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Heterotrimetallic {LnOVPt} complexes with Antiferromagnetic Ln-V Coupling and Magnetic Memory

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Stephanie A. Beach,^a Jesse L. Guillet,^a Sydney P. Lagueux,^a Mauro Perfetti,^b Brooke N. Livesay,^c Matthew P. Shores,^c Jeffrey W. Bacon,^a Arnold L. Rheingold,^d Polly L. Arnold,^e and Linda H. Doerr ^{*a}

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The new PtVO(SOCR)₄ lantern complexes, 1 (R=CH₃) and 2 (R=Ph) behave as neutral O-donor ligands to Ln(OR)₃ with Ln = Ce, Nd. Four heterotrimetallic complexes with linear {LnOVPt} units were prepared: [Ln(ODtbp)₃{PtVO(SOCR)₄}] (Ln=Ce, 3Ce (R=CH₃), 4Ce (R=Ph); Nd, 3Nd (R=CH₃), 4Nd (R=Ph); ODtbp=2,6-ditertbutylphenolate). Magnetic characterization confirms slow magnetic relaxation behaviour and suggests antiferromagnetic coupling across {Ln-O=V} in all four complexes, with variations tunable as a function of Ln and R.

Rare earth elements have become essential in clean energy technologies such as the synthesis of batteries,¹ magnets,² and catalysts³. Due to the inherent magnetic anisotropy of these systems, lanthanide (Ln) complexes are possibly most well known for their potential single molecule magnet (SMM) behaviour which is used in the fields of molecular magnets and spintronics for potential quantum information storage (QIS) technologies.⁴ In the design of SMMs, low-coordinate Ln complexes with high structural anisotropy are preferred for better isolated magnetic centers and slow relaxation.^{5, 6} Recently, the field of SMMs has seen an increase in research on the coupling of *d*-block metals to Ln complexes as a method to increase the magnetic anisotropy of the system. Low coordinate 3*d*-4*f* complexes have been achieved with examples including an unsupported Nd-Fe bond⁷ as well both ferro- and antiferromagnetic coupling in a vanadyl-Gd coupled complex.⁸

More recently, focus has been on a bottom-up approach to the rational design of SMMs through structural and magnetic studies. While solvated LnX₃ complexes are very common, the formation of low coordinate species requires bulkier ligands

such as substituted aryloxides, siloxides, and amides⁹ with monodentate O-donor ligands being most common due to Ln oxophilicity. In mixed-metal complexes, reviews of magnetism consistently show no coupling in trinuclear LnM₂ complexes with triangular metal arrangement but when arranged linearly, coupling is observed. The importance of ligand geometry and different Ln ion *f*-orbital electron distribution shapes (oblate or prolate) can be observed through better stabilization by either greater equatorial or axial ligand contribution, promoting highly anisotropic ground states and greater coupling.¹⁰ This phenomenon is exemplified in the magnetic coupling in dinuclear Tb(III)-Cu(II) complexes with O-donor ligands, which can be tuned through ligand charge as well as the greater equatorial vs axial ligand contributions to prolate Tb(III).⁶

In the present work, we set out to combine low coordinate lanthanide complexes with a vanadyl unit in an effort to effect magnetic coupling between *d*- and *f*-block metals. Design of linear M=O-Ln units is particularly needed since the majority of *d*-block-O-Ln adducts have used 4*d*/5*d* elements and result in diamond {Ln(μ₂-O)M} moieties rather than the desirable linear coordination. A variety of lantern complexes of the formula [PtM(SOCR)₄(L)] (M = Mg, Ca, Cr, Mn, Fe, Co, Ni, Zn; R = CH₃ (SOCMe), Ph (SOCPh); L = substituted pyridines and donating solvents) are known.¹¹ Antiferromagnetic coupling of the 3*d* metals has been consistently observed in the solid state between staggered dimers through a metallophilic interaction. While the late transition metals have been studied in these systems, examples with early transition metals were lacking. We hypothesized that the Lewis basic {V=O} unit, which has already been shown to bind other metal centres,¹²⁻¹⁴ would bind in a linear fashion to Ln. The only reported example of a vanadyl oxo forming a [Ln-O=V] unit is in the chiral visible-light photocatalyst cluster, (nBu₄N)₂[(Ce(DMSO)₃)₂V^{iv}V^v₁₁O₃₃Cl] x2DMSO, but magnetic coupling was not explored. Similarly, the majority of transition metals bound to lanthanides through an oxygen bridge are high coordinate polyoxometalates (M = Mo, W, Re) bound through a metal oxo unit that is rarely linear and by definition does not have a single transition metal center.¹⁵⁻¹⁸ Binding of an uranyl oxo both bent and linear,¹⁹ to Ln has been reported and strong antiferromagnetic coupling

^a Boston University, 590 Commonwealth Ave, Boston, MA 02215.

^b Department of Chemistry, Universitetsparken 5, 2100 Copenhagen.

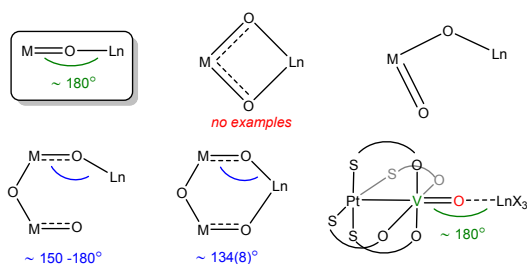
^c Department of Chemistry, Colorado State University, 1301 Center Ave Chemistry B101, Fort Collins, CO 80523

^d University of California San Diego Dept. of Chemistry and Small Molecule Xray Crystallography, 5128 Urey Hall Mc 0358, La Jolla, CA 92093.

^e University of Edinburgh Joseph Black Building, David Brewster Road, Edinburgh, UK EH9 3FJ. Current address: Department of Chemistry, University of California, Berkeley, CA 94720, US; Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA94720, US. pla@berkeley.edu

† Footnotes relating to the title and/or authors should appear here.

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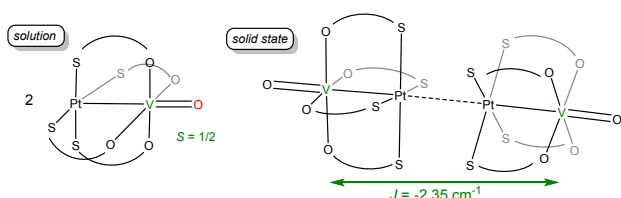


Scheme 1. Known Ln-O-M patterns (M= transition metal) and lantern binding mode.

exists in a U(V)Sm(III) monomer, whereas a U(V)Dy(III) dimer shows magnetic bistability at 3 K.²⁰ As seen in Scheme 1, the majority of known M=O-Ln linkages are bent, whereas a {V=O} lantern can uniquely favour an anisotropic environment and prevent the coordination of other {MO} units.

Anisotropic {V=O}-containing lanterns [PtVO(SOCMe)₄] (**1**) and [PtVO(SOCPh)₄] (**2**) were synthesized similarly to our previously published complexes using VOSO₄ as the starting V(IV) source.¹¹ Rather than forming 1D chains in the solid state, with the terminal oxo interacting with the {PtM} σ* orbital of an adjacent lantern, as seen with an S^N donor ligand,¹⁴ both **1** and **2** form dimers in the solid state with different intermolecular interactions. Complex **1** forms a staggered dimer (~D_{4d}) in which the intermolecular Pt...Pt distances are shorter than the resultant Pt...S contacts and the thiocarboxylate backbones are staggered when viewed along the metal axis (Figure S1). As seen with the other paramagnetic complexes that form staggered dimers, **1** exhibits antiferromagnetic V-V coupling across an intermolecular Pt...Pt metallophilic contact of 3.1747(5) Å. Fitting this data as a dimer leads to an exchange coupling of $J = -2.35 \text{ cm}^{-1}$, consistent with the higher-than-expected Weiss constant calculated from the temperature dependence of $1/c$ (Figure S5), suggesting antiferromagnetic coupling between V(IV) ions in adjacent complexes. Whether this is due to communication via a Pt-Pt contact (Scheme S2) or through space (Figure S1) cannot be determined definitively. Certainly, the near orthogonality of the magnetic (d_{xy}) orbitals in the staggered dimer is consistent with the observation of weak exchange coupling. In comparison, **2** forms a square dimer (~D_{2h}) (Figures S2 and S3) in the solid state, dominated by a close intermolecular Pt...S contact of 3.126(2) Å, rather than a metallophilic interaction or any interdimer coupling (Table S1).

Solution phase Evans method^{21, 22} magnetic moment measurements yielded μ_{eff} values of 1.68 (**1**) and 1.60 (**2**), consistent with the predicted spin-only magnetic moment (1.73) of reported V(IV) complexes with tetradentate ONNO ligands.^{23, 24} Shown in Figure S9, the solid state magnetic susceptibility temperature product of staggered dimer **1** at room temperature ($\chi T = 0.839 \text{ cm}^3 \text{ K mol}^{-1}$) is higher than two magnetically uncoupled V(IV) centers (0.75 cm³ K mol⁻¹ for $g = 2$); however, below 10K, the $\chi_{\text{M}}T$ product shows a sharp decrease (0.103 cm³ K mol⁻¹). Fitting this data leads to an exchange coupling of $J = -2.35 \text{ cm}^{-1}$, suggesting antiferromagnetic coupling between V(IV) ions in adjacent complexes (Figure S1) with competing interactions from other



Scheme 2. Solution and solid-state magnetism for **1**.

close neighbors indicated in the higher-than-expected Weiss constant calculated from the temperature dependence of $1/\chi$ (Figure S5). Details for the magnetic exchange interpretation are provided in the ESI. In sum, both **1** and **2** chemically act as monomers in solution (Scheme 2) and can be tested as discrete monodentate ligands for coordination to Ln ions.

Lanthanide tris-aryloxide complexes, particularly the 2,6-ditertbutylphenolate derivatives (Ln(ODtbp)₃ where Ln=Ce, Nd), have previously served as starting materials in non-donor solvents.^{9, 25, 26} Both **1** and **2** are soluble in non-coordinating solvents; when green toluene solutions of either **1** or **2** and Ln(DBP)₃ (Ce=yellow, Nd=blue) are mixed, an immediate colour change to a dark brown/red is observed in all four cases. Air-sensitive, analytically pure, X-ray quality material was grown from the reaction mixtures and isolated in high yield (~80%). For full synthetic and characterization details, see ESI.

Structural characterization of the products of these reactions revealed the successful coordination of one equivalent of **1** or **2** to both Ce(ODtbp)₃ and Nd(ODtbp)₃, giving [Ce(ODtbp)₃{PtVO(SOCMe)₄}] (**3Ce**), [Ce(ODtbp)₃{PtVO(SOCPh)₄}] (**4Ce**), [Nd(ODtbp)₃{PtVO(SOCMe)₄}] (**3Nd**), and [Nd(ODtbp)₃{PtVO(SOCPh)₄}] (**4Nd**). As exemplified by **3Ce**, shown in Figure 1, these complexes feature coordination of the lantern complex to the Ln center through the {V=O}, resulting in pseudo-tetrahedral geometry about Ln.

The {V=O} stretching frequency shifts from 983 cm⁻¹ in **1** to 912 cm⁻¹ in **3Ce** and **3Nd** and from 953 cm⁻¹ in **2** to 911 cm⁻¹ in **4Ce** and **4Nd**, respectively (Figures S10, S11, and S12), consistent with the weakening of the V-O bonding interaction upon Ln coordination. These values are consistent with extensive prior IR characterization of {V=O} units,²⁷ in the range of 900-1050 cm⁻¹.

Blue shifts are observed for the *d-d* transitions of 580nm and 593 nm in **3Nd** and 583nm and 595nm in **4Nd** when compared

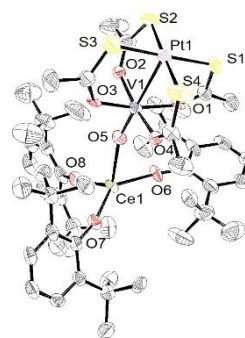


Figure 1. ORTEP of [Ce(DBP)₃{PtVO(SOCMe)₄}] (**3Ce**). Ellipsoids shown at the 50% level. Hydrogen atoms and solvent molecules excluded for clarity.

to the unbound **1** (607nm and 712nm) and **2** (628nm and 726nm), respectively (Figure S13, S14, and S15). In **3Ce** and **4Ce**, however, the broad *f-d* transitions between 400-600nm are strong enough to prevent the weak *d-d* transitions from being observed (Figures S16 and S17).

All six complexes have been characterized via single crystal X-ray diffraction. Important metrical data are collected in Table 1. As previously mentioned, **1** and **2** form dimers in the solid state that do not persist in solution. In the SOCMe-containing **3Ce** and **3Nd**, a slight increase in {V=O} bond distances accompanied by a decrease in {Pt-V} is observed while maintaining a largely linear Pt-VO angle. These changes are consistent with reduction in {V=O} π -bond character, and increased Lewis acidity at V that draws Pt closer. In SOCPH-containing **4Ce** and **4Nd**, there are two independent molecules in the asymmetric unit, denoted as **4Ce-a/b** and **4Nd-a/b**. When comparing **4Ce** and **4Nd** to unbound **2**, the same increase in {V=O} distance is observed but with a smaller decrease in the {Pt-V} bond length than in **3Ce** and **3Nd**.

Table 1: Selected bond distances (Å) and angles (°) of **1**, **2**, **3Ln**, and **4Ln**

	Pt-V (Å)	V-O (Å)	Pt-VO (°)	Ln-OV (Å)	Pt-VO (°)	Ln-OV (°)	O-V-Pt-S torsion (avg)
1	2.8635(6)	1.592(2)	179.7(1)	N/A	179.7(1)	N/A	15.19
2	2.782(1)	1.581(4)	179.8(1)	N/A	179.8(1)	N/A	20.65
3Ce	2.768(1)	1.630(3)	178.6(1)	2.455(4)	178.6(1)	163.7(2)	5.8
4Ce-a	2.7878(9)	1.682(3)	179.0(1)	2.525(3)	179.0(1)	174.4(2)	4.35
4Ce-b	2.7653(9)	1.616(3)	179.4(1)	2.531(3)	179.4(1)	175.8(2)	18.7
3Nd	2.762(1)	1.625(5)	176.7(2)	2.438(5)	176.7(2)	164.8(3)	15.4
5Nd-a	2.7604(6)	1.629(2)	179.37(9)	2.470(2)	179.37(9)	174.2(1)	19.3
5Nd-b	2.7861(6)	1.630(2)	178.99(9)	2.477(2)	178.99(9)	173.6(1)	15.6

The complexes were characterized using dc magnetometry. The Curie constants for a V(IV) ion ($0.375 \text{ emu K mol}^{-1}$) plus that of the Ln(III) ion ($\text{Ce}^{3+}=0.8 \text{ emu K mol}^{-1}$, $\text{Nd}^{3+}=1.64 \text{ emu K mol}^{-1}$) are $1.175 \text{ emu K mol}^{-1}$ and $2.015 \text{ emu K mol}^{-1}$, respectively (see dashed lines in Figure 2). The experimental curves reach values extremely close: 1.176 (**3Ce**), 1.176 (**4Ce**), 2.019 (**3Nd**), 2.000 (**4Nd**), confirming the retained oxidation states of V(IV) and Ln(III) in these air sensitive samples. These data also indicate a relatively small crystal field splitting at Ln, as expected for $4f$ complexes with low symmetry, pseudo-tetrahedral structures. Each complex shows a sharp decrease in χT at low T , and when compared to the M vs H curves (Figure S18), indicate either crystal field splitting and/or possible weak antiferromagnetic interactions of the Ln(III) and V(IV) ions. Compound **4Ce** shows the lowest decrease in χT at low temperatures and has the most well-isolated ground state (see the M vs H/T curves in Figure S19). Interestingly, **3Nd** and **4Ln** reach a very similar χT value at the lowest temperature ($0.8\text{--}0.9 \text{ emu K mol}^{-1}$), while compound **3Ce** drops to $0.45 \text{ emu K mol}^{-1}$. This suggests that either the CF around the Ln stabilizes the same ground state in **3Nd** and **4Ln**, but a different one in **3Ce** or, more likely, the antiferromagnetic interactions in **3Ce** are significantly higher than in the other two compounds. The better coupling in **3Ce** which has the smaller SAc containing lantern paired with the larger ionic radii of Ce(III), confirms the previously discussed importance of ligand size and geometry. To promote better coupling, the steric bulk

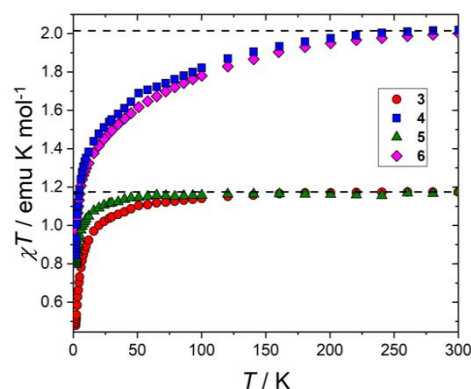


Figure 2. Product of the magnetic susceptibility times the temperature vs. the temperature for **3Ln** and **4Ln**. The black dashed lines are the expected Curie constants for independent V(IV) and Ln(III) ions.

of the lantern or aryloxides would need to be decreased to allow for closer {VO} contact to the Ln. Unfortunately, the measured data are not suitable for a quantitative evaluation due to an over parametrization and correlation problem, impossible to overcome without *ab initio* calculations or a large span of spectroscopic techniques.²⁸ Indeed, for these systems a reasonable fit must include too many parameters (the CF parameters of the Ln, the Ln-V coupling, the g value of V...), that are also difficult to disentangle using only magnetic data.

The metrical parameters of greatest interest are the Ln-O distances and Ln-O-V angles. Depending on the shape of the Ln ion (oblate or prolate), certain ligand environments can stabilize the electron distribution and therefore promote the desired coupling.¹⁰ In the cases of Ce(III) and Nd(III) which are both oblate, strong axial ligand donation is most effective for the stabilization of a high projection of the total angular momentum. In all cases the axial-like Ln-O_{lantern} distances of **3Ln** and **4Ln** are the longest ($2.44\text{--}2.53 \text{ Å}$) while the equatorial-like Ln-O_{ODtbp} lengths are shortest ($2.14\text{--}2.22 \text{ Å}$). These data suggest that the CF around the Ln in these complexes does not effectively stabilize the highest projection of the total angular momentum, thus hinting towards poor slow relaxation behaviour.

The dynamic magnetic behaviour of **3Ln** and **4Ln** have been tested using AC susceptibility measurements. When an external DC field is applied to quench tunnelling and any other relaxation pathways that could lower the anisotropy barrier, all four complexes presented a frequency dependent AC signal with the SOCPH derivatives **4Ce** and **4Nd** being more intense (see Figure 3) than the SOCMe derivatives (Figure S20). This suggests a significantly different ligand field for the two employed lanterns. The longest relaxation time is observed in **3Nd**, with a value of ca. 0.16 ms at $T = 2 \text{ K}$ and $H = 5000 \text{ Oe}$. However, in all cases, the full peak is outside the range of experimental frequencies at the lowest possible temperature (2 K) preventing further investigation.

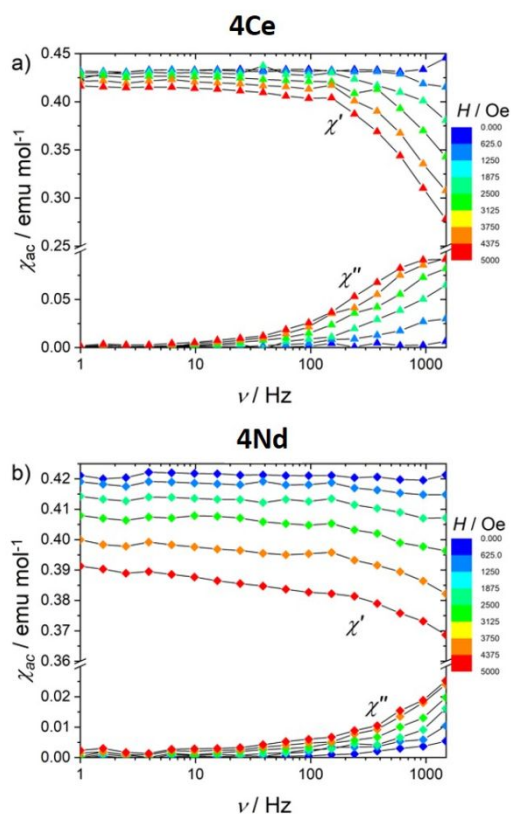


Figure 3. AC magnetic susceptibility of a) **4Ce** and b) **4Nd** obtained at $T = 2$ K and different applied DC fields.

In summary, two new $S = \frac{1}{2}$ [PtVO(SOCR)₄] lantern complexes, **1** (R = Me) and **2** (R = Ph), have been synthesized and magnetically characterized, confirming $S = \frac{1}{2}$ ground states. The monomeric lanterns act as ligands for low coordinate Ln(ODtbp)₃ in new four-coordinate heterotrimetallic {LnOVpt} compounds: [Ln(ODtbp)₃{PtVO(SOCR)₄}] (Ln=Ce, **3Ce** (R=CH₃), **4Ce** (R=Ph); Nd, **3Nd** (R=CH₃), **4Nd** (R=Ph). AC susceptibility measurements show weak slow magnetic relaxation behaviour in **3Ln** and **4Ln**, with each ligand type (SOCMe vs SOCPH) leading to significantly different ligand fields about the Ln, with the slowest relaxation time observed in **3Nd**. Variable-temperature susceptibility measurements indicated antiferromagnetic coupling to be strongest in **3Ce**, which contains the less bulky SAc lantern and larger Ce(III) ionic radii, suggesting that a move to generally less bulky ligands should promote even greater antiferromagnetic coupling in future {Ce-OV} complexes for potential quantum information science systems despite the weaker slow relaxation behaviour.

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Conflicts of interest

There are no conflicts to declare

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

§

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New $\text{PtVO}(\text{SOCR})_4$ lantern complexes combined with $\text{Ce}(\text{OR})_3$ and $\text{Nd}(\text{OR})_3$ form heterotrimetallic $\text{Ln}(\text{ODtbp})_3\{\text{PtVO}(\text{SOCR})_4\}$ with linear Ln-OVpt linkages which exhibit slow magnetic relaxation behavior and likely antiferromagnetic coupling across $\{\text{Ln-O-V}\}$ in all four complexes.

