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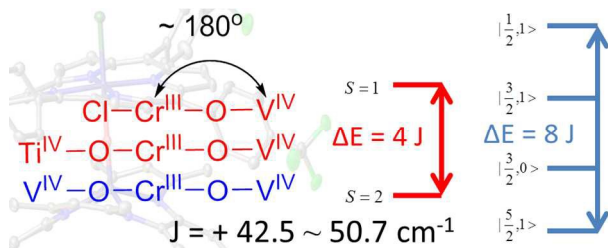


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Linear heterobimetallic oxido-bridged d^1-d^3 compounds are described which are proposed as models for magnetic coupling of MMCT excited states.



Journal Name

ARTICLE

Ferromagnetic Coupling in d^1-d^3 Linear Oxido-Bridged Heterometallic Complexes: Ground-State Models of Metal-to-Metal Charge Transfer Excited States

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Convenient strategies have been developed to synthesize heterobi/trimetallic oxido complexes containing V(IV)–O–Cr(III), V(IV)–O–Cr(III)–O–Ti(IV) and V(IV)–O–Cr(III)–O–V(IV) cores. These compounds can serve as ground state models for probing the magnetic properties of metal-to-metal charge transfer excited states. Each of these complexes represents the first experimental demonstration of ferromagnetic coupling in a d^1-d^3 oxido bridged compound, which confirms a long standing theoretical prediction for such a linkage. Structural characterization reveals a similar structure for each of the bi/trimetallic complexes with identical V=O bond lengths (~1.644 Å) and a linear V–O–Cr geometry. The Cr–O distances (1.943 ~ 1.964 Å) are significantly influenced by the ligands in the *trans* axial positions. Ferromagnetic coupling between the V(IV) and Cr(III) of V–O–Cr is measured by temperature-dependent magnetic susceptibility, showing $J = +42.5$ to $+50.7$ cm^{-1} ($H = -2J\hat{S}_V \cdot \hat{S}_{Cr}$). This is further supported by variable temperature X-band EPR. The values of J are found to be consistent with the function $J = Ae^{Br}$ ($A = 9.221 \times 10^8$ and $\beta = 8.607 \text{ \AA}^{-1}$), where r is the Cr–O bond distance. We propose a model that links either ferromagnetic or antiferromagnetic exchange coupling with long excited state lifetimes in metal-to-metal charge transfer (MMCT) chromophores.

Introduction

Molecules with heterometallic cores demonstrate physical and chemical properties that are not observed in their monometallic analogs.¹⁻⁸ Cooperative effects between two covalently linked metal sites have been extensively explored in cocatalysts,^{9, 10} single molecule magnets^{11, 12} and the solid state.^{13, 14} The unsupported oxido bridged motif^{6, 15, 16} is one of the simplest frameworks among heterometallic complexes and is known to serve as a structural and functional model for many metalloenzymes and cocatalytic reactions.^{9, 12, 17} Despite their seemingly simple structure, unsupported oxido bridge complexes remain synthetically challenging targets,^{3, 17} with a limited number of structurally characterized examples.^{2, 6, 15, 16,}

18-23

Measurement of exchange coupling within oxido-bridged heterobi- and trimetallic complexes is important for fully understanding the magnetic, optical and redox properties of both the ground and excited states.¹³ Among structurally characterized examples, only four include magnetic studies and all possess antiferromagnetic coupling between the metal sites with J values varying from -18.7 to -150 cm^{-1} .^{1, 4, 16, 24} Ferromagnetic exchange coupling is another possible pathway for magnetic coupling in other heterometallic complexes.²⁵⁻²⁷ Empirical, semi-empirical and theoretical calculations have been performed on unsupported oxido bridged heterobimetallic species, and suggest that moderate ferromagnetic interactions should exist in linear d^1-d^3 complexes.²⁸⁻³⁰ To our knowledge no experimental data confirming this hypothesis has been reported. Here, we describe three examples of unsupported oxido heterobi- and trimetallic complexes that are ferromagnetically coupled, allowing experimental determination of the properties in such a system for the first time. In addition, we propose that such molecules can serve as ground-state models for probing

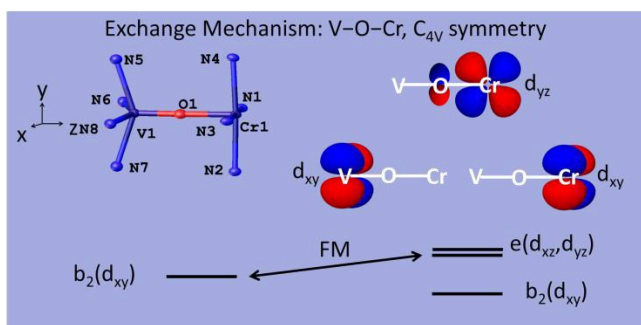
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magnetic and other properties of metal-to-metal charge transfer excited states.

We previously reported the synthesis of heterobi- and trimetallic complexes containing linear Cr(III)–O–Ti(IV) cores.⁵ The d^1 (omtaa)V=O complex (Scheme 2, omtaa: 7,16-dihydro-6,8,11,12,15,17,20,21-octamethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine) is a structural analogue of d^0 (tmtaa)Ti=O that has similar reactivity.^{19, 23} The V(IV) center introduces an additional unpaired electron into the resulting heterometallic systems. The magnetic orbital of this unpaired spin is strictly orthogonal to the occupied orbitals on Cr(III), as suggested by Kahn (Scheme 1).²⁵ Such an orientation of orbitals is known to result in ferromagnetic coupling of paramagnetic metal centers and is discussed in depth elsewhere.^{25–27} The singly occupied d_{xy} orbitals of V(IV) and Cr(III) do not directly interact due to the absence of a symmetrically available orbital in the oxido bridge.³¹

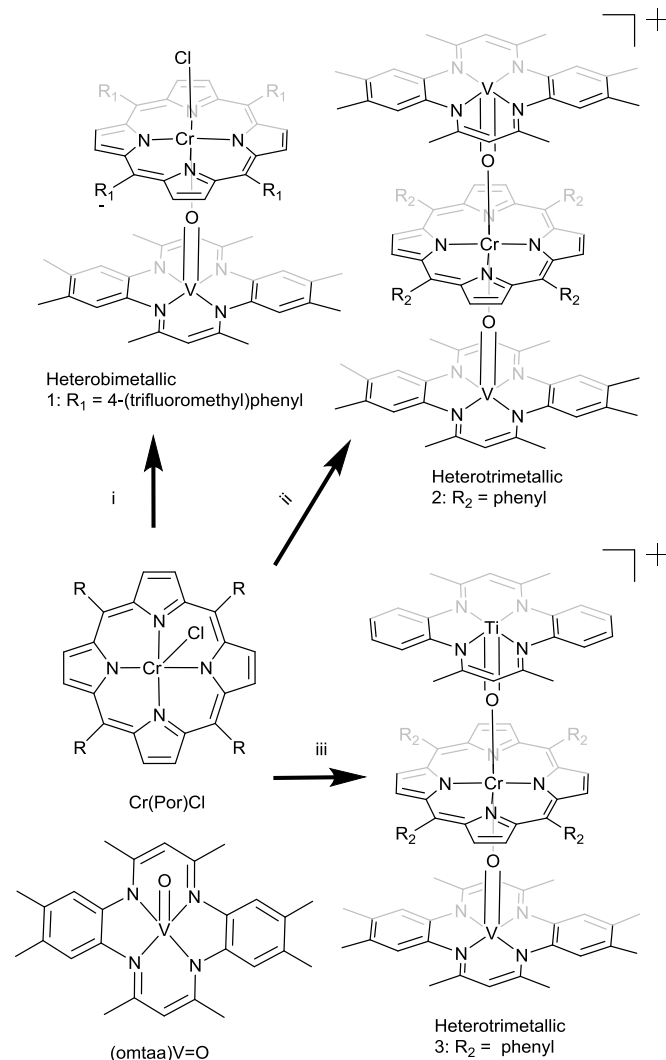


Scheme 1 Simplified molecular geometry of $V^{IV}-O-Cr^{III}$ in C_{4v} symmetry. The d^1 vanadium(IV) $b_2(d_{xy})$ and d^3 chromium(III) $e(d_{xz}, d_{yz})$ orbitals involved in magnetic coupling for linear $V^{IV}-O-Cr^{III}$ are orthogonal (only one Cr magnetic orbital is shown for clarity), which results in a dominant ferromagnetic (FM) exchange interaction through a π -superexchange pathway.^{25, 31}

Result and discussion

Synthesis of bimetallic $V=O \rightarrow Cr$ and trimetallic $[V=O \rightarrow Cr \leftarrow O=V]^+$ are achieved in similar reactions to those previously described,⁵ with careful control of vanadium and chromium stoichiometry (Scheme 2). When Cr(Por)Cl and (omtaa)V=O are combined in a 1:2 ratio, the trimetallic species **2** is isolated with a yield of 62%. In order to synthesize bimetallic $V=O \rightarrow Cr$, the electron withdrawing Cr(TFMP)Cl (TFMP: tetrakis((4-trifluoromethyl)phenyl)porphyrin) was utilized. Mixing this more reactive precursor with (omtaa)V=O in a 1:1 ratio allows bimetallic **1** to be separated with a yield of 22%. As proposed in our earlier study,⁵ the titanium containing bimetallic (tmtaa)Ti=O \rightarrow Cr(Por)Cl can undergo a further exchange reaction to replace its axial chlorido ligand. Thus, the unsymmetrical trimetallic $[Ti=O \rightarrow Cr \leftarrow O=V]^+$ complex **3** can be prepared in 39% yield via a sequential one-pot reaction where one equivalent of (omtaa)V=O is added to $Ti=O \rightarrow Cr$ prepared

in situ. Attempts to synthesize **3** via a one-step, one-pot synthesis using a 1:1:1 ratio of (omtaa)V=O, (tmtaa)Ti=O and Cr(Por)Cl were not successful, yielding a mixture of symmetric trimetallic species.



Scheme 2 Synthesis of $V=O \rightarrow Cr$ bimetallic complex **1** and $[V=O \rightarrow Cr \leftarrow O=M]^+$ trimetallic complexes **2** ($M = V$) and **3** ($M = Ti$). (i) 1:1 ratio of (omtaa)V=O and Cr(Por)Cl in acetonitrile:toluene (1:1); (ii) 1:2:1.1 ratio of (omtaa)V=O, Cr(Por)Cl and NaSbF₆ in acetonitrile:toluene (1:1) (iii) a sequential one pot reaction: a) 1:1 ratio of (tmtaa)Ti=O and Cr(Por)Cl in acetonitrile:toluene (1:1) followed by b) an additional 1:1.1 equivalents of (omtaa)V=O and NaSbF₆.

Crystals suitable for XRD study of **1-3** were obtained by slow vapor diffusion of pentane into a dichloromethane solution. Representative molecular structures of the bi/trimetallic species are shown in Fig. 1. Selected structural parameters and XRD experimental details are listed in Table 1 and Table S1. As can be seen in Fig. 1, the crystal structure of **1** indicates that the Cr(III) porphyrin and (omtaa)V=O are connected by a

Table 1 Selected bond lengths and angles for **1-3**.

Summary	(omtaa)V=O	1	2	3
V–O distance (Å)	1.6120(8)	1.640(2)	1.649(4)	1.644(4)
Cr–N avg. distance (Å)	n/a	2.025(3)	2.026(5)	2.023(4)
V–N avg. distance (Å)	2.0280(9)	1.996(3)	1.997(5)	2.003(5)
Cr–O distance (Å)	n/a	1.964(2)	1.943(4)	1.954(4) ^a 1.929(4) ^b
V–O–Cr angle (°)	n/a	179.10(15)	177.5(3)	177.3(2)
O–V–N avg. angle (°)	108.82(4)	108.18(11)	107.94(2)	107.96(19)
O–Cr–N avg. angle (°)	n/a	88.47(10)	89.98(18)	90.00(16)

^a, Cr–O–V linkage; ^b, Cr–O–Ti linkage

V=O→Cr interaction. The omtaa ligand undergoes a complete saddle inversion when compared to the structure of vanadium monomer (Fig. S5) and the V–O–Cr bond angle is nearly linear with an angle of 179.10(15)°.

These structural details are consistent with previous oxido-bridged bimetallic structures supported by tmtaa and porphyrin ligands.^{2, 5} When comparing bimetallic **1** with (omtaa)V=O, the V=O bond length increases by about 0.03 Å (1.612 Å to 1.640 Å) and the V–N length is shortened by about 0.03 Å (2.028 Å to 1.996 Å). A Cr–O distance of 1.964 Å is observed, which is shorter than that of some weakly bonded O-donor Lewis bases³² but significantly longer than other unsupported oxido bridged complexes.^{2, 5, 15} This explains our observation that bimetallic **1** can dissociate in solution. The Cr–Cl length of 2.3405 Å in **1** is longer than that in Cr(TPP)Cl•H₂O (2.242 Å)³³ but shorter than that in bimetallic Ti=O→Cr–Cl (2.3577 Å).⁵

We conclude that the bond strength of the oxido linkage in Cr(III) porphyrins falls in the order of (tmtaa)Ti=O > (omtaa)V=O > H₂O, with Cr–O distances of 1.941 Å,⁵ 1.964 Å, and 2.239 Å³³ respectively. Such axial structural trans influences have been reviewed in detail elsewhere.³⁴ The molecular structure of trimetallic **2** is depicted in Fig. S3 where two (omtaa)V=O groups connect to a slightly deformed Cr(III) porphyrin in a staggered geometry. A similar geometry is observed for the unsymmetric trimetallic [Ti=O→Cr←O=V]⁺ **3** (Fig. 2), where (tmtaa)Ti=O and (omtaa)V=O are axially connected to the Cr(III) porphyrin. The Cr–O bond is shorter in the Cr–O–Ti linkage (1.929 Å) than that in the Cr–O–V linkage (1.954(4) Å). Due to the different bonding strengths of the *trans* ligands, the bond length of Cr–O in heterometallic **1-3** is: **2** (1.943 Å) < **3** (1.954 Å) < **1** (1.964 Å).

The temperature dependence of the magnetic susceptibility (χ_{mol}) of compounds **1-3** were measured in the temperature range 2–300 K under a constant magnetic field of 0.7 T.

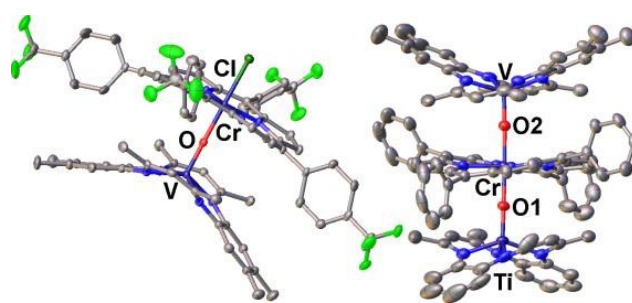


Fig. 1 X-ray crystal structures of **1** and **3**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, counter ions and solvent molecules are omitted for clarity.

In Fig. 2A, the value of χ_{paraT} for **1-3** is shown as a function of temperature *T*. For **1-3**, χ_{paraT} increases monotonically from 300 K to a maximum value at ~ 40 K. This is typical for ferromagnetically coupled systems. For comparison, the maximum values of χ_{paraT} are consistent with the magnetic susceptibility calculated from spin only moments (non-interacting spins for $g = 2.00$) of 2.98 emu*K/mol ($S = 2$) and 4.37 emu*K/mol ($S = 2.5$) for **1-3**, respectively. The value of χ_{paraT} then decreases as the temperature drops to 2.00 K, which can be attributed to weak intermolecular interactions and zero-field-splitting. The field-dependent magnetic behavior data measured at 2 K (Fig. 2B) shows that the ground state is $S = 2$ for **1** and **3**, while $S = 5/2$ for **2**. In order to investigate the exchange coupling between Cr(III) and V(IV), we applied a simple isotropic spin Hamiltonian (equation 1), to fit the data. The final expression³⁵ (equation 2) is derived from the Van Vleck²⁵ equation where N is Avogadro's number, k_B is the Boltzmann constant, T is the temperature, β is the Bohr magneton, g is the electron g -factor, θ is the Weiss constant, and J corresponds to the net magnetic interaction between chromium and vanadium. Effects of zero-field-splitting, spin-orbital coupling, intermolecular interactions and experimental error are reflected in the small differences of the fit value for g .

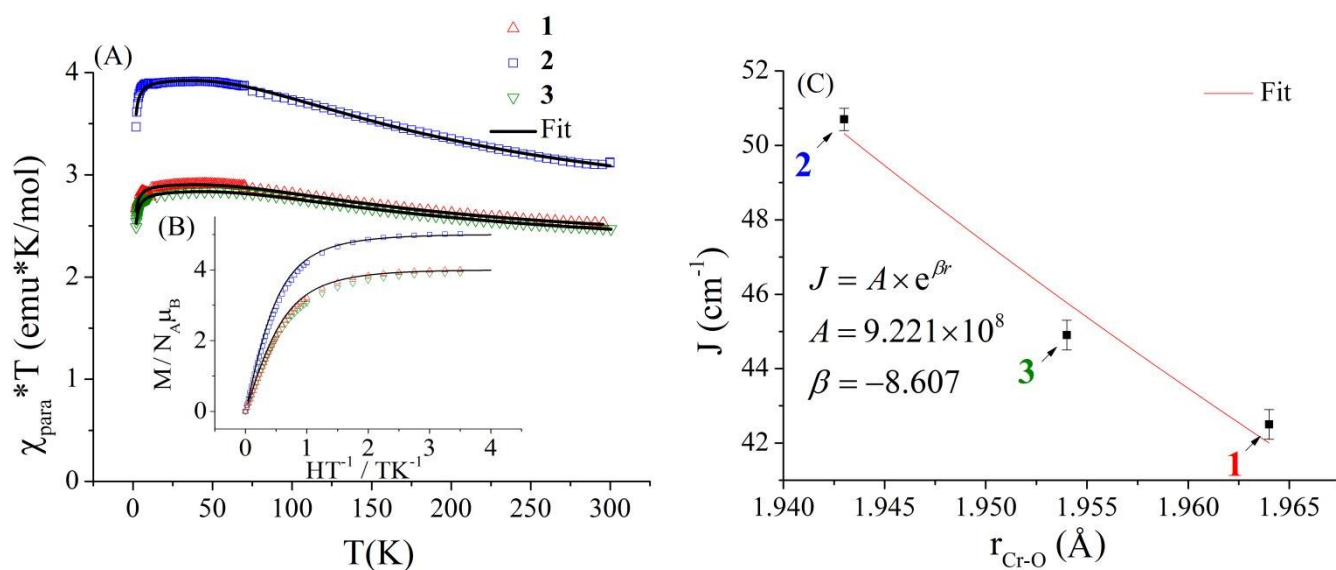


Fig. 2 (A), Molar magnetic susceptibility (χ_{para}) plotted as $\chi_{\text{para}} * T$ vs. T for 1-3. Black lines represent the fit. (B) Variable field dependence of 1-3 at 2 K. (C), Exchange coupling J versus Cr-O bond distance for 1-3.

$$\hat{H}_{\text{VCr}} = -2J\hat{S}_V\hat{S}_{\text{Cr}}, \hat{S}_V = \frac{1}{2}, \hat{S}_{\text{Cr}} = \frac{3}{2} \quad (1)$$

$$\chi T = \frac{Ng^2\beta^2T}{3k_B(T-\theta)} \frac{(6+30e^{\frac{4J}{k_B T}})}{(3+5e^{\frac{4J}{k_B T}})} \quad (2)$$

$$\hat{H}_{\text{VCrV'}} = -2J(\hat{S}_V\hat{S}_{\text{Cr}} + \hat{S}_{V'}\hat{S}_{\text{Cr}}), \hat{S}_V = \hat{S}_{V'} = \frac{1}{2}, \hat{S}_{\text{Cr}} = \frac{3}{2} \quad (3)$$

$$\chi T = \frac{Ng^2\beta^2T}{2k_B(T-\theta)} \frac{1+10e^{\frac{3J}{2k_B T}} + 10e^{\frac{5J}{2k_B T}} + 35e^{\frac{4J}{k_B T}}}{2+4e^{\frac{3J}{2k_B T}} + 4e^{\frac{5J}{2k_B T}} + 6e^{\frac{4J}{k_B T}}} \quad (4)$$

$$J = A \times e^{\beta r} \quad (5)$$

Using this equation for **1**, the values $J = +42.5 \text{ cm}^{-1}$, $\theta = -0.21 \text{ K}$, $g = 1.97$ with $R^2 = 0.9892$ were computed. A similar result was obtained for trimetallic $[\text{Ti}=\text{O} \rightarrow \text{Cr} \leftarrow \text{O}=\text{V}]^+$ **3**, where $J = +44.9 \text{ cm}^{-1}$, $\theta = -0.26 \text{ K}$, $g = 1.95$ and $R^2 = 0.9947$. Trimetallic $[\text{V}=\text{O} \rightarrow \text{Cr} \leftarrow \text{O}=\text{V}]^+$ **2** was studied by a similar approach, but the presence of the second vanadium (IV) necessitated the use of a different isotropic symmetric spin Hamiltonian (equation 3). We omitted any contribution from a d^1 - d^1 intramolecular interaction when computing our results since the distance between the vanadium centers in **2** is quite long (7.2 Å). A simplified expression (equation 4), derived from previous reports,³⁶ was applied to fit the experimental data. Using this equation for **2**, $J = +50.7 \text{ cm}^{-1}$, $\theta = -0.20 \text{ K}$, $g = 1.90$ and $R^2 = 0.9950$ is calculated. These values for J in **1-3** are in good

agreement with both the sign and magnitude of J in previous computational reports for such a d^1 - d^3 linkage.^{29, 30}

Table 2 Molar absorptivity of 1-3 in dichloromethane at 298 K and solid state ATR-FT-IR.

	UV, λ_{max} , nm (log ϵ)	$\nu_{\text{V=O}}$ cm ⁻¹
[a]	316(4.10), 377(4.44), 420 (3.90)	972
1	321(4.58), 377(4.73), 393(4.69), 446(5.20), 519(3.60), 562(3.97), 599(3.84)	933
2	329(4.67), 386(4.74), 408(4.82), 464(4.53), 535(3.75), 576(3.85), 613(3.92), 636(3.80)	912
3	344(4.76), 399(4.82), 423(4.59), 455(4.71), 526(3.76), 574(3.89), 615(3.96), 635(3.86)	928
[a] (omtaa) $\nu=0$		

The distance dependence of the observed exchange coupling was fit to equation 5, with r being the Cr-O distance.³⁷ It has been reported that J is correlated with the longer metal oxide bond length in asymmetric μ -oxido complexes.³⁸ We therefore only considered the distance dependence caused by changes in the Cr-O bond. The value of $A = 9.221 \times 10^8$ and $\beta = -8.607 \text{ \AA}^{-1}$ is obtained by fitting the experimental data to equation 5 (Fig. 2C). A linear fit is provided in the SI for comparison (Fig. S9). We find that our result is consistent with the similar empirical exponential expression computed by Weihe and Güdel for oxido bridged binuclear systems. Using the metric parameters for **1-3**, their model predicts that $A = 2.739 \times 10^8$ and $\beta = -7.909 \text{ \AA}^{-1}$.³⁹ The close match between our experimental result and the

theoretical prediction lends support to both our experimental interpretation and their computational model. However, due to the small variations in Cr–O bond length, this is only an initial treatment for experimentally understanding magnetic coupling in such complexes. Additional compounds that have significantly different bond lengths and/or angles will be necessary to fully model such geometric control of exchange coupling. Since the main structural differences between compounds **1–3** are in the axial ligands, we conclude that the axial ligands influence exchange coupling directly by influencing the strength of the Cr–O bond. This conclusion is consistent with the observed differences in $\nu_{\text{V=O}}$ across this series, where the largest red-shift from the mononuclear (omtaa)V=O ($\nu_{\text{V=O}} = 972 \text{ cm}^{-1}$), and therefore the strongest Cr–O bond, is found for **2** ($\nu_{\text{V=O}} = 912 \text{ cm}^{-1}$, $\Delta = 60 \text{ cm}^{-1}$). The smallest shift is found for **1** ($\nu_{\text{V=O}} = 933 \text{ cm}^{-1}$, $\Delta = 39 \text{ cm}^{-1}$), which has the longest Cr–O bond as determined by crystallography (See Table 2)

Ferromagnetic coupling in the ground state of **2** ($S = 5/2$) is further confirmed by variable temperature EPR (Fig. 3). As seen in Fig. 3, signals observed at 298 K at $g = 15.7$ and $g = 3.60$ disappear when the sample is cooled to 77 K. This is attributed to the differences in Boltzmann populations of the magnetic states, which we calculate utilizing spin ladder energies obtained using the J value determined by magnetometry. The ground state $E(5/2, 1)$ is populated at 69.6% at 298 K, but rises to 96.7% at 77 K. The signals at $g = 15.7$ and 3.60 are assigned to the EPR response from the nearest excited spin state $E(3/2, 0)$ is calculated to be 16.8% populated at 298 K and 2.9% at 77 K. Simulation of these states was performed using the Easyspin package,⁴⁰ resulting in $g = 1.97$, $|D| = 0.047 \text{ cm}^{-1}$, $|E| = 0.015 \text{ cm}^{-1}$ for $E(5/2, 1)$ and $g = 1.96$, $|D| = 0.191 \text{ cm}^{-1}$, $|E| = 0.010 \text{ cm}^{-1}$ for the $E(3/2, 0)$ state.

This work confirms the long standing prediction of ferromagnetic exchange coupling in linear oxido-bridged d^1-d^3 systems.^{28–30} This V(IV)–O–Cr(III) d^1-d^3 oxido bridged system provides the first examples of a ground state analogue for the d^1-d^3 excited state that results from MMCT of a d^0-d^4 species such as Ti(IV)–O–Mn(III) (Scheme 3).⁴¹ We propose that measuring properties such as exchange coupling in these models can provide guidance when designing species with long-lived MMCT transitions.

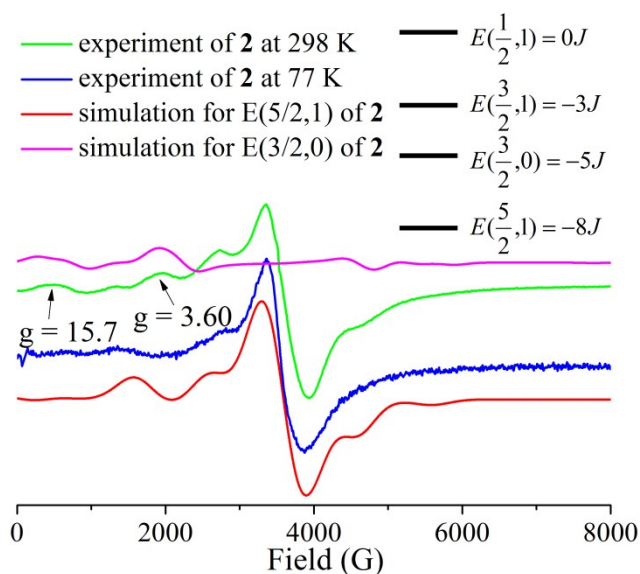
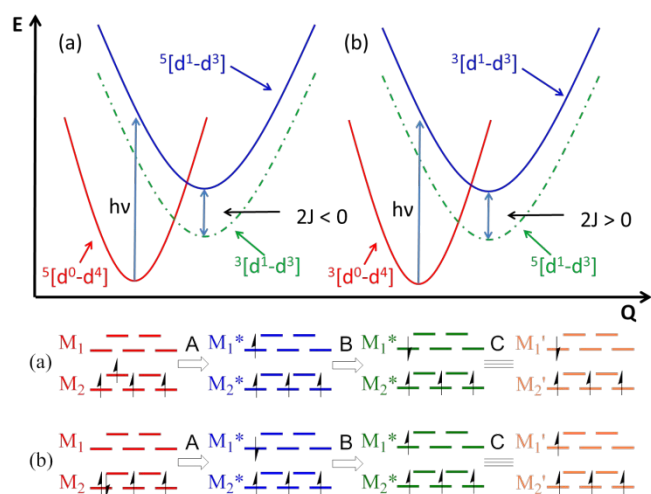


Fig. 3 Experimental CW EPR spectra of **2** at 77 K (blue) and 298 K (green). Simulated spectra are also depicted for the $E(5/2, 1)$ ground (red) and $E(3/2, 0)$ first excited (magenta) magnetic states. $E(S_1, S_2)$ is denoted as $S_1 = S_V + S_{Cr} + S_V$, $S_2 = S_V + S_V$

Processes for light induced MMCT are depicted in Scheme 3. In case A, the ground state has the quintet $^5[d^0-d^4_{\text{hs}}]$ with a high spin d^4 metal site (Scheme 3a). Other systems containing MMCT transitions, such as Cr(III)–O–Ti(IV) (d^0-d^3),⁴² Mn(II)–O–Ti(IV) (d^0-d^5),⁴³ can be modeled in a similar manner. In this simplified model, the initial ground state $^5[d^0-d^4_{\text{hs}}]$ can be excited into the corresponding $^5[d^1-d^3]$ MMCT excited state. Depending on the sign of the exchange coupling between the d^1 and d^3 metal centers in this state, the initially populated $^5[d^1-d^3]$ can intersystem cross to form a $^3[d^1-d^3]$ state of relatively lower energy. If the d^1 and d^3 sites are antiferromagnetically coupled in the excited state ($2J < 0$), the triplet $^3[d^1-d^3]$ will be lower energy than the quintet $^5[d^1-d^3]$ (Scheme 3a). As suggested by McClure and Frei, this subsequently populated spin state would create a spin forbidden barrier for back electron transfer, slowing the rate for repopulation of the ground state.¹³ Known examples of such long-lived chromophores, analogous to organic and inorganic triplet excited states, have been reported.⁴⁴ It has been shown theoretically³⁰ and experimentally⁴⁵ that antiferromagnetic coupling values increase as the angle of the M–O–M' linkages decrease. Based on their determination of a significantly bent $\text{Ti}^{\text{IV}}\text{–O–Mn}^{\text{II}}$ structure ($\sim 110^\circ$) in surface bound MMCT chromophores,^{13, 46} we propose that such excited states should exhibit antiferromagnetic coupling between the photo excited $\text{Ti}^{\text{III}}\text{–}d^1$ and $\text{Mn}^{\text{III}}\text{–}d^4$ metal centers. This geometrically enforced antiferromagnetic coupling is the origin of a low lying $^4[d^1-d^4]$ state, which ultimately slows BET to regenerate the $^6[d^0-d^5]$ ground state in such chromophores.



Scheme 3 A) Formation of a d^1-d^3 MMCT excited state from a d^0-d^4 heterobimetallic chromophore; B) Intersystem crossing to energetically lower state C) Exchange coupling of this excited state can be determined by d^1-d^3 heterobimetallic molecules ground state analogues. In all systems, ground states are shown in red, initial excited states are shown in blue and spin-trapped states are green. Ground state analogues of the spin-trapped states are shown in orange.

A similar spin forbidden BET barrier can be imagined for systems with ferromagnetic coupling, such as the linear systems reported here. As shown in Scheme 3b, such a complex would require a ground state $^3[d^0-d^4_{is}]$ with a low spin d^4 metal site, such as low spin Mn^{III} .⁴⁷ This initial ground state $^3[d^0-d(is)^4]$ can be excited to form its corresponding $^3[d^1-d^3]$ excited state. In this case, ferromagnetic coupling would be present between the excited state d^1 and d^3 centers ($2J > 0$). Therefore, the quintet $^5[d^1-d^3]$ state will be lower in energy when compared with a triplet $^3[d^1-d^3]$ state. It is known that spin multiplicity can be altered in the excited state, with MMCT inducing magnetization changes in solid-state cyano-bridged assemblies.⁴⁸⁻⁵⁰ This new model suggests that such linear heterobimetallic complexes, with low-spin donor metal sites, can also be synthetic targets for realizing chromophores with long-lived MMCT transitions.

Experimental measurements of exchange coupling in MMCT excited states are known to be complicated.^{51, 52} As demonstrated here, measuring exchange coupling in ground state analogues of these excited states is much more straightforward. We speculate that the sign and magnitude of excited state exchange coupling may play important role on the BET rate of MMCT excited states. The sign and magnitude of exchange coupling in charge transfer excited states is known to influence BET in organic chromophores,⁵³⁻⁵⁸ with ground state analogues able to predict such effects.⁵⁹ Recently, our group reported the synthesis of d^1-d^x ($x = 5-9$) unsupported oxido bridged complexes with various M_1-O-M_2 angles

($156^\circ \sim 170^\circ$) and M-O distances ($1.94 \sim 2.09 \text{ \AA}$)²³ which could also serve as ground state analogues of additional MMCT excited states.

The connection between the sign and magnitude of J and MMCT lifetimes in such heterobimetallic compounds remains speculative, however the compounds reported here represent an important step toward providing the quantitative measurements necessary to experimentally and theoretically model the influence of excited state magnetic coupling on the lifetimes of MMCT-based chromophores.

Conclusion

In summary, we have developed approaches to synthesize the first examples of V(IV)-O-Cr(III), V(IV)-O-Cr(III)-O-Ti(IV) and V(IV)-O-Cr(III)-O-V(IV) species. Ferromagnetic exchange coupling is observed between the metal centers in these d^1-d^3 (**1**), $d^1-d^3-d^0$ (**3**) and $d^1-d^3-d^1$ (**2**) systems. The magnitude of this interaction is found to be influenced by the *trans* axial ligand and is consistent with an empirical distance dependent equation: $J = Ae^{\beta r}$, where $A = 9.221 \times 10^8$ and $\beta = -8.607 \text{ \AA}^{-1}$. To our knowledge, this is the first direct experimental evidence of ferromagnetic exchange in an unsupported oxido bridged heterometallic species and confirms that an empirical relationship which depends on angular and distance dependence can be applied to predict exchange coupling between two different paramagnetic centers. Such data is of particular importance for understanding magnetic control of MMCT excited state lifetimes in oxido-bridged heterobimetallic chromophores in both homogeneous and heterogeneous systems.

Experimental section

General Procedures.

All reactions were performed under an atmosphere of nitrogen in an Innovative Technology glovebox or using Schlenk techniques. All chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar or TCI America and used without further purification. All solvents were stored over 4 \AA molecular sieves prior to use. Dichloromethane and pentane were sparged with N_2 and dried over an alumina column using the method of Grubbs.⁶⁰ Toluene was dried over purple sodium benzophenone ketyl, then vacuum transferred and freeze-pump-thawed before storing in Teflon-sealed Schlenk bombs. Acetonitrile was dried over CaH_2 and distilled prior to use. Absorption spectra were recorded on an Olis RSM-1000 spectrometer using 1 cm Teflon-sealed quartz cuvettes. Attenuated total reflectance (ATR)mFTIR spectra were recorded with either a Bruker Vertex 80V infrared spectrometer equipped with a Platinum™ Diamond ATR attachment or a Bruker Alpha ATR-FTIR. Magnetic

susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID Magnetometer. A saturation plot was measured at 2 K with the applied field being varied from 0~70000 oe. Temperature-dependent magnetic susceptibilities were performed from 2-300 K. Crystalline samples (ca. 10-30 mg) were loaded into gelcap/straw sample holders and mounted to the sample rod with Kapton tape for temperature dependence measurements. For compound **1-3**, multiple measurements were performed. The fitting results (such as g-factor, θ and J) from these separate data sets are consistent. The reported error bars for J are based on several separate fitting results from different data sets. Electron paramagnetic resonance spectra were taken with samples at either at room temperature or at 77 K in a Bruker ELEXSYS E500 spectrometer operating at approximately 9.86 GHz (X-band) with a modulation amplitude of 10 G and a modulation frequency of 100 kHz. The experimental time constant was set at 81.92 ms with a 117.19 ms conversion time and a 120 s sweep time. A typical collection of 1024 data points is performed under 2 mW incident microwave power in a range from 0 to 8000 G. Recrystallized polycrystalline solid samples (1 ~ 2 mg) were loaded in Wilmad quartz (CFQ) EPR tubes (O.D. 4 mm, L 100 mm) and sealed under N₂.

The ligands studied in this report are represented by the following abbreviations: TPP, tetraphenylporphyrin; TFMP, tetrakis((4-trifluoromethyl)phenyl)porphyrin; tmtaa: 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine, omtaa: 7,16-dihydro-6,8,11,12,15,17,20,21-octamethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine. The ligands are synthesized according to the reports of Weare and coworkers⁵ and Goedken and coworkers.¹⁹ Cr(III) porphyrin,⁵ (tmtaa)Ti=O and (omtaa)V=O¹⁹ are synthesized as previously reported.

X-Ray crystallography

Crystals were mounted on MiTeGen mounts and cooled to 110 K. X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å). Unit cell dimensions were determined from symmetry constrained fits of the reflections. Frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved using direct methods (Bruker XS) and refined using the Bruker SHELX 2013⁶¹ software package using full-matrix least-squares refinement on F. All non-hydrogen atoms were identified in the original solution, or located from the difference map from refinement results. Hydrogen atoms were placed at idealized positions and allowed to ride on the nearest non-H atom. Figures of the molecular structures were created using Olex2 Crystallographic information files for all

structures are available in the ESI[†] and from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk). CCDC reference number: **1** (1049246), **2** (1049245), **3** (1049247), (omtaa)V=O (1049244).

Synthesis of (omtaa)V=O→Cr(R)Cl binuclear complexes,

(omtaa)V=O→Cr(TFMP)Cl, (1). The synthesis is adopted from a previous publication.² In the glovebox, (omtaa)V=O (50.0 mg, 0.11 mmol) and Cr(TFMP)Cl (104.4 mg 0.11 mmol) were added to 5 mL of a 1:1 acetonitrile:toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. The solution was then cooled slowly to room temperature and was filtered to remove side products. A fine green powder was obtained from the filtrate after removal of the solvent in vacuo. The final product, which is of X-ray quality, was obtained after recrystallization via layered diffusion of pentane (15 mL) into a dichloromethane (3 mL) solution at -25 °C. Yield after recrystallization: 43.6 mg, 28.2%. UV/Vis (CH₂Cl₂) λ_{\max} (nm) (ϵ (M⁻¹cm⁻¹)), 321 (38300), 377 (53500), 393 (48500), 446 (160000), 519 (4000), 562 (9400), 599 (6900). ATR/FTIR $\nu_{\text{V=O}}$ (cm⁻¹): 933(s). Anal. calc'd for C₇₄H₅₄ClCrF₁₂N₈OV • 0.5CH₂Cl₂: C, 60.58; H, 3.75; N, 7.59. Found: C, 60.16; H, 3.63; N, 7.67. HRMS-ESI (M⁺) calc'd for C₇₄H₅₄ClCrF₁₂N₈OV: 1401.3068. Found 1401.3049.

Synthesis of [(omtaa)V=O→Cr(R)←O=V(omtaa)][†] trinuclear complexes,

[(omtaa)V=O→Cr(TPP)←O=V(omtaa)]SbF₆, (2). The compound was synthesized and purified by following a procedure similar to that described above for **1** using two equivalents of (omtaa)V=O (50.0 mg, 0.11 mmol), one equivalent of Cr(TPP)Cl (37.6 mg 0.054 mmol) and 1.1 equivalents of NaSbF₆ (17.5 mg, 0.067 mmol). X-ray quality crystals were obtained via vapor diffusion of pentane into a solution of dichloromethane at room temperature. Yield after recrystallization: 60.9 mg, 62%, UV/Vis (CH₂Cl₂) λ_{\max} (nm)(ϵ (M⁻¹cm⁻¹)): 329 (46300), 386 (55400), 408 (66000), 464 (33700), 535 (5600), 576 (7100), 613 (8300), 636 (6300). ATR/FTIR $\nu_{\text{V=O}}$ (cm⁻¹): 912(s). Anal. calc'd for C₉₆H₈₈CrF₆N₁₂O₂SbV₂, C, 56.77; H, 4.28; N, 8.11. Found: C, 56.10; H, 4.04; N, 8.40. HRMS-ESI (M⁺) calc'd for C₉₆H₈₈CrN₁₂O₂V₂: 1594.5432. Found 1594.5423.

Synthesis of [(tmtaa)Ti=O→Cr(R)←O=V(omtaa)][†] trinuclear complexes,

[(tmtaa)Ti=O→Cr(TPP)←O=V(omtaa)]SbF₆, (3). The compound was synthesized in a sequential two-step, one-pot procedure utilizing methods similar to those described above for **1**. In the glovebox, equimolar amounts of (tmtaa)Ti=O (50.0 mg, 0.12 mmol) and Cr(TPP)Cl (86.0 mg 0.12 mmol) were added to 12 mL of a 1:1 acetonitrile:toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. Following this step, one equivalent of (omtaa)V=O (57.2 mg, 0.12 mmol) and 1.1 equivalents of NaSbF₆ (35.0 mg, 0.14 mmol) were added into mixture and the reaction is stirred for an additional 12 h at 80 °C. The solution was then cooled slowly

to room temperature and was filtered to remove side products. After filtration, a fine green powder was obtained after removal of the solvent *in vacuo*. The resulting solid was purified similarly to **1**. X-ray quality crystals were obtained via vapor diffusion of pentane into a solution of dichloromethane at room temperature. Yield after recrystallization: 85.6 mg, 39.2%. Attempts to make **3** in a single step by adding all of the starting materials at once yielded a mixture of the Ti only (compound **8** in reference 5) and V only (**2**) heterotrimetallic compounds as identified by ESI-MS. UV/Vis (CH₂Cl₂) λ_{max} (nm)(ε (M⁻¹cm⁻¹)): 344 (56900), 389 (65800), 423 (38600), 455 (51000), 526 (5800), 574 (7700), 615 (9100), 635 (7300). ATR/FTIR ν_{V=O} (cm⁻¹): 928(s), ν_{Ti=O} (cm⁻¹): 911(s). Anal. calc'd for C₉₂H₈₀CrF₆N₁₂O₂SbTiV•0.5CH₂Cl₂: C, 61.16; H, 5.00; N, 9.35. Found: C, 61.22; H, 4.50; N, 9.26. HRMS-ESI (M⁺) calc'd for C₉₂H₈₀CrN₁₂O₂TiV: 1535.4845. Found 1535.4857.

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Notes and references

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