schiff base (SB) complex revealed a principal possibility of SCM behaviour in alternating [-Mn^{III}-NC-M^{III}-CN-] systems.⁸ In such chains, where M^{III} signifies a 3d metal ion, the origin of the magnetic anisotropy is zero-field splitting (ZFS) of the [Mn^{III}SB] complex having an easy magnetization axis along the Jahn-Teller distortion direction. It should be especially emphasized that in the case of M^{III} = Ru or Os, there is an additional source of anisotropy caused by spin-orbit coupling in [M(CN)₆]³⁻. The use of heavier transition metal ions offers an extra benefit: presence of more diffuse 4(5)d-orbitals providing stronger exchange interactions.

In this work we present the synthesis, crystal structure and magnetic properties of the first chain heterobimetallic polymer involving, together with [Mn^{III}(SB)], hexacyanoosmate(III). The choice of the paramagnetic constituents was driven by our prior experience. The [Os(CN)₆]³⁻ was selected due to the higher stability of this complex in contrast to its Ru congener.^{9a} Moreover, the SB complex, [Mn(acacen)]⁺, acacen = *N,N'*-ethylenebis(acetylacetylidenaminato), in combination with cyanometallates is able to form 1D structures as shown earlier.^{9b,c}

Mixing of alcohol solutions of [Mn(acacen)(CH₃OH)₂]⁺PF₆⁻ (0.1 mmol, 1 mL) and (Ph₄P)₃[Os(CN)₆]³⁻ (0.1 mmol, 2 mL) gave a white precipitate of Ph₄PPF₆ that was discarded after centrifugation. Diluting the reaction mixture with *i*-propanol (3 mL) led to a complex (Ph₄P)₂[Mn(acacen)Os(CN)₆](H₂O)_{1.5}(C₃H₇O)_{0.7} in the form of large prismatic brown crystals (**1**) after one week storage in the dark. X-ray structural analysis revealed that **1** is a 1D polymer complex (Fig. 1, Table S1 in ESI[†]), containing one Mn and two Os ions in the asymmetric unit. Both symmetrically

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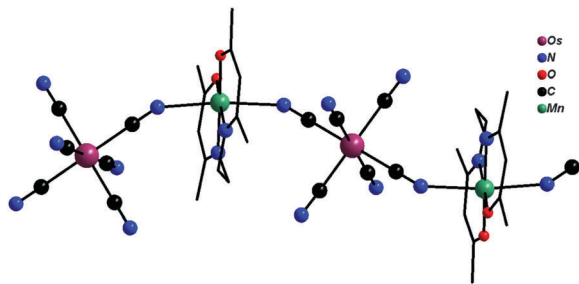


Fig. 1 The chain fragment in **1**; H atoms are omitted for clarity.

non-equivalent osmium centres have an almost non-distorted octahedron coordination environment formed by six CN-groups (Table S1, ESI†). All Os–C bond distances vary within 0.01 Å and all bond angles NC–Os^{III}–CN within 4.4° (Table S2, ESI†). The apical sites of the Mn^{III} ion in the [Mn(acacen)]⁺ moiety are occupied by cyanides in *trans* positions of [Os(CN)₆]^{3–} units, forming a zig-zag chain. The donor atoms of acacen in the basal plane (2O and 2N) are involved in shorter bonds of 1.90–1.98 Å, and two nitrogen atoms of *trans*-disposed CN ligands (N_{CN}–Mn–N_{CN} angle is 173.4°) form much longer (2.29–2.34 Å) Mn–N_{CN} bonds (Table S2, ESI†). The Mn–N–C bond angles are much less than 180° and equal 142.2° and 146.1° alike to those in the cyanide bridged Mn^{III}–Fe complexes.^{9c}

Similarly to compounds (Et₄N)₂[Mn(acacen)Fe(CN)₆]^{9c} and [Mn(SB)Fe(CN)₆]·4H₂O,⁸ in **1**, the parallel chains form hexagonal rod packing¹⁰ (Fig. S3, ESI†). The interstitial space is occupied by Ph₄P⁺ and *i*-PrOH and H₂O solvent molecules. The shortest contacts N_{CN}···H_{Ph} (2.695 and 3.053 Å) in **1** are formed by the same Ph₄P⁺ and [Os(CN)₆]^{3–} of adjacent chains. The hydrogen bonding (HB) network linking neighboring chains is absent. HB details in **1** are presented in the ESI† (Fig. S4). For further interpretation of the magnetic properties of **1** it is important to note that only one of two compounds known to date comprising [Os(CN)₆]^{3–} and Mn^{III}(SB) complex,^{6e,f} a trinuclear complex [Mn₂(SB)₂(MeOH)₂Os(CN)₆][–],^{6e} is very close by their geometric parameters to the repeating unit of **1** (Fig. S5, ESI†).

The magnetic susceptibility of **1** is shown in Fig. 2 as the χT product. At 300 K the value of 3.4 is close to 3.30 cm³ K mol^{–1} expected for Mn^{III} spin $S = 2$ with $g = 2.0$ and Os^{III} spin $s = 1/2$ with $g = 1.8$.^{6e} χT increases monotonously (without a minimum) and reaches 160 cm³ K mol^{–1} at low temperatures, pointing to predominant ferromagnetic interaction between the Mn and Os spins. However, our attempt to describe the high temperature $\chi T(T)$ data using the Seiden model,¹¹ which is often used in the case of alternating Heisenberg spin chains,^{8,12} appeared to be unsuccessful for **1**. This may be related to a complicated interplay between single-ion magnetic anisotropy of Mn^{III} and highly anisotropic three axes exchange interaction between Os and Mn, as observed previously for a chemically and structurally related trinuclear complex^{6e} [Mn₂(SB)₂(MeOH)₂Os(CN)₆][–] (Fig. S5, ESI†) and a recently reported seven-nuclear Os(CN)₆(Mn^{III})₆ molecular cluster.^{6f}

For 1D systems with an anisotropy, which produce a gap in the energy spectrum, the low temperature divergence of susceptibility should follow the relation $\chi T \sim \exp(\Delta_{\xi}/kT)$, where Δ_{ξ} is the

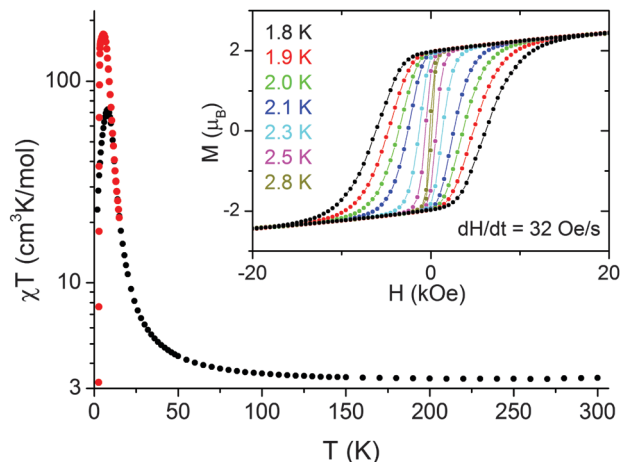


Fig. 2 Temperature dependence of χT for **1** based on dc susceptibility measured at 1 kOe (black points) and ac susceptibility at $H_{ac} = 3$ Oe, 10 Hz (red). Inset: hysteresis loops measured for a powder sample at different temperatures and a constant sweep rate of the magnetic field.

domain wall formation energy.^{1b} For **1** we estimated $\Delta_{\xi} = 38.4(4)$ K from the low field susceptibility data in the temperature range 10–20 K (Fig. S6, ESI†).

As shown in the inset of Fig. 2, a hysteresis loop opens below 2.8 K. The coercive field strongly depends on the temperature and the field sweep rate (Fig. S7, ESI†) and reaches 6 kOe at 1.8 K for a sweep rate of 32 Oe s^{–1}. The ac susceptibility of **1** is presented in Fig. 3. The maxima of the in-phase susceptibility χ' are accompanied by large peaks of the out-of-phase signal χ'' . All maxima shift to higher temperatures with increasing ac frequency. The Mydosh parameter, defined as the temperature shift of the χ' peak on a decade of frequency $\Delta T_m/[T_m \Delta \log(\nu)]$, equals 0.13, which exceeds the value typical for spin-glasses.¹³

For a quantitative study of the magnetic relaxation in **1** we measured the ac susceptibility at fixed temperatures as a function of frequency ν in the range 0.01 to 1000 Hz (Fig. S8, ESI†). The $\chi'(\nu)$ and $\chi''(\nu)$ dependencies were fitted using the generalized Debye model¹⁴ to obtain the relaxation time τ at each temperature. The parameter α , describing a distribution of relaxation times, is in the range 0.12–0.16 (Table S3, ESI†). Such small values point to a single relaxation process. This confirms

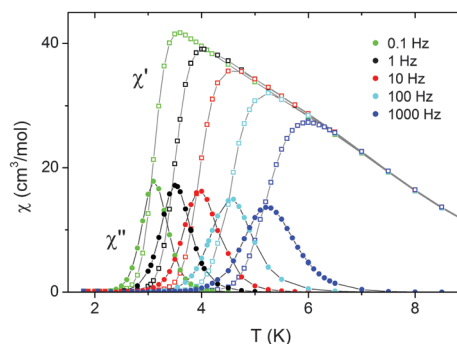


Fig. 3 Temperature dependence of ac susceptibility for **1** measured at $H_{ac} = 3$ Oe and different frequencies.

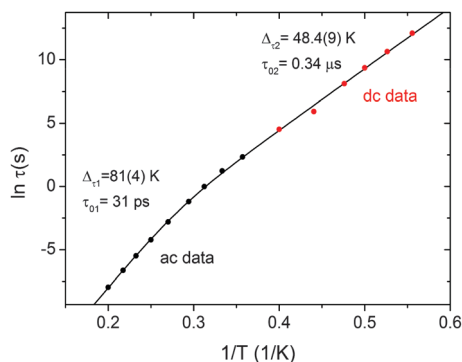


Fig. 4 Relaxation time of **1** derived from frequency dependent ac susceptibility (black points) and time dependent dc magnetization (red points). The solid line was fitted according to the Arrhenius model with two relaxation processes.

good quality of the sample and proves the SCM nature of observed relaxations. Below 2.8 K τ is over 10 s, thus, dc magnetic measurements were used to study the magnetization relaxation following switching off the magnetic field from 10 kOe to 0 (Fig. S9, ESI[†]). A stretched exponential decay model $M(t) = M_0 \exp(-(t/\tau)^{1-n})$ was used to extract τ from these data. The obtained values of n are under 0.4. All measured relaxation times are shown in Fig. 4. A linear dependence of $\ln \tau$ vs. T^{-1} denotes an Arrhenius activation with an energy barrier, the slope changing at the crossover temperature $T^* = 3.5$ K. This is a characteristic behaviour for experimentally studied SCMs, for which a finite size of chains plays a role at low temperatures.^{1a} The energy barrier values, estimated by fitting $\ln(\tau) = -\ln(\exp(-\Delta E_1/T)/\tau_{01} + \exp(-\Delta E_2/T)/\tau_{02})$ to the Arrhenius plot, were found to be $\Delta E_1 = 81(4)$ K and $\Delta E_2 = 48.4(9)$ K, above and below T^* , respectively. These values are significantly higher than the energy barriers reported for the chains composed of hexacyanometallate, $[M(\text{CN})_6]^{3-}$, and Mn^{3+} , e.g. for $M = \text{Mn, Fe, Cr}$, with ΔE_1 values 25, 32, 48 K respectively.⁸ The difference $\Delta E_1 - \Delta E_2 = 33(5)$ K is close to the ΔE_ζ value, as expected. The anisotropy barrier can be derived as $\Delta A = 2\Delta E_1 - \Delta E_2 = 16(5)$ K.

The extrapolation of data measured for **1** at 1.8 K up to 50 kOe gives an anisotropy field H_A exceeding 200 kOe, which is much higher than the values of about 100 kOe reported for Mn^{III} single-ion anisotropy.⁸ Since, in our case, the coordination environment of the Mn ion is similar to those in the $\text{Mn}^{\text{III}}(\text{SB})$ complex,⁸ the Mn^{III} anisotropy contribution should be alike. It is essential to underline that the origin of magnetic behaviour of **1** as SCM is expected to be very complicated due to the unquenched orbital momentum of $[\text{Os}(\text{CN})_6]^{3-}$ resulting in highly anisotropic Os–Mn spin coupling. Importantly, the latter fact has been recently documented both experimentally and theoretically for two related $\text{Os}^{\text{III}}\text{--Mn}^{\text{III}}$ SMs.^{6e,f} In a trinuclear $\text{Os}^{\text{III}}\text{--Mn}_2^{\text{III}}$ compound,^{6e} the Os–Mn spin coupling is described by an extremely anisotropic three-axes spin Hamiltonian $H = -J_x S_x^{\text{Os}} S_x^{\text{Mn}} - J_y S_y^{\text{Os}} S_y^{\text{Mn}} - J_z S_z^{\text{Os}} S_z^{\text{Mn}}$ with opposite signs of exchange parameters ($J_x = -18, J_y = +35$ and $J_z = -33 \text{ cm}^{-1}$).^{6e} Thus, in **1** we have a sophisticated situation coming from a complicated combination of anisotropic Os–Mn exchange interactions and single-ion magnetic anisotropy of Mn^{III} centres with non-collinear orientations of the local magnetic axes x, y , and z . To prove this fact,

magnetic measurements on a single crystal will be performed in near future. To the best of our knowledge, such an unusual and complicated case was not analysed before in the literature for magnetically anisotropic SCM chains; some steps in this direction are underway.

In summary, the first $[\text{Os}(\text{CN})_6]^{3-}$ -based single chain magnet has been synthesized and fully characterized. The SCM characteristics of **1** are the best in comparison to those of heterobimetallic 1D compounds consisting of $[\text{M}(\text{CN})_6]^{3-}$ and $[\text{Mn}^{\text{III}}\text{SB}]$ units known to date. These results represent a significant contribution from the perspective of obtaining higher blocking temperature cyanide based SCMs. Moreover, the appearance of a new complicated system possessing slow magnetic dynamics is important for physicists to elaborate new theoretical SCM models.

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