The synthesis, structural characterization and magnetic properties of a 1D zig-zag coordination polymer based on a cation–cation \([\{UO_2\}Mn^{II}\}] \) repeated unit are reported; it shows single chain magnet (SCM) behaviour with a high energy barrier of 122 K.

Single chain magnets (SCMs) have been attracting increasing attention in the last decade\(^1\) following the first report of slow relaxation of the magnetization in a 1 D coordination polymer.\(^2\) Notably SCMs provide an attractive alternative to 0 D molecular magnets (SMMs) for the development of information storage devices.\(^1a,^3\) The requirements to observe the SCM behaviour first predicted by Glauber\(^4\) are the presence of strong Ising anisotropy, high intra-chain magnetic coupling and weak inter-chain interactions. Notably, the high anisotropy of 5d and 4f ions has been successfully exploited to afford 1 D coordination polymers with SCM behaviour.\(^5,^6\)

Actinide ions have been recently attracting increasing attention for the design of SMMs due to their high anisotropy and their ability to engage in strong magnetic exchange.\(^7,^8\) However only one example of an actinide based single chain magnet has been reported so far.\(^9\)

Our group and others have demonstrated that cation–cation interactions (described as the bonding of an actinyl imido or an oxo group with a metal cation) provide a convenient route to magnetic relaxation and to the assembly of exchange-coupled SMMs.\(^2m,^8b,^9,^10\) In particular, we have recently shown that, depending on the reaction stoichiometry, the cation–cation interaction between the uranyl(v) \([UO_2(salen)(Py)]\] building block and the \([Mn(n)(Py)_3]\) unit leads either to a \(\{U_{12}Mn_4\}\) wheel-shaped uranyl(v) cluster with SMM behaviour\(^7m\) or to a linear 1 D polymer with a SCM behaviour.\(^9\)

Here we report the first actinide based 1D zig-zag coordination polymer \(\{\{UO_2(Mesaldien)\}[Mn(NO_3)(Py)_2]\}_m, 2\) that is built from the cation–cation interaction of the uranyl(v) complex \([UO_2(caldien)]\] with \([Mn(n)(NO_3)(Py)_3]\). Polymer 2 shows slow relaxation of the magnetization with a high relaxation barrier of 122 K and an open magnetic hysteresis loop at \(T < 3\) K, with a coercive field of 1.75 T at 2 K. Compound 2 is thus only the second example of an actinide based polymer showing SCM behaviour which most likely arises from a strong intra-chain coupling combined with the high Ising anisotropy of the uranyl(v) dioxo group.

The monomeric uranyl(v) complex \([UO_2(Mesaldien)][Cp^*Co]_1, 1\), containing the pentadentate Schiff base Mesaldien was prepared in high yield (90%) by reduction of the analogous monomeric uranyl(v) complex with one equivalent of \(Cp^*Co\) in pyridine (see the ESI†). Complex 1 is fully stable in the solid state and in a variety of organic solvents. The stability of complex 1 with respect to the disproportionation reaction is consistent with previously reported spectroscopic and synthetic studies showing that pentadentate Schiff bases stabilize pentavalent uranyl by saturating the equatorial coordination sites and therefore preventing the formation of dimeric disproportionation intermediates.\(^11a–c\) As such complex 1 provides an excellent precursor for the controlled synthesis of heteropolymetallic cation–cation assemblies. Notably, the reaction of 1 with one equivalent of the \(Mn(NO_3)_2\) salt affords the 1D polymer \(\{[UO_2(Mesaldien)]\}[Mn(NO_3)(Py)_2]\}_m, 2\), as a pink microcrystalline powder in 66% yield (Scheme 1). The X-ray crystal structure of 2 is shown in Fig. 1.

In the structure of 2 the oxo groups of the uranyl(v), \([UO_2(Mesaldien)]\] \(^-\) units bridge through a linear cation–cation interaction between two \([Mn(NO_3)(Py)_3]\) cations to yield a zig-zag one-dimensional chain. The asymmetric unit of 2 contains only one uranium and one manganese atoms forming the neutral repeated entity \(\{[UO_2(Mesaldien)]\}[Mn(NO_3)(Py)_2]\). The uranium atom is heptacoordinated with a slightly distorted pentagonal
Scheme 1 Synthesis of 2.

Fig. 1 Mercury view of the structure of 2 (top) and enhanced view of the zig-zag core with associated distances and angles. (bottom) (Ligands were represented in pipes, H and co-crystallised solvent molecules were omitted for clarity, C is represented in grey, O in red, N in light blue, Mn in pink and U in green.)

bipyramidal geometry by the five donor atoms of the Mesaldien ligand situated in the equatorial plane and by the two uranyl oxygens in the axial position. The manganese(n) ion is hexa-coordinated, by two uranyl oxygens from two different uranyl(V) units, two pyridines and the two oxygens of the bidentate nitrate ligand. Due to the U(ν)O2−Mn(n) cation–cation interactions, the U–O bond distances are lengthened (U1–O1U 1.900(3) Å and U1–O2U 1.913(3) Å) compared to those found in [UO2(Mesaldien)](Cp*Co)4 1 (U1–O1U 1.847(6) Å and U1–O2U 1.846(6) Å). The mean Mn–Oyl (where Oyl is the uranyl oxygen) bond distance is 2.15(2) Å but similar Mn–Oyl distances are lengthened (U1–O1U 1.900(3) Å and U1–O2U 1.846(6) Å).

An intra-chain separation between neighbouring U(ν) ions of 6.634 Å and a separation between neighbouring Mn(n) ions of 7.897 Å are found in 2 whereas the mean intramolecular U–Mn distance is 3.96(3) Å. Each chain is separated from the nearest chain with a minimum intermetallic distance of 11.881, 10.336 and 9.019 Å, respectively, for U–U, U–Mn and Mn–Mn. No significant interchain π-stacking is observed in the structure of 2.

Magnetic susceptibility measurements were performed first between 2 and 300 K on a polycrystalline sample of 2 at magnetic fields of 0.01, 0.1, 0.5 and 5 T (see the ESI†). The measured χT value for 2 at room temperature is approximately 4.8 cm3 K mol−1 which is consistent with the values reported for heteropolymetallic Mn(n)–uranyl(v) assemblies containing one spin-only divalent manganese (with S = 5/2 and g close to 2) and one pentavalent uranium ion.9 The χT product remains constant from 300 K to 80 K before reaching a field-dependent maximum (177.8 cm3 K mol−1 at 0.01 T, 77.29 cm3 K mol−1 at 0.1 T, 26.3 cm3 K mol−1 at 0.5 T; 6.7 cm3 K mol−1 at 5 T). At very low temperatures this product drops rapidly probably due to saturation effects, magnetic anisotropy and/or inter-chain antiferromagnetic interactions. The increase of χT below 80 K suggests the presence of a dominant ferromagnetic interaction leading to an aligned-spin ground state.

The scaling of the χT data of 2 (Fig. 2, left) clearly shows the occurrence of a linear regime characteristic of Ising 1D systems. The ln(χT) versus 1/T plot increases linearly between 45 and 16 K (1/T from 0.063 to 0.022 K−1). The experimental data were fitted within this linear regime using the equation $\chi T = C_{\text{eff}} \exp(\Delta/4k_B T)$ which describes a ferromagnetically coupled infinite chain. The fit gives an energy gap $\Delta/k_B$ of 43.4 K and a pre-exponential factor $C_{\text{eff}} = 2.50$. The magnetic susceptibility data of 2 between 16 and 300 K at 0.01 T were also fitted with the equation $\chi T = C_1 \exp(\Delta_1/k_B T) + C_2 \exp(\Delta_2/k_B T)$, where a second negative exponential is added to take into account the high-temperature crystal field effect and possible antiferromagnetic

![Diagram of the structure of 2](image_url)

**Fig. 2** Left: plots of (top) $\chi T$ versus $T$ and (bottom) ln($\chi T$) versus $1/T$ for a polycrystalline sample of 2, measured at 0.01 T applied field. Right: temperature dependence of the (top) real ($\chi'$) and (bottom) imaginary ($\chi''$) ac susceptibilities for 2 measured at zero-dc field and 1.5 G ac field.
The high stability of the [UO$_2$(Mesaldien)]$^-$ building block provides a versatile route to a wide variety of 3d–5f 1D chains that will be investigated in future studies.
Notes and references

1 (a) W. X. Zhang, R. Ishikawa, B. Breedlove and M. Yamashita, RSC Adv., 2013, 3, 3772–3798; (b) H. L. Sun, Z. M. Wang and S. Gao, Coord. Chem. Rev., 2010, 254, 1081–1100; (c) H. Miyasaka, M. Juve, M. Yamashita and R. Clerac, Inorg. Chem., 2009, 48, 3420–3437; (d) S. W. Prybylak, F. Tuna, S. J. Teat and R. E. P. Winpenny, Chem. Commun., 2008, 1983–1985.

2 (a) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Nowak, Angew. Chem., Int. Ed., 2001, 40, 1760–1763; (b) R. Clerac, H. Miyasaka, M. Yamashita and C. Coulon, J. Am. Chem. Soc., 2002, 124, 12837–12844.

3 D. Gatteschi, R. Sessoli and J. Villain, Molecular Nanomagnets, Oxford University Press, Oxford, UK, 2006.

4 R. J. Glauber, J. Math. Phys., 1963, 4, 294–307.

5 (a) E. V. Peresypkina, A. M. Majcher, M. Rams and K. E. Vostrikova, Chem. Commun., 2014, 50, 7150–7153; (b) T. D. Harris, M. V. Bennett, R. Clerac and J. R. Long, J. Am. Chem. Soc., 2010, 132, 3980–3988.

6 (a) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, J. Am. Chem. Soc., 2006, 128, 7947–7956; (b) R. Sessoli and A. K. Powell, Coord. Chem. Rev., 2009, 253, 2328–2341; (c) Y. Z. Zheng, Y. H. Lan, W. Wernsdorfer, C. E. Anson and A. K. Powell, Chem. – Eur. J., 2009, 15, 12566–12570.

7 (a) J. R. Long and K. R. Meihaus, J. Chem. Soc., Dalton Trans., 2015, 44, 2517–2528; (b) N. Magnani, Int. J. Quantum Chem., 2014, 114, 755–759; (c) K. R. Meihaus, S. G. Minasian, W. W. Lukens, Jr., S. A. Kozimor, D. K. Shuh, T. Tyliszczak and J. R. Long, J. Am. Chem. Soc., 2014, 136, 6056–6068; (d) J. D. Rinehart, K. R. Meihaus and J. R. Long, J. Am. Chem. Soc., 2010, 132, 7572–7573; (e) J. D. Rinehart and J. R. Long, J. Am. Chem. Soc., 2009, 131, 12558–12559; (f) M. A. Antunes, L. C. J. Pereira, I. C. Santos, M. Mazzanti, J. Marcalo and M. Almeida, Inorg. Chem., 2011, 50, 9915–9917; (g) T. Coutinho, M. A. Antunes, L. C. J. Pereira, H. Bolvin, J. Marcalo, M. Mazzanti and M. Almeida, J. Chem. Soc., Dalton Trans., 2012, 41, 13568–13571; (h) L. C. J. Pereira, C. Camp, J. T. Coutinho, L. Chatelain, P. Maldivi, M. Almeida and M. Mazzanti, Inorg. Chem., 2014, 53, 11809–11811; (i) N. Magnani, C. Apostolidis, A. Morgenstern, E. Colineau, J. C. Griveau, H. Bolvin, O. Walter and R. Caciuffo, Angew. Chem., Int. Ed., 2011, 50, 1696–1698; (j) N. Magnani, E. Colineau, R. Eloirdi, J. C. Griveau, R. Caciuffo, S. M. Cornet, I. May, C. A. Sharrad, D. Collison and R. E. P. Winpenny, Phys. Rev. Lett., 2010, 104, 197202; (k) N. Magnani, E. Colineau, J. C. Griveau, C. Apostolidis, O. Walter and R. Caciuffo, Chem. Commun., 2014, 50, 8171–8173; (l) S. Carretta, G. Amoretti, P. Santini, V. Mougel, M. Mazzanti, S. Gambarelli, E. Colineau and R. Caciuffo, J. Phys.: Condens. Matter, 2013, 25, 486001; (m) V. Mougel, L. Chatelain, J. Pecaut, R. Caciuffo, E. Colineau, J. C. Griveau and M. Mazzanti, Nat. Chem., 2012, 4, 1011–1017; (n) D. P. Mills, F. Moro, J. McInnes, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, Nat. Chem., 2011, 3, 434–436; (o) D. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes and S. T. Liddle, Angew. Chem., Int. Ed., 2013, 52, 4921–4924.

8 (a) H. Miyasaka, M. Julve, A. Bernot, L. Bogan, A. Caneschi, D. Gatteschi and R. Sessoli, J. Am. Chem. Soc., 2010, 132, 2517–2528; (b) P. L. Arnold, E. Hollis, F. J. White, N. Magnani, R. Caciuffo and J. B. Love, Angew. Chem., Int. Ed., 2011, 50, 887–890; (c) L. Chatelain, V. Mougel, J. Pecaut and M. Mazzanti, Chem. Sci., 2012, 3, 1075–1079; (d) V. Mougel, P. Horeglad, G. Nocton, J. Pecaut and M. Mazzanti, Angew. Chem., Int. Ed., 2009, 48, 8477–8480; (e) G. Nocton, P. Horeglad, J. Pecaut and M. Mazzanti, J. Am. Chem. Soc., 2008, 130, 16633–16645; (f) L. P. Spencer, E. J. Schelter, F. Yang, R. L. Gildea, B. L. Scott, J. D. Thompson, J. L. Kiplinger, E. R. Batista and J. M. Bonecila, Angew. Chem., Int. Ed., 2009, 48, 3795–3798.

9 (a) K. Takao, M. Kato, S. Takao, A. Nagasawa, G. Bernhard, C. Hennig and Y. Ikeda, Inorg. Chem., 2010, 49, 2349–2359; (b) K. Takao, S. Tsushima, S. Takao, A. C. Scheinost, G. Bernhard, Y. Ikeda and C. Hennig, Inorg. Chem., 2009, 48, 9602–9604; (c) V. Mougel, J. Pecaut and M. Mazzanti, Chem. Commun., 2012, 48, 868–870.

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

11 G. Nocton, P. Horeglad, V. Vetere, J. Pecaut, L. Dubois, P. Maldivi, N. M. Edelstein and M. Mazzanti, J. Am. Chem. Soc., 2010, 132, 495–508.