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Spontaneous resolution and absolute configuration of a coordination polymer formed by Mn^{II} and a ferrocene-based bisnitronyl nitroxide radical†

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Crystallisation of a ferrocenyl bis(nitronyl nitroxide) with manganese(II) bis(hexafluoroacetylacetonate) gives rise to spontaneous resolution of a coordination polymer formed by the two units creating seven sources of chirality.

Spontaneous resolution of molecular compounds upon crystallisation is a relatively scarce phenomenon, but one of great importance in a number of research areas.[1] The process leads to crystals which can present optical activity, a particularly contemporary theme in the field of molecular magnetic materials.[2] The preparation of chiral magnets using open shell species can be achieved either by (i) the incorporation of asymmetric groups, (ii) isolation of atropoisomeric or conformational enantiomers, or (iii) a combination of the two. The isolation of their atropoisomers in a crystal environment is relatively simple provided that spontaneous resolution occurs, a situation observed in magnets based on nitronyl nitroxide–manganese(II) bis(hexafluoroacetylacetonate) complexes.[3] Following our interest in the stereochemistry of nitronyl nitroxides[4] and their coordination complexes,[5] we report here the spontaneous resolution and absolute configuration of conformational enantiomers of a coordination polymer (**1**) comprising of a ferrocenyl bis(nitronyl nitroxide) and manganese(II) bis(hexafluoroacetylacetonate). The compound is intriguing in the sense that there are seven interrelated sources of conformational chirality in the system, which presumably propagate along the chain during its formation (see Fig. 1 bottom) and manifest themselves macroscopically in the form of two enantiomorphic crystals.

The complex was crystallised from a dichloromethane solution of ferrocenyl bis(nitronyl nitroxide)[6] and dry Mn^{II} bis(hexafluoroacetylacetonate).† The complex crystallises‡ in the chiral space group $P2_12_12_1$, and the unit cell is comprised of four manganese-diradical moieties and disordered solvent molecules. It is a coordination polymer in which one oxygen atom of the ONCNO unit of each of the radical units coordinate to the paramagnetic metal ion in a *cis* manner (Fig. 1). The bond-lengths and angles in the radical and the metallocene part of the molecule are those expected for this type of complex.[7] The bond-lengths of the coordinating N–O groups are slightly longer than those of the non-coordinated (N1–O1: 1.321(3)Å; N3–O3: 1.312(3)Å; N2–O2: 1.273(4)Å; N4–O4: 1.271(4)Å). The manganese–oxygen distances are also in the normal range (O1–Mn1: 2.148(2)Å; O3–Mn1′: 2.161(2)Å; N1–O1–Mn1: 124.0°; N3–O3–Mn1′: 122.8°; O1–Mn1–O3′: 78.4(1)°; O1–O3′: 2.72Å; N1–O1–O3′: 172.9°; N3–O3–O1′: 171.4°).[7] The polymeric chains run along the *b* axis, with 11.03 Å between Mn^{II} ions within the chains. Very short contacts (3.02–3.40 Å) between the Cp-rings and the hfac ligand CO group, consistent with π–π interactions, seem to play an active role in determining the structure of the polymeric chain.[3]

Both enantiomorphous structures of **1** have been solved (with roughly equal amounts of each, *vide infra*), here we give the data for the one in which the metal centre has the Λ configuration. There are seven elements of chirality in the compound (Fig. 1, where all values for the dihedral angles are given): (1) The manganese(II) ion coordination sphere, as mentioned, with the Λ configuration. (2) The radical substituents on the ferrocene moiety adopt a *cisoid* conformation with *P* helicity, because of weak intramolecular hydrogen bonds between radical-oxygen atoms and methyl groups (2.51–2.59Å), as found in the isolated diradical.[6] (3) The torsion of the angle formed by the Mn–O–N–C(Me) bonds, which here gives *P* helicity. (4–7) The Cp ring and the ONCNO plane form an angle, and the imidazolyl ring has an associated torsion, which according to our previous definitions[4] in this case results in the *MP pseudoeclipsed* arrangement of the Cp-imidazolyl system, with small torsion angles between the planar O–N–C–N–O group and the Cp-rings.

1

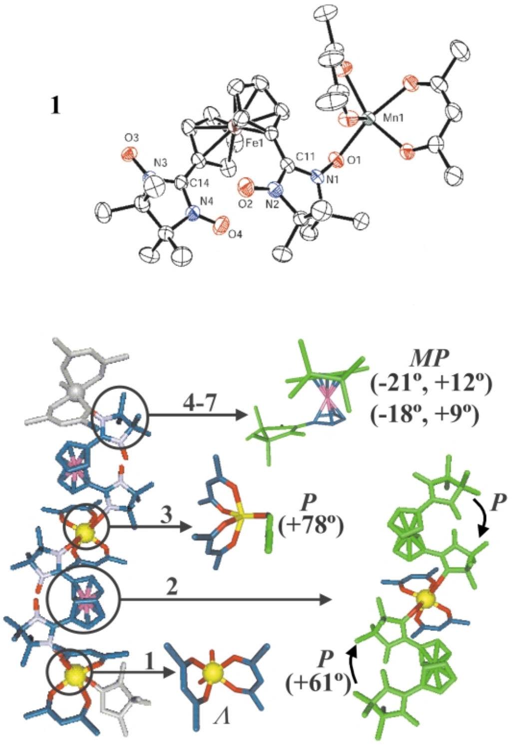

Fig. 1 The crystal structure of **1**. Top: ORTEP[11] view of the monomeric building block (manganese(II) Λ configuration) (F and H atoms and solvent molecule omitted for clarity). Thermal ellipsoids are shown at the 50% probability level. Bottom: The conformations of the seven stereogenic sources and associated angles in **1**.

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† Electronic supplementary information available: Experimental procedure. See http://www.rsc.org/suppdata/cc/b2/b205722k/

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Variable-temperature magnetic susceptibility data for a ground crystalline sample of **1** was measured on a SQUID susceptometer (2–300 K) with an applied external field of 1 kG. The value of χ_mT at 300 K is 2.5 emu K mol^{-1} (Fig. 2). Upon cooling χ_mT gradually decreases down to 70 K, where it reaches a plateau at a value of 1.9 emu K mol^{-1}, in excellent agreement with that expected for a $S = 3/2$ spin ground state (1.875 emu K mol^{-1}) and consistent with the presence of strong antiferromagnetic interactions between the Mn^{II} ion and the two coordinated nitronyl nitroxide moieties. Below 70 K, the χ_mT value abruptly decreases to a χ_mT value of 0.4 emu K mol^{-1} at 2 K, indicating that the resulting $S = 3/2$ units are weakly antiferromagnetically coupled, a characteristic of coordination polymers consisting of metal ions and radical ligands with two or more kinds of exchange interactions where one of them is predominant.[8] The data was fitted to a magnetic model based on a three-spin system radical–Mn^{II}–radical with strong antiferromagnetic exchange coupling (J). The model was corrected by a molecular field approximation (zJ') to take into account the magnetic behavior at low temperatures.[9] Fixing $g = 2.0$, the best fit was obtained for $J/k = -193$ K (in the range of related complexes[3,7]) and $zJ'/k = -10$ K. The combination of spin polarization and direct overlap between SOMOs of the two radical units, as confirmed by X-ray crystallographic studies, leads to the appearance of this weaker antiferromagnetic intramolecular interaction between radicals (in the pure metallocene diradicals this coupling is $J/k \approx -5$ K[6]), rather than weak interchain interactions.

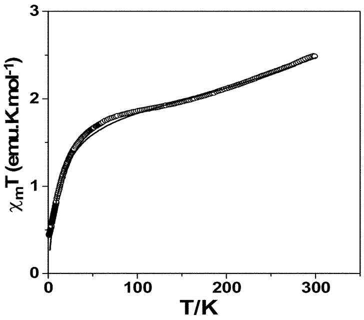

Fig. 2 Temperature dependence of χ_mT *versus* T for a polycrystalline sample of complex **1**. The continuous line is the fit of experimental data (○).

Spontaneous resolution was proved by solving the crystal structure and determining the absolute configuration of nine enantiomorphic single crystals of sufficient size and quality (obtained after many crystallization experiments), taking a collection of these crystals in which the Mn^{II} ion had the same Λ configuration and determining the CD spectrum in KBr matrix.[10] The crystals gave a CD spectrum in which four strong Cotton effects are observed, as witnessed in Fig. 3. The pattern is very similar to that observed for the enantiopure molecular magnet **2** in which the same Λ configuration of the metal ion is present.[5] This observation bears witness to the importance of the conformation of the radical unit in the optical properties of these compounds.

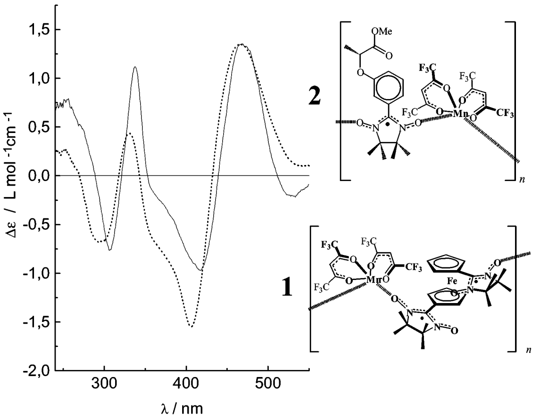

Fig. 3 The CD spectra in KBr matrix of **1** (solid line) and **2** (dotted line).

The complex **1** shows a remarkable structure which resolves spontaneously upon crystallization revealing seven sources of chirality, which are probably determined ultimately by the configuration of the manganese(II) ion, which passes its chirality through the radical moiety and Cp rings *via* π–π interactions to the ferrocenyl ring, contrasting with that in which we used an asymmetrically substituted carbon atom to induce the chirality of the Mn^{II} centre.[5] Despite the lack of either an asymmetric carbon atom or a solution-stable atropoisomer in the complex reported here, the optical activity is equal to that of the enantiopure sample prepared with a chiral radical. However, in order to take advantage of the optical activity in the present case the tedious separation procedure of the enantiomorphs described above has to be undertaken.

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Notes and references

‡ *Crystal data* for **1** : $C_{34}H_{34}F_{12}FeMnN_4O_8 \cdot CH_2Cl_2$, $M = 1050.37$, orthorhombic $P2_12_12_1$ (no. 19), $a = 10.8382(4)$ Å, $b = 19.9028(6)$ Å, $c = 20.5120(4)$ Å , $\alpha = \beta = \gamma = 90°$, $V = 4424.7(2)$ Å^3, $T = 213(2)$ K , $Z = 4$, MoKα ($\lambda = 0.71073$ Å), 5752 reflections collected, 5324 independent reflections with $I > 2\sigma(I)$, $R1$ [$I > 2\sigma(I)$] = 0.0318, $wR2$ (all data) = 0.0766, goodness-of-fit 1.075. Flack parameter (for absolute structure) = 0.00 (2). Data were measured with a Nonius Kappa CCD and the structure was solved by direct methods (SHELXS-86),[12] and refined by full-matrix least-squares methods on F^2 (SHELXL-93).[13] CCDC number 188251. See http://www.rsc.org/suppdata/cc/b2/b205722k/ for crystallographic data in CIF or other electonic format.

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