Coherent Manipulation of a Molecular Ln-Based Nuclear Qudit Coupled to an Electron Qubit

We demonstrate that the [Yb(trensal)] molecule is a prototypical coupled electronic qubit-nuclear qudit system. The combination of noise-resilient nuclear degrees of freedom and large reduction of nutation time induced by electron-nuclear mixing enables coherent manipulation of this qudit by radio frequency pulses. Moreover, the multilevel structure of the qudit is exploited to encode and operate a qubit with embedded basic quantum error correction.
Cr(pyrazine)\textsubscript{2}(OSO\textsubscript{2}CH\textsubscript{3})\textsubscript{2}: A two-dimensional coordination polymer with an antiferromagnetic ground state

A novel two-dimensional (2D) coordination polymer with the formula Cr(pyrazine)\textsubscript{2}(OSO\textsubscript{2}CH\textsubscript{3})\textsubscript{2} has been synthesized and characterized. Powder X-ray diffraction data reveal that this material, which crystallizes in the Pnnm orthorhombic space group, is composed of rectangular grid layers with octahedral CrN\textsubscript{4}O\textsubscript{2} nodes bridged by pyrazine ligands. Since the redox-active pyrazine can be reduced in the presence of transition metals, X-ray absorption spectroscopy and quantum chemical calculations were used to confirm the +II oxidation state of the Cr center. Magnetic susceptibility measurements indicate the presence of antiferromagnetic interactions between the chromium(II) centers through the neutral pyrazine and suggest an antiferromagnetic ordered state below T\textsubscript{N} \approx 10 K, which was confirmed by heat-capacity measurements.
Field-induced single-molecule magnet behavior in ideal trigonal antiprismatic cobalt(ii) complexes: precise geometrical control by a hydrogen-bonded rigid metalloligand

A new cobalt(ii) complex bearing a pair of cobalt(iii) tris-chelate complexes as metalloligands was prepared. The Co-II ion possesses an ideal trigonal antiprismatic geometry because of the intermolecular hydrogen-bonds between the metalloligands via counter anions. This complex exhibits slow magnetic relaxation under a dc field reminiscent of a single-molecule magnet behavior.
Formation of the layered conductive magnet CrCl$_2$(pyrazine)$_2$ through redox-active coordination chemistry

The unique properties of graphene, transition-metal dichalcogenides and other two-dimensional (2D) materials have boosted interest in layered coordination solids. In particular, 2D materials that behave as both conductors and magnets could find applications in quantum magnetoelectronics and spintronics. Here, we report the synthesis of CrCl$_2$(pyrazine)$_2$, an air-stable layered solid, by reaction of CrCl$_2$ with pyrazine (pyz). This compound displays a ferrimagnetic order below ~55K, reflecting the presence of strong magnetic interactions. Electrical conductivity measurements demonstrate that CrCl$_2$(pyz)$_2$ reaches a conductivity of 32mS cm$^{-1}$ at room temperature, which operates through a 2D hopping-based transport mechanism. These properties are induced by the redox-activity of the pyrazine ligand, which leads to a smearing of the Cr 3d and pyrazine π states. We suggest that the combination of redox-active ligands and reducing paramagnetic metal ions represents a general approach towards tuneable 2D materials that consist of charge-neutral layers and exhibit both long-range magnetic order and high electronic conductivity.
[OsF₆]⁻: Molecular Models for Spin-Orbit Entangled Phenomena

Heavy 5d elements, like osmium, feature strong spin-orbit interactions which are at the origin of exotic physical behaviors. Revealing the full potential of, for example, novel osmium oxide materials (“osmates”) is however contingent upon a detailed understanding of the local single-ion properties. Herein, two molecular osmate analogues, [OsF₆]²⁻ and [OsF₆]⁻, are reported as model systems for Os⁴⁺ and Os⁵⁺ centers found in oxides. Using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) techniques, combined with state-of-the-art ab initio calculations, their ground state was elucidated; mirroring the osmium electronic structure in osmates. The realization of such molecular model systems provides a unique chemical playground to engineer materials exhibiting spin-orbit entangled phenomena.

General information
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Organisations: Department of Chemistry, Organic Chemistry, Technical University of Denmark, University of Oxford, Max Planck Institute, Universite de Bordeaux, ESRF-The European Synchrotron
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BFI (2017): BFI-level 2
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Web of Science (2017): Impact factor 5.16
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 5.03 SJR 2.352 SNIP 1.068
Web of Science (2016): Impact factor 5.317
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 4.99 SJR 2.461 SNIP 1.195
Web of Science (2015): Impact factor 5.771
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 5.51 SJR 2.526 SNIP 1.222
Web of Science (2014): Impact factor 5.731
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 5.68 SJR 2.643 SNIP 1.239
Web of Science (2013): Impact factor 5.696
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 5.55 SJR 2.935 SNIP 1.291
Web of Science (2012): Impact factor 5.831
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 5.46 SJR 2.902 SNIP 1.319
Web of Science (2011): Impact factor 5.925
Iridates from the molecular side

New exotic phenomena have recently been discovered in oxides of paramagnetic Ir$^{4+}$ ions, widely known as ‘iridates’. Their remarkable properties originate from concerted effects of the crystal field, magnetic interactions and strong spin-orbit coupling, characteristic of 5d metal ions. Despite numerous experimental reports, the electronic structure of these materials is still challenging to elucidate, and not attainable in the isolated, but chemically inaccessible, [IrO$_6$]$^{8-}$ species (the simplest molecular analogue of the elementary [IrO$_6$]$^{8-}$ fragment present in all iridates). Here, we introduce an alternative approach to circumvent this problem by substituting the oxide ions in [IrO$_6$]$^{8-}$ by isoelectronic fluorides to form the fluorido-iridate: [IrF$_6$]$^{2-}$. This molecular species has the same electronic ground state as the [IrO$_6$]$^{8-}$ fragment, and thus emerges as an ideal model for iridates. These results may open perspectives for using fluorido-iridates as building-blocks for electronic and magnetic quantum materials synthesized by soft chemistry routes.

General information

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Organisations: University of Copenhagen, CNRS, Paul Scherrer Institute, University of Oxford, Moldova Academy of Sciences - Institute of Applied Physics, ESRF-The European Synchrotron
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Publication information
Multifaceted magnetization dynamics in the mononuclear complex \([\text{Re}^{IV}\text{Cl}_4\text{(CN)}_2]^{2-}\)

The mononuclear complex \((\text{Bu}_4\text{N})_2[\text{Re}^{IV}\text{Cl}_4\text{(CN)}_2]\)·2DMA (DMA = N,N-dimethylacetamide) displays intricate magnetization dynamics, implying Orbach, direct, and Raman-type relaxation processes. The Orbach relaxation process is characterized by an energy barrier of 39 K (27 cm\(^{-1}\)) that is discussed based on high-field electron paramagnetic resonance (EPR), inelastic neutron scattering and frequency-domain THz EPR investigations.
We have studied Er(trensal) single-ion magnets adsorbed on graphene/Ru(0001), on graphene/Ir(111), and on bare Ru(0001) by scanning tunneling microscopy and X-ray absorption spectroscopy. On graphene, the molecules self-assemble into dense and well-ordered islands with their magnetic easy axes perpendicular to the surface. In contrast, on bare Ru(0001), the molecules are disordered, exhibiting only weak directional preference of the easy magnetization axis. The perfect out-of-plane alignment of the easy axes on graphene results from the molecule-molecule interaction, which dominates over the weak adsorption on the graphene surface. Our results demonstrate that the net magnetic properties of a molecular submonolayer can be tuned using a graphene spacer layer, which is attractive for hybrid molecule-inorganic spintronic devices.

**General information**

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Organisations: University of Copenhagen, Paul Scherrer Institute, Swiss Federal Institute of Technology Lausanne, CNRS
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**Publication Information**

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Volume: 10
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ISSN (Print): 1936-0851
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 14.29 SJR 7.203 SNIP 2.58
Toward Molecular 4f Single-Ion Magnet Qubits

Quantum coherence is detected in the 4f single-ion magnet (SIM) Yb(trensal), by isotope selective pulsed EPR spectroscopy on an oriented single crystal. At X-band, the spin-lattice relaxation ($T_1$) and phase memory ($T_m$) times are found to be independent of the nuclei bearing, or not, a nuclear spin. The observation of Rabi oscillations of the spin echo demonstrates the possibility to coherently manipulate the system for more than 70 rotations. This renders Yb(trensal), a sublimable and chemically modifiable SIM, an excellent candidate for quantum information processing.

General information
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Organisations: University of Copenhagen, CNRS, University of Manchester
Contributors: Pedersen, K. S., Ariciu, A., McAdams, S., Weihe, H., Bendix, J., Tuna, F., Piligkos, S.
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Journal: Journal of the American Chemical Society
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BFI (2017): BFI-level 2
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Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 13.18 SJR 7.492 SNIP 2.596
Web of Science (2016): Impact factor 13.858
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 12.81 SJR 6.775 SNIP 2.63
Web of Science (2015): Impact factor 13.038
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 11.92 SJR 6.294 SNIP 2.587
Web of Science (2014): Impact factor 12.113
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 11.38 SJR 5.993 SNIP 2.466
Web of Science (2013): Impact factor 11.444
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 10.37 SJR 6.211 SNIP 2.38
Web of Science (2012): Impact factor 10.677
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 9.94 SJR 5.476 SNIP 2.321
Web of Science (2011): Impact factor 9.907
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 5.167 SNIP 2.138
Web of Science (2010): Impact factor 9.023
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 5.06 SNIP 2.16
Web of Science (2008): Indexed yes
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 4.662 SNIP 2.252
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 4.413 SNIP 2.223
[CrIII8MII6]12+ Coordination Cubes (MII=Cu, Co) coordination cubes were constructed from a simple [CrIII3L3] metalloligand and a "naked" MII salt. The flexibility in the design proffers the potential to tune the physical properties, as all the constituent parts of the cage can be changed without structural alteration. Computational techniques (known in theoretical nuclear physics as statistical spectroscopy) in tandem with EPR spectroscopy are used to interpret the magnetic behavior.

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Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 11.31 SJR 6.155 SNIP 2.165
Web of Science (2017): Impact factor 12.102
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 10.8 SJR 5.954 SNIP 2.146
Web of Science (2016): Impact factor 11.994
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 11.13 SJR 5.888 SNIP 2.225
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 10.84 SJR 5.811 SNIP 2.307
Web of Science (2014): Indexed yes
Cyanide Single-Molecule Magnets Exhibiting Solvent Dependent Reversible "On" and "Off" Exchange Bias Behavior

The syntheses, structures, and magnetic properties of four new complex salts, (PPN)[[MnIII(salphen)(MeOH)][II][CN]6]·7MeOH (Mn2M 7MeOH) (M = Fe, Ru, Os and Co; PPN+ = bis(triphenylphosphoranylidene)ammonium cation; H2salphen = N,N-bis(salicylidene)-1,2-diaminobenzene), and a mixed metal Co/Os analogue (PPN)[[MnIII(salphen)(MeOH)]
2\text{[(Co}^{III}_{0.92}\text{Os}^{III}_{0.08}\text{(CN)}_{6}] \cdot 7\text{MeOH} were undertaken. It was found that all compounds exhibit switchable single-molecule magnet (SMM) and exchange-bias behavior depending on the interstitial methanol content. The pristine (PPN)[(\text{Mn}$^{II}$\text{(salphen)}\text{(MeOH)])[2\text{Os(CN)}_{6}]} \cdot 7\text{MeOH} (\text{Mn}_2\text{Os} \cdot 7\text{MeOH}) behaves as an SMM with an effective barrier for the magnetization reversal, ($U_{\text{eff}}/k_B$), of 17.1 K. Upon desolvation, Mn$_2$Os exhibits an increase of $U_{\text{eff}}/k_B$ to 42.0 K and an opening of the hysteresis loop observable at 1.8 K. Mn$_2$Os $\cdot$ 7MeOH shows also exchange-bias behavior with magnetic hysteresis loops exhibiting a shift in the quantum tunneling to 0.25 T from zero-field. The Fe$^{III}$ and Ru$^{III}$ analogues were prepared as reference compounds for assessing the effect of the 5d versus 4d and 3d metal ions on the SMM properties. These compounds are also SMMs and exhibit similar effects but with lower energy barriers. These findings underscore the importance of introducing heavy transition elements into SMMs to improve their slow relaxation of the magnetization properties. The (PPN)[(\text{Mn}^{II}_{0.92}\text{(salphen)}\text{(MeOH)}) \cdot 2\text{Co(CN)}_{6}]} \cdot 7\text{MeOH} (\text{Mn}_2\text{Co} \cdot 7\text{MeOH}) analogue with a diamagnetic Co$^{III}$ central atom and the mixed Co/Os (PPN)[(\text{Mn}^{II}_{0.92}\text{(salphen)}\text{(MeOH)}) \cdot 2\text{Co(Os}^{III}_{0.08}\text{(CN)}_{6}]} \cdot 7\text{MeOH} (\text{Mn}_2\text{Co/Os} \cdot 7\text{MeOH}) magnetically diluted system with a $9:1$ Co/Os metal ratio were prepared in order to further probe the nature of the energy barrier increase upon desolvation of Mn$_2$Os. In addition, inelastic neutron scattering and frequency-domain Fourier-transform THz electron paramagnetic resonance spectra obtained on Mn$_2$Os $\cdot$ 7MeOH and Mn$_2$Os in combination with the magnetic data revealed the presence of anisotropic exchange interactions between Mn$^{III}$ and Os$^{III}$ ions.

General information
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Organisations: University of Copenhagen, Jagiellonian University in Kraków, Texas A and M University, CNRS, Swiss Federal Institute of Technology Lausanne, Helmholtz–Zentrum Berlin für Materialien und Energie, Technical University of Munich, Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung
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BFI (2017): BFI-level 2
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Web of Science (2017): Impact factor 14.357
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 13.18 SJR 7.492 SNIP 2.596
Web of Science (2016): Impact factor 13.858
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 12.81 SJR 6.775 SNIP 2.63
Web of Science (2015): Impact factor 13.038
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 11.92 SJR 6.294 SNIP 2.587
Web of Science (2014): Impact factor 12.113
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 11.38 SJR 5.993 SNIP 2.466
Web of Science (2013): Impact factor 11.444
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 10.37 SJR 6.211 SNIP 2.38
Web of Science (2012): Impact factor 10.677
ISI indexed (2012): ISI indexed yes
Design of Single-Molecule Magnets: Insufficiency of the Anisotropy Barrier as the Sole Criterion

Determination of the electronic energy spectrum of a trigonal symmetry mononuclear Yb$$^{3+}$$ single-molecule magnet (SMM) by high-resolution absorption and luminescence spectroscopies reveals that the first excited electronic doublet is placed nearly 500 cm$$^{-1}$$ above the ground one. Fitting of the paramagnetic relaxation times of this SMM to a thermally activated (Orbach) model ($T = T_0 \times \exp [\Delta_{Orbach}/(k_B T)]$) affords an activation barrier, $\Delta_{Orbach}$, of only 38 cm$$^{-1}$$. This result is incompatible with the spectroscopic observations. Thus, we unambiguously demonstrate, solely on the basis of experimental data, that Orbach relaxation cannot a priori be considered as the main mechanism determining the spin dynamics of SMMs. This study highlights the fact that the general synthetic approach of optimizing SMM behavior by maximization of the anisotropy barrier, intimately linked to the ligand field, as the sole parameter to be tuned, is insufficient because of the complete neglect of the interaction of the magnetic moment of the molecule with its environment. The Orbach mechanism is expected dominant only in the cases in which the energy of the excited ligand field state is below the Debye temperature, which is typically low for molecular crystals and, thus, prevents the use of the anisotropy barrier as a design criterion, for the realization of high-temperature SMMs. Therefore, consideration of additional design criteria that address the presence of alternative relaxation processes beyond the traditional double-well picture is required.
Fluoride-coordination chemistry in molecular and low-dimensional magnetism

We review the past and current efforts towards interesting molecular, magnetic systems encompassing inter-metallic fluoride bridging. The efficacy of fluoride as mediator of magnetic interactions is addressed and the use of the structure-directing properties of the fluoride ion as a synthetic handle for polymetallic systems is established. Finally, the magnetic properties of selected examples of systems of increasing complexity are discussed.

General information
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Contributors: Pedersen, K. S., Sørensen, M. A., Bendix, J.
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Web of Science (2017): Impact factor 14.499
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 11.43 SJR 4.298 SNIP 3.107
Web of Science (2016): Impact factor 13.324
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 12.29 SJR 3.951 SNIP 3.305
Magnetic and magnetocaloric properties of an unusual family of carbonate-panelled \([\text{Ln}^{III}_6\text{Zn}^{II}_2]\) cages

The reaction of the pro-ligand \(\text{H}_4\text{L}\), which combines the complementary phenolic oxime and diethanolamine moieties within the same organic framework, with \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) and \(\text{Ln(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}\) in a basic methanolic solution generates a family of isostructural heterometallic coordination compounds of general formula \([\text{Ln}_{6}\text{Zn}_{2}(\text{CO}_3)^{5}\text{(OH)}_{(\text{H}_2\text{L})_{4}}\text{(H}_3\text{L})_{2}\text{(H}_4\text{L})_{(\text{Gd})}}\cdot\text{xMeOH}\) \(\text{Ln} = \text{Gd, x = 30 (1), Ln = Dy, x = 32 (2), Ln = Sm, x = 31 (3), Ln = Eu, x = 29 (4), Ln = Tb, x = 30 (5)}\). The octametallic skeleton of the cage describes a heavily distorted \([\text{Gd}^{III}_6]\) octahedron capped on two faces by \(\text{Zn}^{II}\) ions. The metal core is stabilised by a series of \(\mu^3\text{-}\text{and} \mu^4\text{-CO}_3^{2-}\) ions, originating from the serendipitous fixation of atmospheric \(\text{CO}_2\). The magnetic properties of all family members were examined via SQUID magnetometry, with the \(\chi_{MT}\) product and VT/VB data of the Gd analogue \(\text{(1)}\) being independently fitted by numerical diagonalisation to afford the same best-fit parameter \(J_\text{Gd-Gd} = -0.004\text{ cm}^{-1}\). The MCE of complex \(\text{(1)}\) was elucidated from specific heat data, with the magnetic entropy change reaching a value of 22.6 J kg\(^{-1}\) K\(^{-1}\) at \(T = 1.7\text{ K}\), close to the maximum entropy value per mole expected from six \(\text{Gd}^{III}\) spins (\(\chi_{Gd} = 7/2\)), 23.7 J kg\(^{-1}\) K\(^{-1}\).

General information

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Organisations: University of Copenhagen, University of Edinburgh, Universidad de Zaragoza
One-dimensional coordination polymers of $[\text{Co}_3(\text{dpa})_4]^{2+}$ and $[\text{MF}_6]^{2-}$ ($\text{M} = \text{Re}^{IV}, \text{Zr}^{IV}$ and $\text{Sn}^{IV}$)

One-dimensional coordination polymers of alternating metal-metal bonded trinuclear $[\text{Co}_3(\text{dpa})_4]^{2+}$ (dpa = the anion of 2,2'-dipyridylamine) building blocks and $[\text{ReF}_6]^{2-}$ (1), $[\text{ZrF}_6]^{2-}$ (2) or $[\text{SnF}_6]^{2-}$ (3) linkers have been self-assembled and crystallographically characterized. Magnetic measurements reveal a significant ferromagnetic coupling ($J/k_B = +9.9$ K) between $S = 1/2 \{\text{Co}^{3+}\}$ and $S = 3/2 \text{Re}^{IV}$ magnetic sites through a single, unsupported fluoride bridge in 1.

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Organisations: University of Copenhagen, CNRS
Contributors: Bulicanu, V., Pedersen, K. S., Rouzieres, M., Bendix, J., Dechamboenit, P., Clerac, R., Hillard, E. A.
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Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 6.06 SJR 2.538 SNIP 1.16
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Scopus rating (2015): CiteScore 6.7 SJR 2.601 SNIP 1.295
Zero-Field Splitting in \((\text{Mn}^{\text{III}}(\mu_3-O))\) Core Single-Molecule Magnets Investigated by Inelastic Neutron Scattering and High-Field Electron Paramagnetic Resonance Spectroscopy

The global zero-field splitting (ZFS) parameters of three, ferromagnetically coupled, \(\mu_3-K^3\)-\([XO_4]^–\) (\(X = \text{Cl, Re}\)) capped, manganese(III) oximate single-molecule magnets, \([\text{Mn}_3\text{O}(\text{R-sao})_3(2,4’\text{-bipyridine})_3]XO_4\] \(X = \text{Cl, R = Me, Et; X = Re, R = Me; Me-sao = 2\text{-hydroxyphenylethanone oximate}(2-)}\), with crystallographic trigonal symmetry were determined by use of inelastic neutron scattering and high-field/high-frequency electron paramagnetic resonance spectroscopy. \(\text{ReO}_4^–\) (\(\text{O}…\text{O} \approx 1.7 \text{ Å}\)) is larger than \(\text{ClO}_4^–\) (\(\text{O}…\text{O} \approx 1.4 \text{ Å}\)), which allows more parallel alignment of the local ZFS tensors. However, this chemical modification results in concomitant distortions in the equatorial ligand plane. Consistent parametrization of all spectroscopic data was achieved, and effective spin-reversal barriers determined from alternating current susceptibility data were shown to be in good accordance with the energy barriers deduced from spectroscopy.

**General information**

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**Organisations:** University of Copenhagen, Paul Scherrer Institute, CNRS, University of Bern, Institut Laue-Langevin  
**Contributors:** Sigrist, M., Tregenna-Piggott, P. L. W., Pedersen, K. S., Sørensen, M. A., Barra, A., Hauser, J., Liu, S., Decurtins, S., Mutka, H., Bendix, J.  
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Web of Science (2018): Indexed yes  
BFI (2017): BFI-level 1  
Scopus rating (2017): CiteScore 2.28 SJR 0.828 SNIP 0.626  
Web of Science (2017): Impact factor 2.507  
Web of Science (2017): Indexed yes  
BFI (2016): BFI-level 1  
Scopus rating (2016): CiteScore 2.26 SJR 0.838 SNIP 0.649  
Web of Science (2016): Impact factor 2.444  
BFI (2015): BFI-level 1  
Scopus rating (2015): CiteScore 2.58 SJR 0.983 SNIP 0.728  
Web of Science (2015): Impact factor 2.686  
BFI (2014): BFI-level 1  
Scopus rating (2014): CiteScore 2.7 SJR 1.055 SNIP 0.813  
Web of Science (2014): Impact factor 2.942  
Web of Science (2014): Indexed yes  
BFI (2013): BFI-level 1  
Scopus rating (2013): CiteScore 2.82 SJR 1.067 SNIP 0.809  
Web of Science (2013): Impact factor 2.965  
ISI indexed (2013): ISI indexed yes  
Web of Science (2013): Indexed yes  
BFI (2012): BFI-level 1  
Scopus rating (2012): CiteScore 2.88 SJR 1.249 SNIP 0.901  
ISI indexed (2012): ISI indexed yes  
BFI (2011): BFI-level 1  
Scopus rating (2011): CiteScore 2.81 SJR 1.189 SNIP 0.804
Exchange Interaction of Strongly Anisotropic Tripodal Erbium Single-Ion Magnets with Metallic Surfaces

We present a comprehensive study of Er(trensal) single-ion magnets deposited in ultrahigh vacuum onto metallic surfaces. X-ray photoelectron spectroscopy reveals that the molecular structure is preserved after sublimation, and that the molecules are physisorbed on Au(111) while they are chemisorbed on a Ni thin film on 0(100) single-crystalline surfaces. X-ray magnetic circular dichroism (XMCD) measurements performed on Au(111) samples covered with molecular monolayers held at temperatures down to 4 K suggest that the easy axes of the strongly anisotropic molecules are randomly oriented. Furthermore XMCD indicates a weak antiferromagnetic exchange coupling between the single-ion magnets and the ferromagnetic Ni/Cu(100) substrate. For the latter case, spin-Hamiltonian fits to the XMCD M(H) suggest a significant structural distortion of the molecules. Scanning tunneling microscopy reveals that the molecules are mobile on Au(111) at room temperature, whereas they are more strongly attached on Ni/Cu(100). X-ray photoelectron spectroscopy results provide evidence for the chemical bonding between Er(trensal) molecules and the Ni substrate. Density functional theory calculations support these findings and, in addition, reveal the most stable adsorption configuration on Ni/Cu(100) as well as the Ni-Er exchange path. Our study suggests that the magnetic moment of Er(trensal) can be stabilized via suppression of quantum tunneling of magnetization by exchange coupling to the Ni surface atoms. Moreover, it opens up pathways toward optical addressing of surface-deposited single-ion magnets.

General information
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Organisations: University of Copenhagen, Swiss Federal Institute of Technology Lausanne, Paul Scherrer Institute, Uppsala University
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The reaction of fac-[MIIIF₃(Me₃tacn)]⋅x H₂O with Gd(NO₃)₃⋅5H₂O affords a series of fluoride-bridged, trigonal bipyramidal \{Gd^{III}_{3}M^{III}_{2}\} (M=Cr (1), Fe (2), Ga (3)) complexes without signs of concomitant GdF₃ formation, thereby demonstrating the applicability even of labile fluoride-complexes as precursors for 3d–4f systems. Molecular geometry enforces weak exchange interactions, which is rationalized computationally. This, in conjunction with a lightweight ligand sphere, gives rise to large magnetic entropy changes of 38.3 J kg⁻¹ K⁻¹ (1) and 33.1 J kg⁻¹ K⁻¹ (2) for the field change 7 T→0 T. Interestingly, the entropy change, and the magnetocaloric effect, are smaller in 2 than in 1 despite the larger spin ground
state of the former secured by intramolecular Fe–Gd ferromagnetic interactions. This observation underlines the necessity of controlling not only the ground state but also close-lying excited states for successful design of molecular refrigerants.

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**Magnetic Interactions Through Fluoride: Magnetic and Spectroscopic Characterization of Discrete, Linearly Bridged [Mn^{III}]_{2}(μ-F)_{4}(Me_{3}tacn)_{2}(PF_{6})**

The nature of the magnetic interaction through fluoride in a simple, dinuclear manganese(III) complex (1), bridged by a single fluoride ion in a perfectly linear fashion, is established by experiment and density functional theory. The magnitude of the antiferromagnetic exchange interaction and the manganese(III) zero-field-splitting parameters are unambiguously determined by inelastic neutron scattering to yield $J = 33.0(2) \text{ cm}^{-1}$ ($\hat{H} = J\hat{S}_{1}\cdot\hat{S}_{2}$ Hamiltonian definition) and single-ion $D = -4.0(1) \text{ cm}^{-1}$. Additionally, high-field, high-frequency electron paramagnetic resonance and magnetic measurements support the parameter values and resolve $|E| \approx 0.04 \text{ cm}^{-1}$. The exchange coupling constant $(J)$ is 1 order of magnitude smaller than that found in comparable systems with linear oxide bridging but comparable to typical magnitudes through cyanide, thus underlining the potential of fluoride complexes as promising building blocks for novel magnetic systems.
Magnetic properties of ultra-small goethite nanoparticles

Goethite (α-FeOOH) is a common nanocrystalline antiferromagnetic mineral. However, it is typically difficult to study the properties of isolated single-crystalline goethite nanoparticles, because goethite has a strong tendency to form particles of aggregated nanograins often with low-angle grain boundaries. This nanocrystallinity leads to complex magnetic properties that are dominated by magnetic fluctuations in interacting grains. Here we present a study of the magnetic properties of 5.7 nm particles of goethite by use of magnetization measurements, inelastic neutron scattering and Mössbauer spectroscopy. The ‘ultra-small’ size of these particles (i.e. that the particles consist of one or only a few grains) allows for more direct elucidation of the particles’ intrinsic magnetic properties. We find from ac and dc magnetization measurements a significant upturn of the magnetization at very low temperatures most likely due to freezing of spins in canted spin structures. From hysteresis curves we estimate the saturation magnetization from uncompensated magnetic moments to be $\sigma_s = 0.044 \text{ A m}^2 \text{ kg}^{-1}$ at room temperature. Inelastic neutron scattering measurements show a strong signal from excitations of the uniform mode (q = 0 spin waves) at temperatures of 100-250 K and Mössbauer spectroscopy studies show that the magnetic fluctuations are dominated by ‘classical’ superparamagnetic relaxation at temperatures above ~170 K. From the temperature dependence of the hyperfine fields and the excitation energy of the uniform mode we estimate a magnetic anisotropy constant of around $1.0 \times 10^5 \text{ J m}^{-3}$. 

General information

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Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.07 SJR 1.135 SNIP 1.122
Web of Science (2016): Impact factor 2.588
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 2.1 SJR 0.886 SNIP 1.25
Web of Science (2015): Impact factor 2.772
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 2.53 SJR 1.096 SNIP 1.408
Web of Science (2014): Impact factor 2.721
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 2.6 SJR 1.194 SNIP 1.452
Web of Science (2013): Impact factor 2.521
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 2.31 SJR 1.279 SNIP 1.414
Web of Science (2012): Impact factor 2.528
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): CiteScore 2.36 SJR 1.266 SNIP 1.399
Web of Science (2011): Impact factor 2.544
ISI indexed (2011): ISI indexed yes
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BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.292 SNIP 1.28
Web of Science (2010): Impact factor 2.109
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.269 SNIP 1.327
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 1.427 SNIP 1.549
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 1.38 SNIP 1.612
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.406 SNIP 1.742
Web of Science (2006): Indexed yes
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Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 1.133 SNIP 1.438
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 0.912 SNIP 1.221
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 1.033 SNIP 1.233
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 0.925 SNIP 1.212
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 0.842 SNIP 1.125
Modifying the properties of 4f single-ion magnets by peripheral ligand functionalisation

We study the ligand-field splittings and magnetic properties of three ErIII single-ion magnets which differ in the peripheral ligand sphere but exhibit similar first coordination spheres by inelastic neutron scattering (INS) and SQUID magnetometry. The INS spectra of the three compounds are profoundly different pointing at a strong response of the magnetic behavior to minor structural changes, as they are e.g. encountered when depositing molecules on surfaces. The observation of several magnetic excitations within the J = 15/2 ground multiplet together with single-crystal magnetic measurements allows for the extraction of the sign and magnitude of all symmetry-allowed Stevens parameters. The parameter values and the energy spectrum derived from INS are compared to the results of state-of-the-art ab initio CASSCF calculations. Temperature-dependent alternating current (ac) susceptibility measurements suggest that the magnetisation relaxation in the investigated temperature range of 1.9 K < T < 5 K is dominated by quantum tunnelling of magnetisation and two-phonon Raman processes. The possibility of observing electron paramagnetic resonance transitions between the ground-state doublet states, which can be suppressed in perfectly axial single-ion magnets, renders the studied systems interesting as representations of quantum bits.
[ReF$_6$]$^{2-}$: A Robust Module for the Design of Molecule-Based Magnetic Materials
A facile synthesis of the [ReF$_6$]$^{2-}$ ion and its use as a building block to synthesize magnetic systems are reported. Using dc and ac magnetic susceptibility measurements, INS and EPR spectroscopies, the magnetic properties of the isolated [ReF$_6$]$^{2-}$ unit in (PPh$_4$)$_2$[ReF$_6$]·2H$_2$O (1) have been fully studied including the slow relaxation of the magnetization observed below ca. 4 K. This slow dynamic is preserved for the one-dimensional coordination polymer [Zn(viz)$_4$(ReF$_6$)]$_n$ (2, viz = 1-vinylimidazole), demonstrating the irrelevance of low symmetry for such magnetization dynamics in systems with easy-plane-type anisotropy. The ability of fluoride to mediate significant exchange interactions is exemplified by the iso-structural [Ni(viz)$_4$(ReF$_6$)]$_n$ (3) analogue in which the ferromagnetic Ni$^{II}$-Re$^{IV}$ interaction (+10.8 cm$^{-1}$) dwarfs the coupling present in related cyanide-bridged systems. These results reveal [ReF$_6$]$^{2-}$ to be an unique new module for the design of molecule-based magnetic materials.
Single-molecule magnet engineering: building-block approaches

Tailoring the specific magnetic properties of any material relies on the topological control of the constituent metal ion building blocks. Although this general approach does not seem to be easily applied to traditional inorganic bulk magnets, coordination chemistry offers a unique tool to delicately tune, for instance, the properties of molecules that behave as "magnets", the so-called single-molecule magnets (SMMs). Although many interesting SMMs have been prepared by a more or less serendipitous approach, the assembly of predesigned, isolatable molecular entities into higher nuclearity
complexes constitutes an elegant and fascinating strategy. This Feature article focuses on the use of building blocks or modules (both terms being used indiscriminately) to direct the structure, and therefore also the magnetic properties, of metal ion complexes exhibiting SMM behaviour.

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BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 6.03 SJR 2.555 SNIP 1.127
Web of Science (2017): Impact factor 6.29
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 6.06 SJR 2.538 SNIP 1.16
Web of Science (2016): Impact factor 6.319
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 6.7 SJR 2.601 SNIP 1.295
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 6.83 SJR 2.692 SNIP 1.436
Web of Science (2014): Impact factor 6.834
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 6.73 SJR 2.752 SNIP 1.372
Web of Science (2013): Impact factor 6.718
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 6.21 SJR 3.118 SNIP 1.35
Web of Science (2012): Impact factor 6.378
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 5.96 SJR 2.889 SNIP 1.323
Web of Science (2011): Impact factor 6.169
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 2.781 SNIP 1.255
Web of Science (2010): Impact factor 5.787
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 2.669 SNIP 1.31
Angular dependence of the exchange interaction in fluoride-bridged Gd\textsuperscript{III}-Cr\textsuperscript{III} complexes

The observed angular variation of the magnetic exchange coupling parameter in a series of fluoride-bridged chromium(III)-gadolinium(III) complexes is explained by DFT calculations.
Scopus rating (2016): CiteScore 6.06 SJR 2.538 SNIP 1.16
Web of Science (2016): Impact factor 6.319
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 6.7 SJR 2.601 SNIP 1.295
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 6.83 SJR 2.692 SNIP 1.436
Web of Science (2014): Impact factor 6.834
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 6.73 SJR 2.752 SNIP 1.372
Web of Science (2013): Impact factor 6.718
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 6.21 SJR 3.118 SNIP 1.35
Web of Science (2012): Impact factor 6.378
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 5.96 SJR 2.889 SNIP 1.323
Web of Science (2011): Impact factor 6.169
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 2.781 SNIP 1.255
Web of Science (2010): Impact factor 5.787
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 2.669 SNIP 1.31
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 2.909 SNIP 1.286
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.957 SNIP 1.278
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.487 SNIP 1.264
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 2.265 SNIP 1.225
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 2.071 SNIP 1.251
Scopus rating (2003): SJR 1.828 SNIP 1.2
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 2.04 SNIP 1.29
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 2.036 SNIP 1.215
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 1.843 SNIP 1.193
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 1.777 SNIP 1.162
Original language: English
We have investigated the single-molecule magnets $[\text{Mn}^{\text{III}}_2(\text{5-Brsalen})_2(\text{MeOH})_2\text{M}^{\text{III}}(\text{CN})_6]\text{NEt}_4$ ($\text{M}=\text{Os}$ (1) and $\text{Ru}$ (2); 5-Brsalen=N,N-ethylenebis(5-bromosalicylidene)iminate) by frequency-domain Fourier-transform terahertz electron paramagnetic resonance (THz-EPR), inelastic neutron scattering, and superconducting quantum interference device (SQUID) magnetometry. The combination of all three techniques allows for the unambiguous experimental determination of the three-axis anisotropic magnetic exchange coupling between Mn$^{\text{III}}$ and Ru$^{\text{III}}$ or Os$^{\text{III}}$ ions, respectively. Analysis by means of a spin-Hamiltonian parameterization yields excellent agreement with all experimental data. Furthermore, analytical calculations show that the observed exchange anisotropy is due to the bent geometry encountered in both 1 and 2, whereas a linear geometry would lead to an Ising-type exchange coupling.
XMCD study of the magnetic exchange coupling in a fluoride-bridged Dy-Cr molecular cluster

We have studied the fluoride-bridged Dy-Cr molecular nanomagnet [Dy(hfac)₄-CrF₂(py)₄]·1/2CHCl₃ by x-ray magnetic circular dichroism (XMCD). The obtained element-specific magnetization curves allow for a quantification of the sign and strength of the magnetic exchange coupling between the Dy and the Cr ions. In an effective spin-1/2 formalism only taking into account the ground Kramers doublet of the DyIII ion, we find a coupling strength of \( j_{eff,z} = -2.3(1) \text{ cm}^{-1} \). Further, we find that the ground Kramers doublet is nearly perfectly axial with \( g_{eff,z,Dy} = 19.6(6) \) and \( g_{eff,xy,Dy} = 0(2) \). The coupling value corresponds to a "true", non-effective isotropic coupling of \( j = -0.16 \text{ cm}^{-1} \) when taking into account a full \( J = 15/2 \) angular momentum. This coupling strength is comparable to that of \( j = -0.18 \text{ cm}^{-1} \) previously found in the related fluoride-bridged compound Dy-Cr-Dy.

General information
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Contributors: Dreiser, J., Piamonteze, C., Nolting, F., Pedersen, K. S., Bendix, J., Rusponi, S., Brune, H.
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Publication date: 2013
Peer-reviewed: Yes
An oxide-bridged Dy-ReV-Dy single-molecule magnet

The reaction of diamagnetic trans-[Re\((O)\_2(py)\_4\)]NO\_3 with [Ln(hfac)\_3(H\_2O)\_2] (Ln = Dy, Y, Tb; hfac\(^-\) = 1,1,1,5,5,5-hexafluoroacetylacetonate(1-)) in chloroform yields oxide-bridged, trinuclear [Ln(hfac)\_3(H\_2O)-Re(O)\_2(py)\_4-Ln(hfac)\_3(NO\_3)] (DyReDy, YReY, TbReTb). The series is isostructural to a fluoride-bridged \{Dy-Cr-Dy\} complex previously reported (Dreiser et al., Chem. Sci. 3 (2012) 1024) but, notably, DyReDy exhibits frequency-dependent out-of-phase ac susceptibility (\(\chi''\)) signals at higher temperatures than the chromium analogue. Magnetic investigations of a solid solution of Dy\(^{3+}\) in YReY reveal the presence of a small Dy-Dy exchange interaction in DyReDy.
Direct observation of a ferri-to-ferromagnetic transition in a fluoride-bridged 3d-4f molecular cluster

We report on the synthesis, crystal structure and magnetic characterisation of the trinuclear, fluoride-bridged, molecular nanomagnet [Dy(hfac)$_9$]$_2$(H$_2$O)-CrF$_2$(py)$_4$-Dy(hfac)$_9$(NO$_3$)] (1) (hfacH = 1,1,1,5,5,5-hexafluoroacetylacetone, py = pyridine) and a closely related dinuclear species [Dy(hfac)$_4$-CrF$_2$(py)$_4$]·1/2 CHCl$_3$ (2). Element-specific magnetisation curves obtained on 1 by X-ray magnetic circular dichroism (XMCD) allow us to directly observe the field-induced transition from a ferrimagnetic to a ferromagnetic arrangement of the Dy and Cr magnetic moments. By fitting a spin-Hamiltonian model to the XMCD data we extract a weak antiferromagnetic exchange coupling of $j$ = -0.18 cm$^{-1}$ between the Dy$^{III}$ and Cr$^{III}$ ions. The value found from XMCD is consistent with SQUID magnetometry and inelastic neutron scattering measurements. Furthermore, alternating current susceptibility and muon-spin relaxation measurements reveal that 1 shows thermally activated relaxation of magnetisation with a small effective barrier for magnetisation reversal of $\Delta_{\text{eff}}$ = 3 cm$^{-1}$. Density-functional theory calculations show that the Dy-Cr couplings originate from superexchange via the fluoride bridges.

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BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 8.54 SJR 4.508 SNIP 1.666
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 8.44 SJR 4.516 SNIP 1.659
Web of Science (2016): Impact factor 8.668
BFI (2015): BFI-level 1
Fluoride-bridged \(\{\text{Ln}_2\text{Cr}_2\}\) polynuclear complexes from semi-labile mer-[CrF\(_3\)(py)\(_3\)] and [Ln(hfac)\(_3\)(H\(_2\)O)\(_2\)]

The trifluorido complex mer-[CrF\(_3\)(py)\(_3\)] (py = pyridine) reacts with 1 equiv. of [Ln(hfac)\(_3\)(H\(_2\)O)\(_2\)] and depending on the solvent forms the tetranuclear clusters [Cr\(_2\)Ln\(_2\)(μ-F)\(_4\)(μ-OH)\(_2\)(py)\(_4\)(hfac)\(_6\)] \(\text{1Ln}\) and [Cr\(_2\)Ln\(_2\)(μ-F)\(_4\)F\(_2\)(py)\(_6\)(hfac)\(_6\)] \(\text{2Ln}\) in acetonitrile and 1,2-dichloroethane, respectively (Ln = Y, Gd, Tb, Dy, Ho, and Er; hfacH = 1,1,1,5,5,5-hexafluoroacetylacetone). Reaction with [Dy(hfac)\(_3\)(H\(_2\)O)\(_2\)] in dichloromethane produces the dinuclear cluster [CrDy(μ-F)(OH\(_2\))(py)\(_3\)(hfac)\(_4\)] \(\text{3Dy}\). All the clusters feature fluoride bridges between the chromium(III) and lanthanide(III) centres. Fits of susceptibility data for 1Gd and 2Gd reveal the fluoride-mediated chromium(III)-lanthanide(III) exchange interactions to be 0.43(5) cm\(^{-1}\) and 0.57(7) cm\(^{-1}\), respectively (in the \(H = JS(J)\) convention). Heat capacity measurements on 2Gd reveal a moderate magneto-caloric effect (MCE) reaching \(-ΔS_m(T) = 11.4\ J\ kg^{-1}\ K^{-1}\) for \(ΔB_0 = 9\ T \rightarrow 0\ T\) at \(T = 4.1\ K\). Out-of-phase alternating-current susceptibility (chi '') signals are observed for 1Dy, 2Dy and 2Tb, demonstrating slow relaxation of the magnetization.

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Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 3.93 SJR 1.306 SNIP 0.904
Web of Science (2017): Impact factor 4.099
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.85 SJR 1.229 SNIP 0.918
Web of Science (2016): Impact factor 4.029
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 4.1 SJR 1.302 SNIP 1.006
Web of Science (2015): Impact factor 4.177
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 4.06 SJR 1.389 SNIP 1.064
Web of Science (2014): Impact factor 4.197
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 4.07 SJR 1.441 SNIP 1.08
Web of Science (2013): Impact factor 4.097
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 3.79 SJR 1.364 SNIP 0.865
Web of Science (2012): Impact factor 3.806
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): CiteScore 3.68 SJR 1.163 SNIP 0.751
Web of Science (2011): Impact factor 3.838
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.002 SNIP 0.602
Web of Science (2010): Impact factor 3.647
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.766 SNIP 0.596
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.689 SNIP 0.528
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 0.754 SNIP 0.578
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.061 SNIP 0.907
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 1.21 SNIP 0.869
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 1.154 SNIP 1.032
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 1.221 SNIP 1.199
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 1.265 SNIP 1.122
Scopus rating (2001): SJR 1.35 SNIP 1.06
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 1.158 SNIP 1.036
Mn\textsuperscript{III} zero-field splitting parameters and weak exchange interactions in a cyanide-bridged \{Mn\textsuperscript{III}-Ir\textsuperscript{III}-Mn\textsuperscript{III}\} cluster

The reaction of [Mn\textsuperscript{III}(5-Brsalen)(MeOH)](ClO\textsubscript{4}) (5-Brsalen2-=N,N'-ethylenebis(5-bromosalicylidene-iminate)) with [Ir\textsuperscript{III}(CN)\textsubscript{6}]3- yields a trinuclear, cyanide-bridged Mn\textsuperscript{III}-(Ir\textsuperscript{III}-Mn\textsuperscript{III}) cluster which is a member of an isostructural series of Mn\textsuperscript{III}-Mn\textsuperscript{III}-Mn\textsuperscript{III} clusters. The presence of the large, diamagnetic [Ir\textsuperscript{III}(CN)\textsubscript{6}]3- bridging unit facilitates a precise determination of the Mn\textsuperscript{III} zero-field splitting (zfs) parameters by the combined use of inelastic neutron scattering, high-field, high-frequency EPR spectroscopy and magnetic measurements. The single-ion axial (D) and rhombic (E) zfs parameters are found to be $D = -3.72(5)$ cm\textsuperscript{-1} and vertical bar $E$ vertical bar=021(1) cm\textsuperscript{-1}. The experimental data are consistent with a small, antiferromagnetic exchange interaction between the two Mn\textsuperscript{III} ions.

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Scopus rating (2017): CiteScore 1.68 SJR 0.43 SNIP 0.474
Web of Science (2017): Impact factor 1.81
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Scopus rating (2016): CiteScore 1.55 SJR 0.436 SNIP 0.481
Web of Science (2016): Impact factor 1.64
Scopus rating (2015): CiteScore 1.68 SJR 0.474 SNIP 0.54
Web of Science (2015): Impact factor 1.762
Scopus rating (2014): CiteScore 1.81 SJR 0.515 SNIP 0.597
Web of Science (2014): Impact factor 1.777
Scopus rating (2013): CiteScore 1.9 SJR 0.551 SNIP 0.68
Web of Science (2013): Impact factor 2.062
Scopus rating (2012): CiteScore 2.04 SJR 0.655 SNIP 0.772
Web of Science (2012): Impact factor 2.016
Scopus rating (2011): CiteScore 2.03 SJR 0.579 SNIP 0.735
Web of Science (2011): Impact factor 1.972
Scopus rating (2010): SJR 0.648 SNIP 0.746
Web of Science (2010): Impact factor 1.974
Scopus rating (2009): SJR 0.661 SNIP 0.868
Scopus rating (2008): SJR 0.731 SNIP 0.816
Scopus rating (2007): SJR 0.737 SNIP 0.861
Scopus rating (2006): SJR 0.709 SNIP 0.882
Scopus rating (2005): SJR 0.754 SNIP 0.729
Scopus rating (2004): SJR 0.715 SNIP 0.806
Scopus rating (2003): SJR 0.637 SNIP 0.728
Scopus rating (2002): SJR 0.734 SNIP 0.676
Scopus rating (2001): SJR 0.616 SNIP 0.496
X-ray Magnetic Circular Dichroism (XMCD) Study of a Methoxide-Bridged DyIII-CrIII Cluster Obtained by Fluoride Abstraction from cis-[CrIIIF2(phen)2]+

An isostructural series of dinuclear chromium(III)-lanthanide(III) clusters is formed by fluoride abstraction of cis-[CrF2(phen)2]+ by Ln³⁺ resulting in LnF3 and methoxide-bridged Cr-Ln clusters (Ln = Nd (1), Tb (2), Dy (3)) of formula [CrIII(phen)2(μ-MeO)2Ln(NO3)4]·xMeOH (x = 2-2.73). In contrast to fluoride, methoxide bridges in a nonlinear fashion, which facilitates chelation. For 3, X-ray magnetic circular dichroism (XMCD) provides element-specific magnetization curves that are compared to cluster magnetization and susceptibility data acquired by SQUID magnetometry. The combination of XMCD and SQUID is able to resolve very small magnetic coupling values and reveals a weak CrIII-DyIII coupling of J = -0.04(3) cm⁻¹. The DyIII ion has a ground-state Kramers doublet of mJ = ±√3/2, and the first excited doublet is found to be mJ = ±13/2 at an energy of δ = 57(21) cm⁻¹. The CrIII ion exhibits a uniaxial anisotropy of DCr = 1.7(1.0) cm⁻¹. Further, we observe that a weak anisotropic coupling of dipolar origin is sufficient to model the data, suggesting that methoxide bridges do not play a significant role in the magnetic coupling for the present systems.

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Web of Science (2018): Indexed yes
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Scopus rating (2017): CiteScore 2.75
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Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.64
Web of Science (2016): Impact factor 2.847
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 2.78
Web of Science (2015): Impact factor 2.883
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 2.65
Web of Science (2014): Impact factor 2.693
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 2.84
Web of Science (2013): Impact factor 2.775
A linear single-molecule magnet based on [Ru\textsuperscript{III}(CN)$_6$]\textsuperscript{3-}

We report the synthesis, structure and magnetic properties of the first molecular cluster and single-molecule magnet to incorporate [Ru\textsuperscript{III}(CN)$_6$]\textsuperscript{3-}. Frequency-domain Fourier-transform THz-EPR (FDFT THz-EPR) and magnetic susceptibility measurements indicate strongly anisotropic Mn-Ru exchange interactions.
Frequency-Domain Fourier-Transform Terahertz Spectroscopy of the Single-Molecule Magnet (NEt₄)[Mn₂(5-Brsalen)₂(MeOH)₂Cr(CN)₆]

We have investigated the novel single-molecule magnet (NEt₄)[Mn₂(5-Brsalen)₂(MeOH)₂Cr(CN)₆] (1; 5-Brsalen= N, N'-ethylenebis(5-bromosalicylidene) iminato anion) using spectroscopic as well as magnetization and susceptibility measurements. Frequency-domain Fourier-transform terahertz electron paramagnetic resonance (FDFT THz-EPR) based on the generation of THz radiation from a synchrotron in combination with inelastic neutron scattering (INS) allows for the discrimination between intermultiplet and intramultiplet transitions. Together with ac/dc magnetic susceptibility measurements the obtained set of data provides a complete characterization of the lowest energetic magnetic excitations. We find that the new compound 1 exhibits much weaker intermolecular interactions than found in the closely related compound: K[Mn₂(5-Brsalen)₂(H₂O)₂Cr(CN)₆] (2). Furthermore, two phonon lines in the vicinity of the magnetic excitations are detected.

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Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 5.03 SJR 2.352 SNIP 1.068
Web of Science (2016): Impact factor 5.317
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 4.99 SJR 2.461 SNIP 1.195
Web of Science (2015): Impact factor 5.771
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 5.51 SJR 2.526 SNIP 1.222
Web of Science (2014): Impact factor 5.731
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 5.68 SJR 2.643 SNIP 1.239
Web of Science (2013): Impact factor 5.696
Magnetic Properties of a Manganese(III) Chain with Monoatomic Bridges: catena-MnF(salen)

In the solid state, MnF(salen) forms chains wherein fairly linear fluoride bridges between high-spin Mn\textsuperscript{III} centers are observed. We interpret the magnetic properties of these chains by use of the classical Fisher model and by use of the high-temperature expansion approach, as well as by exact matrix diagonalization of the spin Hamiltonian, of model rings. In solution, electron paramagnetic resonance shows the chains to be symmetrically cleaved to monomeric MnF(salen).

**General information**

**State:** Published

**Organisations:** University of Copenhagen

**Contributors:** Birk, T., Pedersen, K. S., Piligkos, S., Thuesen, C. A., Weihe, H., Bendix, J.

**Pages:** 5312-5314
Enhancing the Blocking Temperature in Single-Molecule Magnets by Incorporating 3d-5d Exchange Interactions

We report the first single-molecule magnet (SMM) to incorporate the [ Os(CN)₆ ]³⁻ moiety. The compound (1) has a trimeric, cyanide-bridged Mn³⁺-Os³⁺-Mn³⁺ skeleton in which Mn³⁺ designates a [ Mn(5Brsalen)(MeOH)]⁺ unit (5-Brsalen= N,N'-ethylenebis(5-bromosalicylideneiminato)). X-ray crystallographic experiments reveal that 1 is isostructural with the Mn³⁺-Fe³⁺-Mn³⁺ analogue (2). Both compounds exhibit a frequency-dependent out-of-phase X″(T) alternating current (ac) susceptibility signal that is suggestive of SMM behaviour. From the Arrhenius expression, the effective barrier for 1 is found to be \( \Delta_{\text{eff}}/k_B=19 \text{ K} \) (\( \tau(0)=5.0 \times 10^{-7} \text{ s} \); \( k_B \) = Boltzmann constant), whereas only the onset (1.5 kHz, 1.8 K) of \( X''(T) \) is observed for 2, thus indicating a higher blocking temperature for 1. The strong spin-orbit coupling present in Os³⁺ isolates the \( E'_1\text{g}(1/2)(\text{Oh})^* \) Kramers doublet that exhibits orbital contributions to the single-ion anisotropy. Magnetic susceptibility and inelastic neutron-scattering measurements reveal that substitution of [Fe(CN)₆ ]³⁻ by the [Os(CN)₆ ]³⁻ anion results in larger ferromagnetic, anisotropic exchange interactions going from quasi-Ising exchange interactions in 2 to pure Ising exchange for 1 with \( J(\parallel\text{to})(\text{MnOs})=-30.6 \text{ cm}^{-1} \). The combination of diffuse magnetic orbitals and the Ising-type exchange interaction effectively contributes to a higher blocking temperature. This result is in accordance with theoretical predictions and paves the way for the design of a new generation of SMMs with enhanced SMM properties.

General information

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Web of Science (2017): Impact factor 5.16
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 5.03 SJR 2.352 SNIP 1.068
Projects:

**Organometallic Polynuclear Chemistry**
Nielsen, M. T., PhD Student, Department of Chemistry
Mossin, S., Main Supervisor, Department of Chemistry
Nielsen, M., Supervisor, Department of Chemistry
Pedersen, K. S., Supervisor, Department of Chemistry
Fonde
01/09/2018 → 31/08/2021
Award relations: Organometallic Polynuclear Chemistry
Project: PhD

**Macroscopic Quantum States in Low-Dimensional Materials**
Wan, W., PhD Student, Department of Physics
Christensen, N. B., Main Supervisor, Department of Physics
Pedersen, K. S., Supervisor
Rønnow, H. M., Supervisor
Institut stipendie (DTU)
01/08/2018 → 31/07/2021
Award relations: Macroscopic Quantum States in Low-Dimensional Materials
Project: PhD

**Advancing 2D Materials by Metal-Organic Framework Engineering**
Voigt, L., PhD Student, Department of Chemistry
Pedersen, K. S., Main Supervisor, Department of Chemistry
Mossin, S., Supervisor, Department of Chemistry
Samfinansieret - Andet
01/08/2017 → 31/07/2020
Award relations: Advancing 2D Materials by Metal-Organic Framework Engineering
Project: PhD