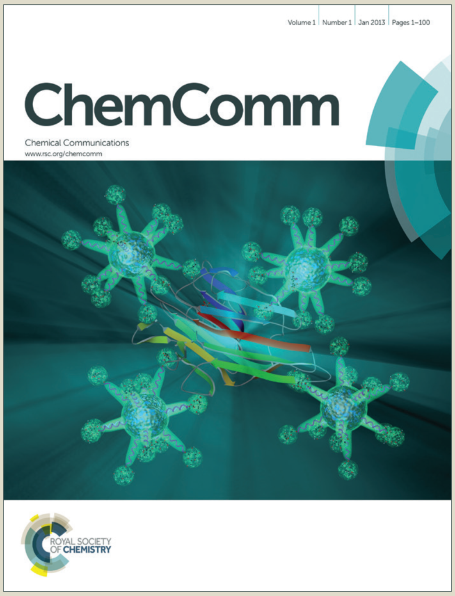

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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

A single chain magnet involving hexacyanoosmate

Eugenia V. Peresypkina,[a] Anna Majcher,[b] Michał Rams*,[b] and Kira E. Vostrikova*,[a,§]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 axis anisotropic coupling of $[Os(CN)_6]^{3-}$ with zero field splitted Mn^{3+}.

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 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 Mn^{III} Schiff base (SB) complex as anisotropic unit, $[Mn_2(SB)_2Ni(pao)_2]^{2+}$,[3c-e] one of which having been the first SCMs described by the Glauber model. Since that time SCMs study 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 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 SCM 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 heterobimetalic 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 with its Ru congener.[9a]Moreover, the SB complex, $[Mn(acacen)]^+$, acacen = N,N′-ethylenebis(acetylacetonylideneaminato), in combination with cyanometallates is able to form 1D structures as it was shown earlier,.[9b,c]

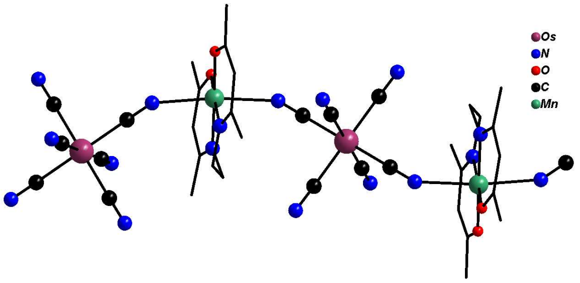


Figure 1. The chain fragment in **1**, H atoms are omitted for clarity.

Mixing of alcohol solutions of $[Mn(acacen)(CH_3OH)_2]PF_6$ (0.1 mmol, 1 mL) and $(Ph_4P)_3[Os(CN)_6]$ (0.1 mmol, 2 mL) gave a white precipitation of Ph_4PPF_6 that was discarded after centrifugation. Diluting of the reaction mixture with *i*-propanol (3 mL) led to a complex $(Ph_4P)_2[Mn(acacen)Os(CN)_6](H_2O)_{1.5}(C_3H_7O)_{0.7}$ 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 (Figure 1, Table S1 in ESI†), containing one Mn and two Os ions in the asymmetric unit. Both symmetrically non-equivalent osmium centres have an almost non-distorted octahedron coordination environment formed by six CN-groups (Table S1). All Os–C bond distances vary within 0.01 Å and all bond angles NC–Os^{III}–CN within 4.4° (Table S2). 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 ($_{NC}N$–Mn–N_{CN} angle is 173.4°) form much longer (2.29-2.34 Å) Mn–N_{CN} bonds (Table S2). 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 $(Et_4N)_2[Mn(acacen)Fe(CN)_6]$[9c] and $[Mn(SB)Fe(CN)_6]\cdot 4H_2O$,[8] in **1**, the parallel chains form hexagonal rod packing[10] (Figure S3). The interstitial space is occupied by Ph_4P^+ and *i*-PrOH and H_2O solvent molecules. The shortest contacts $N_{CN}\ldots H_{Ph}$ (2.695 and 3.053 Å) in **1** are formed by the same Ph_4P^+ 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 ESI (Figure S4). For further interpretation of the magnetic properties of **1** it is important to note that only one of two known to date compounds comprising $[Os(CN)_6]^{3-}$ and Mn^{III}(SB) complex,[6e,f] a trinuclear complex $[Mn_2(SB)_2(MeOH)_2Os(CN)_6]^-$,[6e] is very close by their geometric parameters to the repeating unit of **1** (Figure S5).[9c]

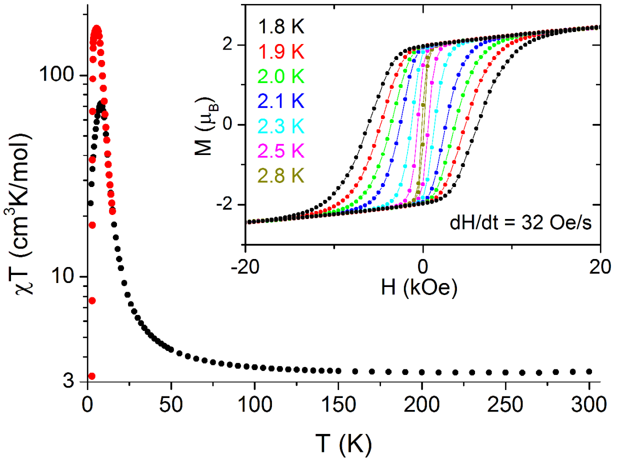


Figure 2. Temperature dependence of χT for **1** based on *dc* susceptibility measured at 1 kOe (black points) and *ac* susceptibility at H_{ac} = 3 Oe, 10 Hz (red). Inset: hysteresis loops measured for a powder sample at different temperatures and a constant sweep rate of the magnetic field.

The magnetic susceptibility of **1** is shown in Figure 2 as the χT product. At 300 K the value of 3.4 is close to 3.30 cm^3K/mol 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 cm^3K/mol 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] occurred 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] $[Mn_2(SB)_2(MeOH)_2Os(CN)_6]^-$ (Figure S5) and 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 domain wall formation energy.[1b] For **1** we estimated Δ_ξ = 38.4(4) K from the low field susceptibility data in the temperature range 10–20 K (Figure S6).

As shown in the inset of Figure 2, a hysteresis loop opens below 2.8 K. The coercive field strongly depends on temperature and the field sweep rate (Figure S7) and reaches 6 kOe at 1.8 K for the sweep rate of 32 Oe/s. The *ac* susceptibility of **1** is presented in Figure 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 lower temperatures with *ac* frequency increasing. The Mydosh parameter, defined as the temperature shift of χ' peak on a decade of frequency $\Delta T_m/[T_m\Delta\log(\upsilon)]$, equals 0.13, which exceeds the value typical for spin-glasses.[13]

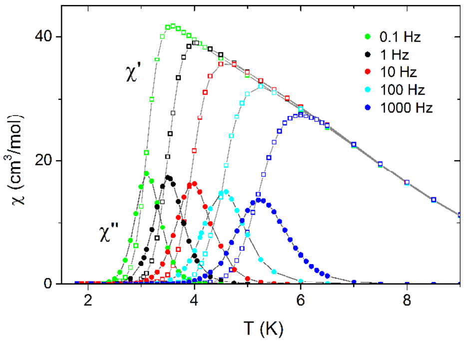


Figure 3. Temperature dependence of *ac* susceptibility for **1** measured at H_{ac} = 3 Oe and different frequencies.

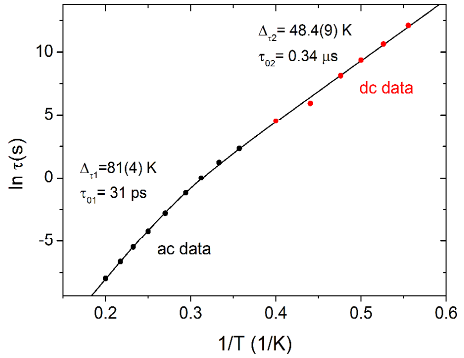


Figure 4. Relaxation time of **1** derived from frequency dependent *ac* susceptibility (black points) and time dependent *dc* magnetization (red points). The solid line was fitted according to the Arrhenius model with two relaxation processes.

For a quantitative study of the magnetic relaxation in **1** we measured the *ac* susceptibility at fixed temperatures as a function of frequency υ in the range 0.01 to 1000 Hz (Figure S8). The $\chi'(\upsilon)$ and $\chi''(\upsilon)$ dependencies were fitted using the generalized Debye model[14] 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 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 (Figure S9).

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 Figure 4. A linear dependence of lnτ 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 feature behaviour for experimentally studied SCMs, for which a finite size of chains plays a role at low temperatures.[1a] The energy barriers values, estimated by fitting $\ln(\tau) = -\ln(\exp(-\Delta\tau_1/T)/\tau_{01} + \exp(-\Delta\tau_2/T)/\tau_{02})$ to the Arrhenius plot, were found to be $\Delta_{\tau1}$ = 81(4) K and $\Delta_{\tau2}$ = 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, $[M(CN)_6]^{3-}$, and Mn^{3+}, *e.g.* for M = Mn, Fe, Cr, with $\Delta_{\tau 1}$ values 25, 32, 48 K respectively.[8] The difference $\Delta\tau_1$-$\Delta\tau_2$ = 33(5) K is close to the Δ_ξ value, as expected. The anisotropy barrier can be derived as $\Delta_A = 2\Delta\tau_1-\Delta\tau_2 = 16(5)$ K.

The extrapolation of data measured for **1** at 1.8 K up to 50 kOe gives the 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 Mn^{III}(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 unquenched orbital momentum of $[Os(CN)_6]^{3-}$ resulting in highly anisotropic Os-Mn spin coupling. Importantly, the latter fact has been recently documented both experimentally and theoretically for two related Os^{III}-Mn^{III} SMMs.[6e,f] In a trinuclear Os^{III}-Mn_2^{III} compound,[6e] the Os-Mn spin coupling is described by an extremely anisotropic three-axis spin Hamiltonian $H = -J_xS^x_{Os}S^x_{Mn} - J_yS^y_{Os}S^y_{Mn} - J_zS^z_{Os}S^z_{Mn}$ with opposite signs of exchange parameters ($J_x = -18$, $J_y = +35$ and $J_z = -33$ 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 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 $[Os(CN)_6]^{3-}$-based single chain magnet has been synthesized and fully characterized. The SCM characteristics of **1** are the best in comparison to those of known to date heterobimetallic 1D compounds consisting of $[M(CN)_6]^{3-}$ and $[Mn^{III}SB]$ units. 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 the physicists to elaborate new theoretical SCM models.

This work was partially supported by RFBR (08-03-00459-a), REA (FP7-PEOPLE-2011-IIF-301689) and by the Polish National Science Centre (2011/01/B/ST5/00716). EVP thanks Prof Dr M. Scheer for an access to the Gemini R Ultra diffractometer. KEV acknowledge V. S. Mironov for useful discussions.

Notes and references

[a] *Nikolaev Institute of Inorganic Chemistry, 3 Acad. Lavrentiev avenue, Novosibirsk, 630090, Russia; E-mail: E-mail: vosk@niic.nsc.ru*
[b] *Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland; E-mail: m.rams@uj.edu.pl*
[c] *Current address: LMI (UMR 5615), Université Claude Bernard Lyon 1, Campus de la Doua, 69622 Villeurbanne Cedex, France*

† Electronic Supplementary Information (ESI) available: Experimental section, crystallographic details (CIF), supplementary tables, structural figures and additional magnetic data. See DOI: 10.1039/b000000x/

1 (a) D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, 2006. (b) C. Coulon, H. Miyasaka and R. Clérac, in *Structure and Bonding*, ed. R. Winpenny, Springer, 2006, 163.

2 R. Glauber, *J. Math. Phys.*, 1963, **4**, 294.

3 (a) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760. (b) R. Lescouëzec, J. Vaissermann, C. Ruiz-Pérez, F. Lloret, R. Carrasco, M. Julve, M. Verdaguer, Y. Dromzee, D. Gatteschi and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2003, **42**, 1483. (c) R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* 2002, **124**, 12837. (d) H. Miyasaka, R. Clérac, K. Mizushima, K. Sugiura, M. Yamashita, W. Wernsdorfer and C. Coulon, *Inorg. Chem.*, 2003, **42**, 8203. (e) C. Coulon, R. Clérac, L. Lecren, O. Wernsdorfer and H. Miyasaka, *Phys. Rev. B*, 2004, **69**, 132408.

4 W.-X. Zhang, B. Breedlove, R. Ishikawa and M. Yamashita, *RSC Advances*, 2013, **3**, 3772.

5 V. S. Mironov, L. F. Chibotaru and A. Ceulemans, *J. Am. Chem. Soc*. 2003, **125**, 9750; V. S. Mironov, *Dokl. Phys. Chem.* 2006, **408**, 130; V. Mironov, *Dokl. Phys. Chem.* 2007, **415**, 199.

6 (a) D. E. Freedman, D. M. Jenkins, A. T. Iavarone and J. R. Long, *J. Am. Chem. Soc.* 2008, **130**, 2884; (b) X. Y. Wang, C. Avendaño and K. R. Dunbar, *Chem. Soc. Rev.*, 2011, **40**, 3213 and references therein; (c) K. S. Pedersen, M. Schau-Magnussen, J. Bendix, H. Weihe, A. V. Palii, S. I. Klokishner, S. Ostrovsky, O. S. Reu, H. Mutka, P. L. W. Tregenna-Piggott, *Chem. Eur. J.* 2010, **16**, 13458. (d) K. S. Pedersen, J. Dreiser, J. Nehrkorn, M. Gysler, M. Schau-Magnussen, A. Schnegg, K. Holldack, R. Bittl, S. Piligkos, H. Weihe, P. Tregenna-Piggott, O. Waldmann and J. Bendix, *Chem. Commun.*, 2011, **47**, 6918; (e) J. Dreiser, K. S. Pedersen, A. Schnegg, K. Holldack, J. Nehrkorn, M. Sigrist, P. Tregenna-Piggott, H. Mutka, H. Weihe, V. S. Mironov, J. Bendix and O. Waldmann, *Chem. Eur. J.*, 2013, **19**, 3693; (f) V. Hoeke, A. Stammler, H. Bögge, J. Schnack and T. Glaser, *Inorg. Chem.*, 2014, **53**, 257. (g) J. M. Zadrozny, D. E. Freedman, D. M. Jenkins, T. D. Harris, A. T. Iavarone, C. Mathonière, R. Clérac and J. R. Long, *Inorg. Chem.*, 2010, **49**, 8886; (h) K. Qian, X.-C. Huang, C. Zhou, X.-Z. You, X.-Y. Wang and K. R. Dunbar, *J. Am. Chem. Soc.*, 2013, **135**, 13302.

7 (a) J. Ru, F. Gao, T. Wu, M.-X. Yao, Y. Li and J.-L. Zuo, *Dalton Trans.*, 2014, **43**, 933; (b) T. Harris, M. Bennett, R. Clérac and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 3980; (c) X. Feng, T. D. Harris and J. R. Long, *Chem. Sci.*, 2011, **2**, 1688; (d) X. Feng, J. Liu, T. D. Harris, S. Hill and J. R. Long, *J. Am. Chem. Soc.*, 2012, **134**, 7521; (e) T. S.Venkatakrishnan, S. Sahoo, N. Bréfuel, C. Duhayon, C. Paulsen, A.-L. Barra, S. Ramasesha and J.-P. Sutter, *J. Am. Chem. Soc.*, 2010, **132**, 6047; (f) S. Sahoo, J.-P. Sutter and S. Ramasesha, *J. Stat. Phys.*, 2012, **147**, 181; (g) S. W. Choi, H. Y. Kwak, J. H. Yoon, H. C. Kim, E. K. Koh.and C. S. Hong, *Inorg. Chem.*, 2008, **47**, 10214; (h) H. S. Yoo, H. H. Ko, D. W. Ryu, J. W. Lee, J. H. Yoon, W. R. Lee, H. C. Kim, E. K. Koh and C. S. Hong, *Inorg. Chem.* 2009, **48**, 5617; (i) J. W. Lee, K. S. Lim, Yoon, J J. H.Yoon, D. W. Ryu, Koo, B. H. Koo, E. K. Koh and C. S. Hong, *Sci. China Chem.*, 2012, **55**, 1012;

8 H. Miyasaka, T. Madanbashi, A. Saitoh, N. Motokawa, R. Ishikawa, M. Yamashita, S. Bahr, W. Wernsdorfer, R. Clérac, *Chem. Eur. J.,* 2012, **18**, 3942.

9 (a) E. V. Peresypkina and K. E. Vostrikova, *Eur. J. Inorg. Chem.*, **2011**, 811; (b) E. V. Peresypkina and K. E. Vostrikova, *Dalton Trans.*, 2012, **41**, 4100. (c) Re, E. Gallo, C. Floriani, H. Miyasaka and N. Matsumoto, *Inorg. Chem.,* 1996, **35**, 6004.

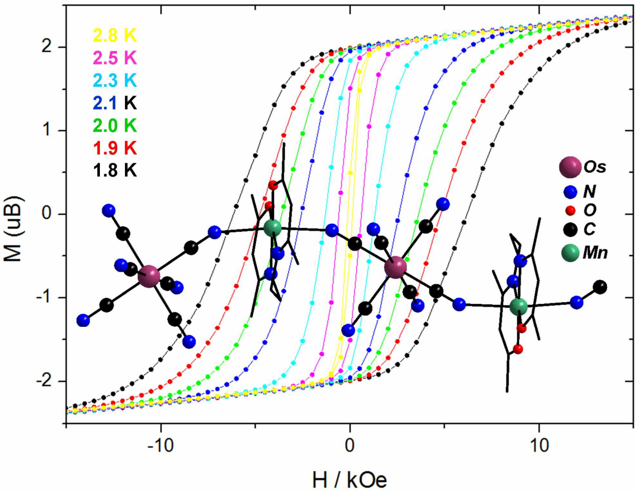
10 M. O'Keeffe and S. Andersson, *Acta Cryst.,* 1977, **A33**, 914.

11 (b) J. J. Seiden, *Phys. Lett.*, 1983, **44**, 947.

12 (a) R.Georges, J. J. Borras-Almenar, E. Coronado, J. Curely, M. Drillon in *Magnetism: Molecules to Materials*, Willey 2001. (b) M. Bałanda, M. Rams, S. K. Nayak, Z. Tomkowicz, W. Haase, K. Tomala, J. V. Yakhmi, *Phys. Rev. B* 2006, **74**, 224421. (c) T. D. Harris, C. Coulon, R. Clérac, J. R. Long, *J. Am. Chem. Soc.* 2011, **133,** 123.

13 J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor and Francis: London, 1993, 67.

14 K. S. Cole, R. H. Cole, *J. Chem. Phys.* 1941, **9**, 341.



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