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Magnetic Memory Effect in a Transuranic Mononuclear Complex**

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Molecular nanomagnets that display magnetic bistability are the subject of intensive investigation due to their unique potential in ultrahigh-density memory components and spintronic devices.[1] So far, the best practical realization of such single-molecule magnets (SMMs) are polymetallic transition-metal complexes with strong intramolecular exchange coupling, giving rise to a high-spin ground state and negligible intercluster interactions.[2] However, 3d metals are restricted by their comparatively low anisotropy, and SMMs with better performance could be produced by exploiting the higher single-ion anisotropy typical of f-electron ions.[3] This possibility has been practically demonstrated by Ishikawa et al., who discovered that mononuclear rare earth metal bis-phthalocyanine compounds (Pc_2RE) display magnetic hysteresis under favorable conditions.[4]

On these grounds, the use of actinides in molecular magnetism appears timely, and indeed slow relaxation effects have recently been reported in a mononuclear uranium-based molecule.[3d] Future SMMs displaying magnetic hysteresis could benefit from the fact that, whilst the 5f electron shell can remain relatively well localized, its larger radial extension with respect to the 4f shell can result both in an increased ligand-field potential (and therefore a higher anisotropy energy barrier) and in the possibility to trigger a sizeable exchange coupling in polynuclear complexes, usually precluded to trivalent rare earth metal ions.[5] Moreover, discrete molecules based on 5f ions should allow much greater understanding of the peculiar behavior observed in actinide materials, including multipolar superexchange coupling.[6]

Recently, we obtained evidence that a neptunium trimetallic compound displays slow magnetic relaxation and superexchange interaction;[3f] nevertheless, we were unable to find any signs of hysteresis in the measured magnetization curves. Here we report the first observation of such low-temperature magnetic memory effects in another transuranic molecular complex, namely, bis(cyclooctatetraenyl)neptunium(IV), commonly known as neptunocene $[Np(COT)_2]$ ($COT = C_8H_8^{2-}$), which was first described in 1970[7] and belongs to the whole actinocene row.[8] The molecule has a single Np^{IV} ion between two planar COT rings in a sandwich structure (Figure 1) with D_{8h} symmetry.[9] The degeneracy of the lowest $J = 9/2$ manifold belonging to the $5f^3$ configuration is partially removed by the axial ligand-field potential, which isolates a $J_z = \pm 5/2$ doublet as the ground state.[10] The presence of slow relaxation of the magnetization was suggested by the splitting of zero-field ^{237}Np Mössbauer spectra between 4.2 and 40 K, but never confirmed experimentally.[7]

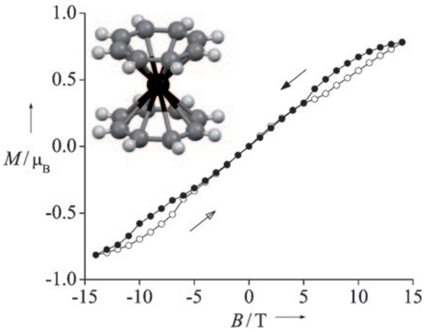

Figure 1. Isothermal magnetization curves for neptunocene, measured at 1.8 K with increasing (empty circles) and decreasing (filled circles) magnetic field. A schematic view of the molecular structure is shown in the inset (Np black, C dark gray, H light gray atoms).

Figure 1 shows magnetization curves measured after zero-field cooling of the sample at $T = 1.8$ K, the lowest attainable temperature (the estimated self-heating due to radioactive decay is $2.03\ \mathrm{mW\,g_{Np}^{-1}}$). Memory effects, clearly visible in the open high-field regions, give rise to a butterfly-shaped hysteresis cycle. At the maximum field of 14 T the magnetic moment is still far from saturation, and reaches a value of $0.8\ \mu_B$ (about half that expected for a $J_z = \pm 5/2$ doublet, an indication of the strong magnetic anisotropy present in this

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compound). Increasing the temperature to 2 K is enough to close the hysteresis cycle under the same measurements conditions.

The occurrence of slow magnetic relaxation of molecular origin, which gives rise to the high-field magnetization hysteresis, is confirmed by the appearance of a frequency-dependent peak in the out-of-phase component of the ac magnetic susceptibility which is clearly visible in the temperature range 2–60 K when a static external magnetic field larger than 0.1 T is applied. The results obtained with a static field of 0.5 T are shown in Figure 2 for different frequencies of the oscillating field. The χ'' curves were divided by the dc susceptibility χ_{dc} measured at 0.5 T on the SQUID magnetometer, so that the relaxation time τ matches the inverse of the angular frequency ω exactly at the peak temperature of the corresponding curve.[4d] Without application of a static field, only extremely weak frequency-independent features appear in χ'' (see Supporting Information); this is a relatively common behavior for rare earth metal complexes and might be a consequence of the low total spin value of the neptunocene molecule.[3a] The overall behavior of the peaks in χ''/χ_{dc} closely resembles the data of Ishikawa et al.[4] on diluted Pc_2RE samples rather than on pure ones, and confirms that (as also inferred by analysis of the static susceptibility curve) intermolecular interactions are extremely weak for neptunocene.

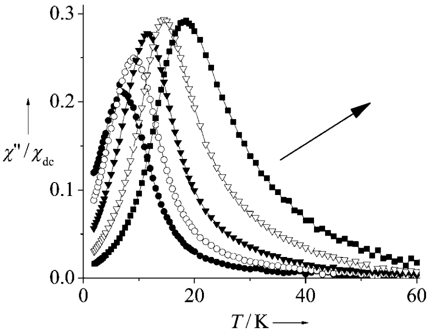

Figure 2. Imaginary component of the ac magnetic susceptibility of neptunocene χ'' measured as a function of temperature with a 0.5 T static magnetic field. The curves correspond to different frequencies of the 5×10^{-4} T driving field: 591 (full circles), 1085 (empty circles), 2072 (full triangles), 4541 (empty triangles), and 9479 (full squares), in increasing order following the arrow. The χ'' data are normalized at each temperature by the corresponding value of χ_{dc}.

The temperature dependence of the relaxation time τ is shown in Figure 3 for different values of the applied static magnetic field. Several different regimes can be recognized, arising from the simultaneous presence of multiple relaxation channels: at low fields (0.5–2 T), the high-temperature region is approximately linear in the $\ln\tau$ versus $1/T$ plot, whereas at low temperatures a significant deviation from this behavior can be observed, reminiscent of quantum tunneling of the magnetization (QTM). At intermediate fields (3 T) the $\ln\tau$ versus $1/T$ plot is essentially linear in the whole range; the solid line is a linear fit to the expression $\tau=\tau_0\exp(\Delta/k_B T)$, which is valid assuming that thermally activated processes are dominant, with $\Delta=41$ K and $\tau_0=1.1\times10^{-5}$ s. At larger fields (above 5 T) a marked slowing down in the magnetization dynamics is observed for low temperatures, where T_{max} becomes essentially independent of the frequency; this is the region in which magnetization hysteresis is observed.

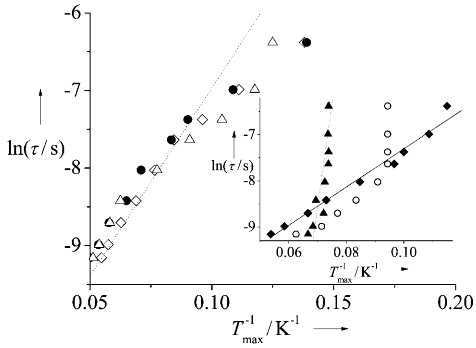

Figure 3. Natural logarithm of the relaxation time as a function of reciprocal temperature measured for different values of the static magnetic field: 0.5 (empty diamonds), 1 (full circles), and 2 T (empty triangles). Inset: 3 (full diamonds), 5 (empty circles), and 7 T (full triangles).

The above-described phenomena can be understood by considering the combined effect of the different possible relaxation mechanisms. In particular, the value of Δ obtained for the relaxation curves with an applied field below 5 T is not compatible with a process involving excited ligand-field states, since our analysis of the dc susceptibility curve (see Supporting Information) places them at an energy not lower than 1400 cm^{-1}. On the other hand, the presence of two slow frequency-dependent relaxation processes in actinide complexes was recently put in light for an U^{3+}-based molecule,[3e] but the case of neptunocene is further complicated by the presence of a nonzero nuclear moment, which breaks the time-reversal symmetry of the ground Kramers doublet even in absence of an applied magnetic field.[11a] The electronic $J_z=\pm5/2$ doublet ground state is split by the Zeeman term, but due to the hyperfine interaction with the $I=5/2$ nuclear magnetic moment several crossing points are present at low field values between states with opposite J_z. These are expected to provide a very efficient relaxation channel, in a way that is similar to QTM.[4c] For fields above 2 T this mechanism becomes ineffective, because almost no molecules in the sample display crossing points in this region (see Supporting Information); therefore, the most efficient relaxation channel is either a direct process between states with opposite J_z, with emission of a phonon, or a two-phonon process involving excited ligand-field states.[11] The latter is eventually favored for fields larger than 5 T and gives rise to the extremely steep linear increase of $\ln\tau$ as a function of $1/T$ (see the dotted line tracing the measurements at 7 T in the inset of Figure 3) due to the very large gap separating the ground doublet and the first excited energy level. Only under these conditions is magnetic hysteresis experimentally observed.

A QTM-like deviation from linear $\ln\tau$-vs-$1/T$ behavior at low fields was also observed for U^{3+}-based single-ion molecules,[3d,e] for which no hyperfine splitting is present.

This can be attributed to their lower point symmetry at the 5f site, which allows the ligand field to mix different J_z components, and to the smaller energy gap, which induces a larger contribution of the excited states to the ground-state wavefunction when the Kramers doublet is split by the magnetic field.

In conclusion, we have shown that neptunocene displays an open magnetic hysteresis cycle at low temperatures, making it the first reported transuranic complex to display magnetic memory effects. A study of the frequency-dependent ac susceptibility allowed us to infer that several relaxation channels are present and active, and that a slow two-phonon process involving excited ligand-field states is the main relaxation mechanism at high magnetic fields. Orbach processes are responsible for slow relaxation effects observed in phthalocyanine-based rare earth single-ion magnets,[4] where they have been proven to be effective even at zero applied field; on the other hand, in these cases a large ground-state magnetic moment is necessary for magnetic memory effects to appear,[3,4a] while neptunocene displays a relatively low-spin ground state and is still quite far from saturation when a magnetic field of 14 T is applied. These peculiar properties are experimental proof that 5f-based molecular magnets could indeed have significant advantages over 4f-based ones, not only from the point of view of the exchange interaction but also by allowing for higher anisotropy energy barrier and larger coercive fields.

Experimental Section

Np(COT)$_2$ samples were prepared by stirring freshly prepared potassium cyclooctatetraenide and neptunium tetrachloride in dry THF under argon atmosphere. The solvent was removed after stirring at room temperature overnight. Extraction with pentane for one day resulted in 20 % yield of prismatic crystallites of very intense dark color suitable for X-ray analysis. A further 70 % of the product was obtained by benzene extraction for one day leading to a dark red brown powder of [Np(COT)$_2$]. A single crystal of suitable size was selected for X-ray diffraction measurements in order to check the sample quality. The obtained structural parameters are in agreement with published results[9] and could be refined to a $R1$ value of 0.0200 due to the excellent crystal quality (CCDC 743428 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif). IR samples were analyzed as KBr pellets and FIR samples as polyethylene pellets on a Perkin-Elmer 2000-FT-IR spectrometer. UV/VIS absorption spectra were measured in quartz cuvettes equipped with Teflon sealable stop cocks (liquid samples) or as polyethylene pellets (solid samples) and recorded on a Perkin-Elmer Lambda 9 spectrometer.

All magnetic measurements were performed on a polycrystalline sample of 65.8 mg encapsulated in a sealed Plexiglas tube, the magnetic contribution of which was determined and subtracted after the experiments. Magnetization cycles and ac susceptibility curves were measured on a 14 T PPMS Quantum Design platform. Data points for the former were collected with steps of 1 T, and the whole hysteresis cycle required a total measuring time of about two hours. The temperature dependence of the dc susceptibility was measured on a 7 T SQUID platform; an applied field of 1 T was found to give the best compromise between obtaining a large signal-to-noise ratio and minimizing low-temperature saturation effects. The ac susceptibility measurements were performed with a driving field of amplitude 5×10^{-4} T, superimposed on a static magnetic field of different values (from 0 to 7 T). The temperature and field dependences of the relaxation time τ were obtained by taking into account the fact that the magnetic susceptibility of neptunocene cannot be considered to be weakly dependent on T within the studied temperature range; therefore, $\tau(T_{\mathrm{max}}) = 1/\omega$ if $\chi''/\chi_{\mathrm{dc}}$ (and not χ'') has a maximum for $T = T_{\mathrm{max.}}$[4d]

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