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Hybrid lanthanide double-deckers based on calixarene and polyoxometalate units†

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Complementarity of calixarene (H2L) and polyoxometalate ligands results in the first organic-inorganic [MIIIL{Mo5O13(OMe)4(NO)}]2– (M = Y, Gd and Dy) hybrid, directing the formation of a distorted square-antiprismatic MO8 ligand field, producing slow relaxation of the magnetisation for the Dy derivative.

Synthetic chemists continue to exploit the wide range of coordination environments of *f*-elements to design molecules with interesting physical properties, including Single-Ion Magnets (SIMs).1 These molecules exhibit slow relaxation of the magnetisation and have been suggested for potential applications in quantum computation or molecular spintronics.2 In this context, rare earth metal ions feature large intrinsic magnetic anisotropy and the possibility to manipulate the alignment and magnitude of the anisotropy axis *via* ligand field design.3 Specific symmetries such *D*4d, *D*5h and *D*6d are proposed in the design of high-performance LnIII-SIMs.4 Following this rational design, sandwich-type complexes based on late lanthanide metals with polydentate organic ligands (*e.g.* phthalocyanines, porphyrins, Schiff-base, organometallic) have shown great success, allowing changes in the magnetic properties upon chemical modification of the peripheral substituents.5 Inorganic analogues, where the lanthanide ion is encapsulated between two tetradentate polyoxometalates (*i.e.* LnIII(POM)2) have also been described, displaying a disparity in the magnetic properties upon structural distortions from the *D*4d symmetry.6 Reports of the exchange of one POM by an organic ligand featuring a hybrid organic-inorganic single lanthanide double-decker complex remain scarce, with just three examples. Two of these molecules exhibit SIM characteristics: [TbIII(HPW11O39)(phen)2]3– and [TbIII(Pc)(PW11O39)]6–.7 These heteroleptic systems are particularly interesting as they combine tuneable organic ligands with robust inorganic polyoxometalates, characterised by high thermal stability and redox-active properties.

 *p-tert*-Butylcalix[4]arene (TBC[4]) represents a highly versatile ligand towards metal complexation. While initially our interest lay in developing a library of polynuclear complexes with transition metals (TM), lanthanides (Ln) and mixed TM-Ln species (*e.g.* [Tb6] cluster in Fig. 1a),8 we have recently started mapping out strategies towards the synthesis of mononuclear lanthanide complexes with TBC[4]. This area has received much less attention, with just two examples showing SIM behaviour, both comprising a TBC[4] ligand methylated in the 1,3-phenolic positions, *i.e.* *p*‐*tert*-butylcalix[4](OMe)2(OH)2arene(= H2L).9 Importantly, the bulky lower-rim methyl groups overcome the predisposition of the calixarene to bridge to neighbouring metal centres (Fig. 1b); this behaviour is also observed with the

**Fig. 1. (a)** [TbIII6(TBC[4])2O2(OH)3.32Cl0.68(HCO2)2(dmf)8(H2O)0.5], an example of a TBC[4]-based polynuclear cluster, highlighting the typical µ2-O2– binding mode of the phenoxide groups coordinating to Ln ions. **(b)** Structure of [DyIIIL(acac)2]– demonstrating the preference of bis-methylated TBC[4] to coordinate to a single Ln ion. Colour code: LnIII: purple, O: red, Cl: yellow and C: black. H atoms and N(*n*Bu)4 cation in (b) omitted for clarity; terminal dmf molecules coordinated to equatorial terbium atoms in (a) only represented by their coordinating oxygen atoms for better visibility.



**Fig. 2.** 1H NMR spectra (400 MHz, 300 K) in CD3CN of **(a)** the [YIIIL{Mo5O13(OMe)4(NO)}]2– anion in **1**, and **(b)** the starting material (N(*n*Bu)4)[YIIIL(acac)2]. Colour code: H–aromatics: brown, H–CH3O(POM): dark magenta, H–CH2*axial*: light green, H–CH3O: blue, H–CH2*equatorial*: green, and H–*t*butyl: orange.

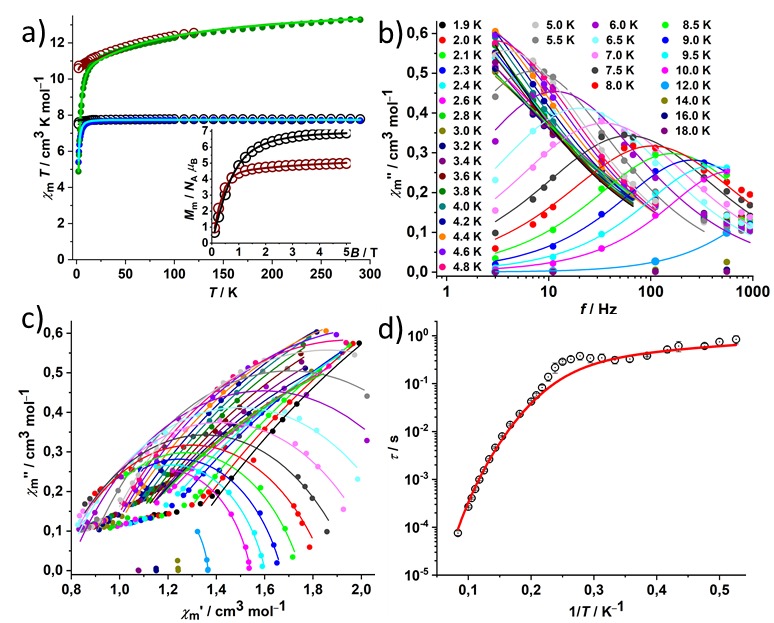
methylated version of *p*‐*tert*-butylthiacalix[4]arene.10 A small number of Ln-based mononuclear complexes with TBC[4] ligands have also been synthesised to investigate luminescence,11 metal extraction12 and synthetic methodology.13 Although polyoxometalates and calixarenes are of significant importance in coordination chemistry with lanthanides in their own right, there are no reports of these two moieties linked together through a single-metal ion. Solid-state networks of polyoxometalate and calixarene units mediated by weak hydrogen bonds and ionic interactions exist as well.14 Herein we describe the synthesis and characterisation of a new class of organic-inorganic Ln double-decker species isolated as (N(*n*Bu)4)2[MIIIL{Mo5O13(OMe)4(NO)}], M = Y (**1**), Gd (**2**) and Dy (**3**), as well as selected magnetic properties of **2** and **3**. These complexes were synthesised by an acetate metathesis reaction of our recently reported (N(*n*Bu)4)[MIIIL(acac)2] complexes (Fig. 1b) with the monolacunary Lindqvist-type pentamolybdate [Mo5O13(OMe)4(NO)Na(MeOH)]2– (in 1:1 stoichiometry,15 see ESI† for details).

Key in developing this synthetic strategy was the initial investigation of the diamagnetic analogue (N(*n*Bu)4)2[YIIIL{Mo5O13(OMe)4(NO)}] (**1**) in CD3CN solution *via* 1H NMR spectroscopy (Fig. 2). Upon coordination with the POM, (N(*n*Bu)4)[YIIIL(acac)2] presents a downfield shift of the aromatic proton signals of 0.08 and 0.05 ppm with singlets at 6.98 and 6.93 ppm, while the methoxy groups are more affected, displaying a large upfield shift of 0.34 ppm (3.76 ppm, C*H*3O-calixarene). Diastereotopic calixarene methylene protons display both upfield and downfield shifts upon ligand exchange. The *axial* protons display a very small upfield shift of 0.06 ppm (to 4.34 ppm, C*H*2*ax*), but the *equatorial* protons show a larger downfield shift of 0.16 ppm (3.03 ppm, C*H*2*eq*). The two unique *tert*-butyl groups are almost unchanged with singlets at 1.22 and 1.07 ppm, due to the long distance to the POM. The disappearance of the signals corresponding to acetylacetonate and the presence of four POM-related methoxy groups (4.64 ppm, C*H*3O-POM) confirms the metathesis reaction. The presence of two tetrabutylammonium counter cations agrees with the integration ratio. Both the starting material (N(*n*Bu)4)[YIIIL(acac)2] and **1** present resonance signals typical of a pinched *C*2v-symmetric conformation of the calixarene ligand, where two distal aromatic groups are pinched and the remaining two splayed (Fig. 1b).

Brown rod-like single crystals of **1** – **3** were obtained by slow evaporation of a dichloromethane/*n*-hexane (1/3, v/v) solution of each complex over a week. The complexes crystallise in the triclinic (**1**) and monoclinic systems (**2** and **3**) in space groups *P*-*1* (**1**) and *C*2/*c* (**2** and **3**; Table S3, ESI†). The three complexes are structurally analogous, we therefore only discuss the representative molecular structure of **3**. The monolacunary Lindqvist pentamolybdate [Mo5O13(OMe)4(NO)]3– contains a central oxygen atom (µ5-Oc), bridging to four equatorial MoVI ions (MoVI–Oc: 2.303(3)–2.357(3) Å) and one axial [Mo(NO)]3+ unit (Mo–Oc: 2.117(3) Å). On the periphery, the MoVI ions are connected by four µ2-Ob bridging oxygen atoms (MoVI–Ob: 1.907(3)–1.931(3) Å) and link to the axial [Mo(NO)]3+ unit via four µ2-OOMe methoxy groups (MoVI–OOMe: 2.238(4)–2.284(4); Moaxial–OOMe: 1.991(3)–2.016(4)). The remaining coordination sites are completed by four terminal oxo groups (MoVI–Ot: 1.700(3)–1.705(4) Å) and one linear nitrosyl group (Moaxial–NNO: 1.768(4) Å). [Mo5O13(OMe)4(NO)]3– provides a nearly regular O4 square (O···O: 2.766(4)–2.869(4) Å; MoVI−O: 1.734(3)–1.744(4) Å) to coordinate to the [DyIIIL]+ unit (DyIII–OPOM: 2.432(3)–2.509(3) Å), completing the [DyIIIL{Mo5O13(OMe)4(NO)}]2– ion in **3** (Fig. 3). The [DyIIIL]+ unit itself comprises the fully deprotonated calix[4]arene, coordinated to the Dy3+ ion as a tetradentate ligand (O···O: 2.839(4)–2.985(4) Å) through the



**Fig. 3. (a)** Molecular structure of the [DyIIIL{Mo5O13(OMe)4(NO)}]2– anion in **3** with the distorted square-antiprismatic DyIIIO8 coordination environment highlighted as transparent magenta polyhedron; dashed yellow lines indicate the *C*2v-symmetric O4 donor arrangement of L. **(b)** Top view of the molecule along its *C*2 axis showcasing the pinched conformation of the TBC[4] unit. Colour code as in Fig. 1; MoVI: turquoise, Moaxial–[Mo(NO)]3+: blue, N: dark blue. H atoms, N(*n*Bu)4 counter cations and a DCM solvent molecule encapsulated in the TBC[4] cavity are omitted for clarity.

lower-rim O atoms (DyIII–OPh: 2.177(3) and 2.136(3) Å; DyIII–OMePh: 2.534(3) and 2.561(3) Å), again showing a *C*2v symmetric pinched-cone conformation (Fig. 3b). The combination of both ligands locks the Dy centre as eight-coordinate, adopting a distorted square-antiprismatic DyIIIO8 environment, rotated by a skew angle of 43.20, 46.03, 42.57 and 48.67° (45.11° as a mean angle) *vs.* an eclipsed geometry (Fig. 3b). Continuous shape measurements of the DyO8 environment yield CShM = 2.172 for a regular square antiprism (*D*4d) and identify a biaugmented triangular prism (*C*2v; Johnson solid 50) with CShM = 1.151 as the most accurate coordination polyhedron (with CShM = 0 corresponding to an exact match).16 The molecule in the solid-state displays a small distortion from the *C*2v symmetry as observed in solution NMR experiments of the yttrium derivative **1** and in CShM. In the crystal lattice the complexes are packed in an antiparallel bilayer array with interdigitated molecules, as also seen for the starting material (N(*n*Bu)4)[MIIIL(acac)2] and solvates of TBC[4].17 This leads to a significant separation of the magnetic sites belonging to neighbouring molecules (DyIII···DyIII: 12.5 Å), with shortest contacts mediated by N*O*–*C*H3(POM) and *C*H3(POM)–*C*H3(POM) interactions at 3.865 and 4.189 Å, respectively. Dichloromethane solvent molecules are located in the TBC[4] cavities with the charge-balancing N(*n*Bu)4 cations located in the interstitial spaces (Fig. S6, ESI†).

The electronic absorption spectra of **1** – **3** in CH3CN present one peak with λmax at 306 nm, attributed to π → π\* electronic transition centred on the phenyl rings of the calixarene ligand, and one shoulder peak with λmax at 244 nm corresponding to the intense n → π\* transition of the nitroso group in the [Mo5O13(OMe)4(NO)]3– unit (Fig. S1, ESI†). FT-IR spectra of **1** – **3** display the following vibrations (cm-1): ~2958–2873 (m, C–H str. ), ~1622 (m, N–O str.), ~1479–1431 (m, arC–Cstr./CH2bend./CH3 bend.), ~1334 (m, CH3 bend.), ~1213 (w, C–O str.), ~1037 (m, C–OPOM str.), ~928–864 (s, (Mo–Ot)POM str.) and~ 681 (vs, (Mo–O–Mo)POM str.) (Fig. S3, ESI†). High-resolution negative ion-mode ESI-MS data for **1** – **3** show the presence of two ions, the singly and doubly charged [M – N(*n*Bu)4]1– (*m*/*z* region of 1830–1940) and [M – 2 N(*n*Bu)4]2– (*m*/*z* region of 790–850) respectively, where M = (N(*n*Bu)4)2[MIIIL{Mo5O13(OMe)4(NO)}]. Relative abundance is 100% for the singly charged species of Gd and Dy (7.6% for Y), with small peaks of the doubly charged [M – 2N(*n*Bu)4]2– {MIII = Y (34.3 %), Gd (32.9%) and Dy (12.1%)}. The ionic fragments have a well-resolved isotopic distribution for each constituent metal ion, with the calculated species matching with the *m*/*z* values of the experimental data (Fig. S7–9, ESI†). Elemental analyses of **1** – **3** agree with the empirical formula C82H142N3O22Mo5M (M = Y, Gd and Dy) within 0.2% (see ESI†).

Direct current (dc) magnetic susceptibility and magnetisation measurements for **2** and **3** are shown as *χ*m*T* *vs.* *T* at 0.1 and 1 T, as well as *M*m *vs.* *B* at 2.0 K and *B* = 0.1 – 5.0 T (Fig. 4a,b). At 290 K, the *χ*m*T* values of 7.80 cm3 K mol–1 (**2**) and 13.28 cm3 K mol–1 (**3**) are within the expected18 ranges of 7.6–7.9 cm3 and 13.0–14.1 cm3 K mol–1 for isolated GdIII and DyIII centres, respectively. Upon cooling, the *χ*m*T* value of **2** remains

**Fig. 4.** **(a)** Dc data: *χ*m*T* *vs*. *T* data at 0.1 T (empty circles: **2** black and **3** brown) and 1 T (filled circles: **2** blue and **3** green) and, molar magnetisation *M*m *vs*. *B* at 2.0 K (inset, right) for **2** (black open circles) and **3** (brown empty circles); solid lines represent the least-squares fit. **(b)** Out-of-phase molar magnetic susceptibility *χ*m'' *vs*. *f* for **3** at dc= 300 Oe (filled circles: data, lines: fits to generalised Debye expression). **(c)** Ac data for **3**: Cole-Cole plot in the range of 1.9–18.0 K at a static bias field of 300 Oe (filled circles: data, solid lines: fits to a generalised Debye expression). Colour code as in Fig. 4b. **(d)** Plot of relaxation time *τ* *vs*. *T*–1 (open circles at 1.9 K ≤ *T* ≤ 12.0 K) for **3**; the solid red line shows a combined fit considering a direct and a Raman relaxation processes.

constant to 15 K, wherefrom it decreases to a value of 7.50 (5.40) under *B* = 0.1 (1.0) T at 2.0 K. Complex **3** displays a progressive decrease in the *χ*m*T* value to 11.15 cm3 K mol–1 at 25 K. At lower temperatures, the different contributions of the Zeeman effect become visible, leading to a decrease down to 10.59 (0.1 T) and 4.88 cm3 K mol–1 (1.0 T) at 2.0 K. Gd3+ is (almost) isotropic *S* = 7/2 (8*S*7/2), hence, the Curie-like temperature-invariant *χ*m*T* value is readily explained. The *χ*m*T* *vs*. *T* data of **3** are mostly characterised by the thermal depopulation of the significantly split *mJ* substates of the (mainly) 6*H*15/2 ground term of the DyIII centre. The splitting and mixing of the eigenstates is primarily caused by electron-electron repulsion, spin-orbit coupling and the ligand field. The different magnetic characteristics of both Ln centres are also reflected in the *M*m *vs*. *B* curves. At 2 K, *M*m increases almost linearly up to approx. 1.0 T (Fig. 4a, inset), and the curve gradually flattens toward higher fields, reaching 6.9 (**2**) and 5.0 *N*A*μ*B (**3**) at 5.0 T, respectively. As such, for the isotropic spin-like GdIII compound, *M*m approaches the saturation value of 7.0 *N*A *μ*B (= *g*eff×*S* *N*A*μ*B, *g*eff ≈ 2) at 5.0 T. For DyIII, *M*m reaches about half of the saturation value (*gJ*×*J* *N*A*μ*B = 10 *N*A*μ*B) at 5.0 T, in line with the magnetic anisotropy and the measurement of a powder sample, *i.e.* of randomly oriented crystallites of **3**. We fitted the data for **2** and **3** using the computational framework CONDON19 (explained in detail in the ESI†). For **2** we used the isotropic spin-only option, while we employed the ‘full’ model option for **3** assuming a *C*2v-symmetric ligand field. The quality of the simultaneous fit (relative root mean squared error) of the *χ*m*T* *vs*. *T* data at 0.1 and 1.0 T and the *M*m *vs*. *B* data at 2.0 K is *SQ* = 0.93% and 0.78% for **2** and **3**, respectively. This fit yields *g*eff = 1.98±0.01 for the effective spin *S*eff = 7/2 system of a GdIII centre. For **3**, the calculated energies and the wave functions of the ground term (2*J*+1 = 16 states) are shown in Table S2, ESI†. The states are strongly mixed, although a respective main contribution of at least 57 % can be identified for every state. As a further feature, the ground doublet and first excited doublet are almost degenerate states. They are separated by only ~0.2 cm–1, which might explain the need to apply a static bias field for improved out-of-phase signals in the following ac measurements.

Dynamic (ac) susceptibility measurements of **2** and **3** in revealed significant out-of-phase components for **3**, particularly at a static bias field of 300 Oe. We analysed the data in terms of a generalised Debye expression20 by simultaneously fitting *χ*m' *vs*. *f* (Fig. S12a, ESI†) and *χ*m'' *vs*. *f* (Fig. 4b). The fits yield the solid lines shown in Fig. 4b,c and S12, ESI†. The corresponding relaxation times *τ* with the distribution *α* = 0.071±0.035 are plotted against the inverse temperature *T* as shown in Fig. 4d. The value of *α* = 0.408±0.123 suggests several active relaxation pathways. The best fit to the *τ* *vs*. 1/*T* data is found for the combination of a direct and a Raman relaxation process, *i.e*. using the equation *τ*–1 = *A*nK*T* + *CTn*, with *A*nK = (0.81±0.08) s–1 K–1 for the direct relaxation process, as well as *C* = (2.39±0.09)×10–4 s–1 K–*n* and the exponent *n* = 7.1±0.1 for the Raman process. This is close to *n* = 7, in line with spin-two-phonon interaction with phonon energies larger than the energy between the ground and excited state.21 In comparison to our previously reported hybrid Dy complex (Fig. 1b),9a the substitution of two acac ligands by the {Mo5} unit leads to a more pronounced slow relaxation behaviour. The corresponding homoleptic POM-based double-decker complex [DyIII(Mo5O13(OMe)4(NO))2]3– also deviates from D4d symmetry, requiring an static bias field of 1k Oe to observe out-of-phase signals in the temperature range 2.8–4.4K.22 In this work, a static field of 300 Oe is applied to observe frequency-dependent signals between 1.9–12K. However, the found process parameters and, in particular, the temperature range of out-of-phase signal detection are overall similar to other Dy-based systems.7c, 9b, 10, 23

Conclusions

In summary, we present the synthesis, characterisation and magnetic properties of a family of new organic-inorganic hybrid complexes of formula [MIIIL{Mo5O13(OMe)4(NO)}]2– formed by an acetate ligand metathesis of our previously synthesised [MIIIL(acac)2]2– species with a monolacunary Lindqvist pentamolybdate, [Mo5O13(OMe)4(NO)]3–. The two tetradentate ligands differ in their donor atom configurations: whereas the pinched-cone conformation of the calix[4]arene L2– group results in a bent rhombic *C*2v-symmetric O4 geometry, the methylated monolacunary polyoxomolybdate provides a nearly regular O4 square. Yet both conformations are compatible to create an approx. square-antiprismatic MIIIO8 environment, resulting in slow magnetisation dynamics for the Dy derivative. We plan to extend this study to other tetradentate calixarene and functionalized polyoxometalate ligands for a systematic variation of axial ligand fields with highly negatively charged species.

Author Contributions

Y.J. performed the experimental work; N.V.I. measured and solved the SXRD data; J.vL. simulated the magnetic data; S.S., S.J.D., E.K.B. and P.K. conceived the idea. All authors contributed to the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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