The Journal of Chemical Physics

# Long-range spin dependent delocalization promoted by the pseudo Jahn-Teller effect

Cite as: J. Chem. Phys. **151**, 201103 (2019); https://doi.org/10.1063/1.5128117
Submitted: 24 September 2019 . Accepted: 18 October 2019 . Published Online: 25 November 2019

Benjamin W. Stein, Diane A. Dickie, Sachin Nedungadi, David J. R. Brook, David A. Shultz, and Martin L. Kirk

The Journal of Chemical Physics

COMMUNICATION

scitation.org/journal/jcp

# Long-range spin dependent delocalization promoted by the pseudo Jahn-Teller effect

Cite as: J. Chem. Phys. 151, 201103 (2019); doi: 10.1063/1.5128117
Submitted: 24 September 2019 • Accepted: 18 October 2019 •
Published Online: 25 November 2019

View Online Export Citation CrossMark

Benjamin W. Stein,[1,a)] Diane A. Dickie,[1,b)] Sachin Nedungadi,[2] David J. R. Brook,[2] David A. Shultz,[3,c)] and Martin L. Kirk[1,c)]

## AFFILIATIONS

[1] Department of Chemistry and Chemical Biology, The University of New Mexico, MSC03 2060, 1 University of New Mexico, Albuquerque, New Mexico 87131-0001, USA

[2] Department of Chemistry, San José State University, One Washington Square, San José, California 95192, USA

[3] Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, USA

**Note:** The paper is part of the JCP Special Topic on Spin Chemistry.

[a)] **Present address:** Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.

[b)] **Present address:** Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319, USA.

[c)] **Authors to whom correspondence should be addressed:** shultz@ncsu.edu and mkirk@unm.edu

## ABSTRACT

Strong spin-dependent delocalization (double exchange) was previously demonstrated for the complexes, NN-Bridge-SQ-$Co^{III}(py)_2$Cat-Bridge-NN (where NN = S = ½ nitronylnitroxide, Bridge = 1,4-phenylene and single bond, SQ = S = ½ orthobenzosemiquinone, $Co^{III}$ = low-spin $d^6$ cobalt 3+, and Cat = diamagnetic catecholate). The mixed-valent S = ½ SQ-$Co^{III}$-Cat triad results in ferromagnetic alignment of localized (pinned) NN spins which are ~22 Å apart (Bridge = Ph). Herein, we report similar ferromagnetic coupling of localized verdazyl (Vdz) radical spins. The origin of the magnetic exchange results from a *second order* vibronic effect (pseudo Jahn-Teller effect) in $[\text{Vdz-diox-Ru(py)}_2\text{-diox-Vdz}]^0$, which possesses a diamagnetic $[\text{diox-Ru-diox}]^0$ triad by virtue of strong antiferromagnetic SQ-$Ru^{III}$ exchange.

## INTRODUCTION

Developing a deeper insight into long-range electron correlation, specifically how electron spins can be exchange coupled over long distances, is important for obtaining a greater spin polarization in electronic ground states,[1–3] carrier-mediated ferromagnetism, spintronics,[4–9] and quantum information science.[10,11] One mechanism by which remote electron spins can be correlated over long distances is by coupling them to an itinerant or a delocalized electron spin.[3] In solid-state materials, this is commonly observed in dilute magnetic semiconductors,[8,12,13] where exchange interactions are manifested between the itinerant electron(s) and doped magnetic impurities. This is referred to as double exchange[3,14–17] and it is observed in mixed-valent dyads of di- or multinuclear transition metal complexes.[14,15,18–22] While a multitude of systems that possess double-exchange have been described, limitations on electronic coupling imposed by organic ligands restrict the delocalization between metal centers to short distances.[3]

The ability to ferromagnetically exchange couple organic electron spins over long distances via a delocalized spin was realized a decade ago in NN-SQ-$Co^{III}(py)_2$Cat-NN and NN-Ph-SQ-$Co^{III}(py)_2$Cat-Ph-NN (NN = nitronylnitroxide radical, SQ = semiquinone radical, Cat = catecholate, py = pyridine, and Ph = 1,4-phenylene).[3] In this system, the spin bearing units are purely organic NN and SQ radicals, while the $Co^{III}$ ion is in a low-spin $d^6$ electronic configuration and is therefore diamagnetic. Ferromagnetic SQ-Bridge-NN exchange results from an SQ → NN superexchange pathway.[23–25] The high-spin S = 3/2 ground state for NN-SQ-$Co^{III}(py)_2$Cat-NN and NN-Ph-SQ-$Co^{III}(py)_2$Cat-Ph-NN arises from delocalization of the electron in the mixed-valent organic SQ-Cat system.[3] A spin-dependent delocalization or an organic double exchange mechanism effectively couples the remote NN spins allowing for their ferromagnetic alignment over distances greater than 22 Å.[3]

We have sought new opportunities to facilitate this long-range electron correlation via photoexcitation, triggering spin-dependent electron delocalization in the electronic excited state. This allows for the spin polarization of remote electron spins to persist upon relaxation to the electronic ground state with characteristic longitudinal ($T_1$) and transverse ($T_2$) relaxation rates that are determined by the underpinning electronic structure of the system and controlled by the molecular design. Such a system is realized within the [diox-Ru-diox]$^0$ core [i.e., SQ-Ru$^{III}$(py)$_2$Cat ↔ SQ-Ru$^{II}$(py)$_2$SQ].[26] This framework possesses an $S = 1/2$ mixed-valent ligand dyad that is strongly coupled to the $S = 1/2$ spin of the low-spin Ru$^{III}$ core such that the resultant description of the delocalized ground state electronic structure is that of a closed-shell singlet. These systems possess a low-energy Cat → SQ IVCT (intervalence charge transfer) transition,[26] the intensity of which is characteristic of the delocalization within the mixed-valent SQ/Cat dyad ($H_{SQ\text{-}Cat}$).

## RESULTS AND DISCUSSION

The X-ray structure of verdazyl (Vdz) radical-elaborated [Vdz-diox-Ru(*t*-Bu-py)$_2$diox-Vdz]$^0$ (**Vdz**) (diox = dioxolene = catechol/semiquinone) is displayed in Fig. 1 and compared to that of the "parent" core molecule (i.e., ***t*-Bu$_2$**) that lacks the verdazyl radical substituents on the dioxolene ligands. In these structures, the ruthenium ion is six-coordinate and bound axially by two 4-*tert*-butylpyridine ligands (i.e., *t*-Bu-py or py) with the two dioxolene chelates coordinating to the metal ion in the equatorial plane. The two verdazyl radicals in **Vdz** are separated by ~13 Å, while a combination of locational disorder and electron delocalization within the Ru(diox)$_2$ core results in average (of SQ and Cat) values for the measured dioxolene bond lengths. The Ru–O bond lengths determined here are consistent with those of the corresponding cobalt complexes, NN-diox-Co$^{III}$(*t*-Bu-py)$_2$diox-NN and NN-Ph-diox-Co$^{III}$(*t*-Bu-py)$_2$diox-Ph-NN, where the substituent appended to the dioxolene ligand is a nitronylnitroxide radical or a phenyl-substituted nitronylnitroxide radical, respectively.[3] Isoelectronic verdazyl and nitronylnitroxide radicals possess similar singly-occupied molecular orbital (SOMO) spin density distributions and nodal character at the bridgehead carbon. Interestingly, the Ru(diox)$_2$ cores of **Vdz** and ***t*-Bu$_2$** are not planar (xy plane), but are distorted such that one dioxolene ligand plane is tilted up along the +z axis of the molecule with the other dioxolene plane bending down along the -z direction. This ligand fold distortion is measured as the angle (θ) between the O–Ru–O and O–C–C–O planes of the respective five-membered chelate rings. The magnitude of this out-of-plane distortion in the parent ***t*-Bu$_2$** compound is $\theta = 10°$, and θ is noticeably suppressed in the x-ray structure of **Vdz** ($\theta = 2°$).

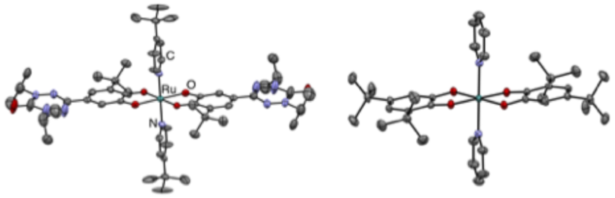

**FIG. 1**. Thermal ellipsoid plots of **Vdz** (left) and ***t*-Bu$_2$** (right). SQ/Cat disorder and delocalization average the dioxolene bond lengths. The verdazyl radicals in **Vdz** are ~13 Å apart.

Although **Vdz** does not display a room-temperature EPR spectrum, one can be observed at low-temperature (5 K), Fig. 2. The spectrum consists of a sharp resonance at g ~ 2 that is superimposed on a much broader g ~ 2 resonance. A low-field resonance is observed at g ~ 4. The presence of a half-field g ~ 4 transition is consistent with a zero-field split $S = 1$ triplet state,[27] where the axial zero-field splitting (ZFS) parameter, D, is the splitting between the $m_s = \pm 1$ and $m_s = 0$ components of the triplet. This $\Delta m_s = 2$ transition is forbidden between the $m_s = \pm 1$ components of the triplet, but is made allowed in the perpendicular direction due to off-diagonal Zeeman mixing between the $m_s = \pm 1$ and $m_s = 0$ states. Thus, for the biradical **Vdz** complex, the half-field transition indicates that the two verdazyl spins must be magnetically exchange coupled in the electronic ground state. The data in Fig. 2 have been simulated[28] assuming that only the $S = 1$ state is populated with a mean axial ZFS parameter, $|D/hc|$, which is equal to 0.1 cm$^{-1}$.

The room-temperature electronic absorption and variable-temperature (3.3–18.9 K) MCD spectra have been overlaid in Fig. 3 for comparative purposes. An energetically isolated and intense NIR band is observed in the electronic absorption spectra of the **Vdz** and parent ***t*-Bu$_2$** complexes. This band has previously been assigned[26] in ***t*-Bu$_2$** as an intraligand charge transfer (ILCT) transition between symmetric and antisymmetric combinations of delocalized dioxolene pair orbitals. An analogous assignment has been made for NN-diox-Co$^{III}$(py)$_2$diox-NN and NN-Ph-diox-Co$^{III}$(py)$_2$diox-Ph-NN, and has been used to show the Class-III dioxolene ligand mixed

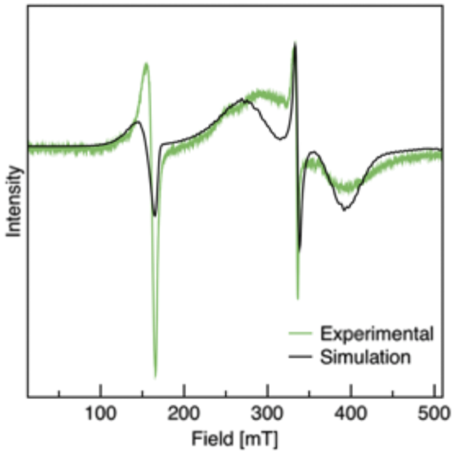

**FIG. 2**. 5 K X-band EPR spectrum of **Vdz**. The simulation is a weighted (normal distribution) average of 100 individual simulations consisting of varied D-values ($g = g_{el} = 2.0023$, mean $|D/hc| = 0.1$ cm$^{-1}$, FWHM = 0.1 cm$^{-1}$). **Vdz** is EPR silent at 300 K. The spectral simulation was performed using *EasySpin*.

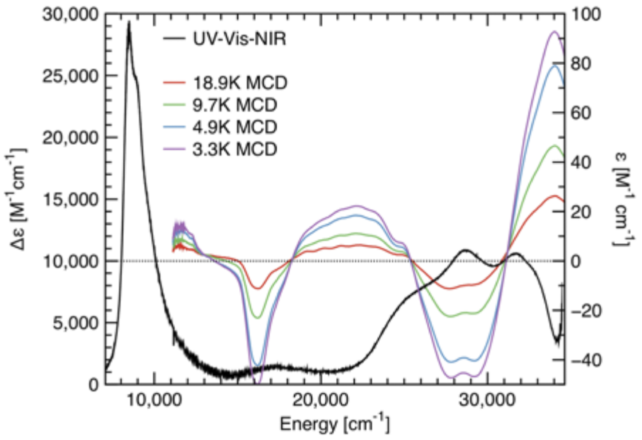

**FIG. 3**. Room temperature UV-Vis-NIR absorption (black) and low temperature (3.3 K–18.9 K) magnetic circular dichroism spectra of **Vdz**. Neither the parent ***t*-Bu$_2$** nor free Vdz ligands show any detectable MCD intensity.

valency.[3] Thus, the pendant NN spins in NN-diox-Co$^{III}$(py)$_2$diox-NN and NN-Ph-diox-Co$^{III}$(py)$_2$diox-Ph-NN are ferromagnetically aligned with the spin of the mixed-valent SQ-Cat dyad in the S = 3/2 ground states of these molecules.[3] Temperature dependent C-term MCD spectra are observed for **Vdz** that, when evaluated in the context of the EPR data, clearly indicate that the S = 1 triplet state is populated at 3.3 K. Additionally, the observation of C-term MCD requires the presence of spin-orbit coupling (SOC),[29,30] and it is therefore typically not observed for organic radicals due to the small SOC constants for their constituent C, O, and N centers. Thus, the C-term MCD activity observed for **Vdz** provides strong evidence that Ru character is admixed into the ground-state wavefunction. This conclusion is corroborated by the axial ZFS parameter ($|D/hc|$ ~ 0.1 cm$^{-1}$) being two orders of magnitude greater than the dipolar prediction for two Vdz radicals separated by ~13 Å ($D_{calc}$ ~ $10^{-3}$ cm$^{-1}$).[31]

A combination of ground state exchange coupling between verdazyl radicals separated by ~13 Å, a large axial ZFS parameter, and the observation of C-term MCD activity suggest significant open-shell Ru-character in the triplet ground state of **Vdz**. A key question emerges as to how this is achieved since there is no orbital overlap between the pendant verdazyl radical SOMOs and the [Ru(py)$_2$(diox)$_2$]$^0$ core in ***t*-Bu$_2$**, which possesses a closed-shell $A_g$ ground state in the nondistorted $D_{2h}$ geometry (i.e., no ligand folding). A partial molecular orbital diagram for this high-symmetry undistorted $D_{2h}$ core that is consistent with the results of DFT computations is shown in Figs. 4(a) and 4(b). Here, the $a_g$ highest-occupied molecular orbital (HOMO) possesses a large degree of Ru d(xy) orbital character in addition to some in-plane dioxolene orbital character, and the $b_{3g}$ HOMO-1 orbital is predominantly Ru d(yz) in nature with a small amount of out-of-plane dioxolene orbital character. The $b_{1u}$ HOMO-2 orbital does not possess any Ru d-orbital character and represents the symmetric combination of the two dioxolene out-of-plane orbitals. The corresponding $b_{2g}$ lowest-unoccupied molecular orbital (LUMO) comprises the antisymmetric combination of these two dioxolene orbitals, which possess an antibonding interaction with the Ru(xz) orbital. This molecular orbital description reveals that there are no low-lying $A_g$ excited states with Ru character that can mix with the $A_g$ ground state. Thus, configuration interaction is *not* a viable mechanism by which significant open shell Ru-character is mixed into the ground state configuration.

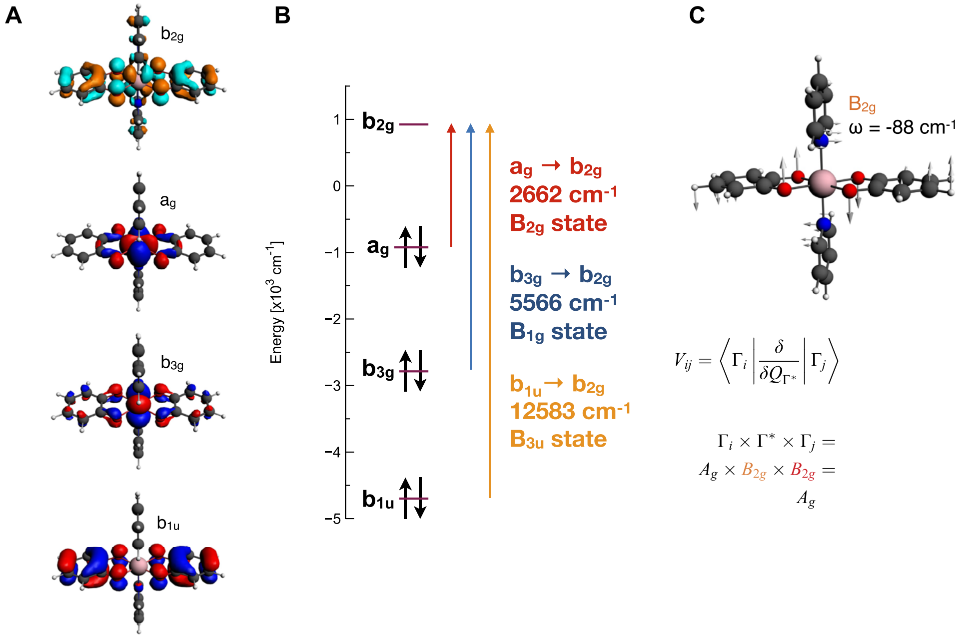

**FIG. 4**. Pseudo-Jahn-Teller analysis of the Ru(diox)$_2$(py)$_2$ core, prior to vibronic distortions. (a): Frontier Kohn-Sham orbitals. (b): Molecular orbital energies and nature of the dominant one-electron promotions in the computed TD-DFT transitions that involve the three highest-lying occupied orbitals and the $b_{2g}$ LUMO. Molecular orbital energies are for the nonvibronically distorted molecule and are given relative to the midpoint of the HOMO-LUMO gap. (c): Vibronically-active $b_{2g}$ mode in the high symmetry $D_{2h}$ geometry.

However, a mechanism to admix excited state open-shell $[Ru(py)_2(diox)_2]^0$ core character into the ground state configuration and increase the degree of Ru-dioxolene covalency may be understood in the context of a pseudo Jahn-Teller (*pJT*) distortion. A *pJT*-mediated distortion derives from vibronic coupling that mixes the electronic ground state ($\Psi_0$) with excited states ($\Psi_i$) according to[32,33]

$$F_{0i} = \langle \Psi_0 | \partial H / \partial Q | \Psi_i \rangle, \tag{1}$$

where $F_{0i}$ represents matrix elements of the vibronic contribution ($K_v$) to the force constant, $K$,

$$K_v = -2 \sum_i \frac{|\langle \Psi_0 | \partial H / \partial Q | \Psi_i \rangle|^2}{E_i - E_0}. \tag{2}$$

The $K_v$ term in Eq. (2) has been shown to represent the only source of instability in polyatomic systems relative to a high-symmetry geometry involving nondegenerate states.[32,33] Thus, a large value for $F_{0i}$, a small energy gap between the ground and excited states ($E_i$–$E_0$), and a small primary (nonvibronic) force constant ($K_0$) can drive a system into a more stable lower symmetry configuration with an increased covalency.[32,33] The results of our time-dependent DFT (TD-DFT) computations indicate the existence of a very low energy (2662 $cm^{-1}$) Ru-dioxolene core-centered HOMO($a_g$) → LUMO($b_{2g}$) one-electron promotion ($A_g \rightarrow B_{2g}$ transition) to create a $B_{2g}$ excited-state configuration [Fig. 4(b)]. The computed molecular orbital and state energies of the system strongly support a dominant single excited state ($\Psi_i = B_{2g}$) contribution to a *pJT* distortion in the $A_g$ ground state along a $b_{2g}$ vibrational coordinate, Q (e.g., $\Gamma_{Ag}$ x $\Gamma_Q$ x $\Gamma_{B2g}$ = totally symmetric $A_g$ for $\Gamma_Q = b_{2g}$). This *pJT* distortion will allow for open-shell $[Ru(py)_2(diox)_2]^0$ core character to be admixed into the $A_g$ ground state and enhance the degree of Ru-character that is covalently mixed into the ground state (note the Ru character in the $b_{2g}$ orbital). The *pJT* effect will manifest itself in an effective symmetry reduction within the $Ru(diox)_2$ core from $D_{2h}$ to $C_{2h}$. Proof that *the pJT* effect is operative in **Vdz** and ***t*-Bu₂** is given by the observation of ligand folding distortions [Fig. 4(a)] in the crystal structures of both **Vdz** and ***t*-Bu₂**.[34] This experimentally-observed low-symmetry distortion in **Vdz** and ***t*-Bu₂** is consistent with a static, vibronically-induced pseudo *pJT* distortion promoted by a $b_{2g}$ vibration.[33,35–37] Indeed, the pJT effect is the *only* possible origin of distortions from high symmetry geometries in systems with nondegenerate ground states.[32,33] Consistent with this $D_{2h} \rightarrow C_{2h}$ distortion in **Vdz**, a single $b_{2g}$ vibration with a negative force constant is computed at 88 $cm^{-1}$ for the high-symmetry $D_{2h}$ structure [Fig. 4(c)].

We have previously studied the related NN-diox-$Co^{II}(py)_2$diox-NN and NN-Ph-diox-$Co^{II}(py)_2$diox-Ph-NN complexes, which possess one more electron than **Vdz**. This results in a ground-state electronic configuration where the LUMO of Figs. 4(a) and 4(b) is occupied by a single unpaired electron. The presence of an electron spin in the LUMO of the $Co^{III}$ complexes is important, since this has been shown to be the origin of the spin-dependent delocalization behavior that leads to ferromagnetic alignment of the two pendant NN spins in the S = 3/2 ground states of NN-diox-$Co^{II}(py)_2$diox-NN and NN-Ph-diox-$Co^{II}(py)_2$diox-Ph-NN.[3] In marked contrast, the occurrence of spin-dependent delocalization in the high-symmetry $D_{2h}$ ground state of **Vdz** is not possible since the $b_{2g}$ orbital is unoccupied. However, a ground-state exchange interaction that couples the two pendant Vdz radical spins can be mediated by the $b_{2g}$ orbital through mixing of the $B_{2g}$ $a_g{}^1 b_{2g}{}^1$ excited configuration with the ground-state via the *pJT* effect. Thus, the admixture of the excited state open-shell SQ-CAT mixed valent character into the electronic ground state promotes long-range electron correlation in **Vdz** that manifests itself in a ligand fold distortion, the observation of magnetic exchange coupling between distant radical spins, and a large zero-field splitting of the triplet component of the ground state.

## CONCLUSION

It is quite remarkable to observe correlated Vdz spins in **Vdz**.[26] However, **Vdz** possesses a dominant mixed-valent Cat/SQ core character in its lowest-energy excited state, which is similar to that found in the ground states of NN-diox-$Co^{III}(py)_2$diox-NN and NN-Ph-diox-$Co^{III}(py)_2$diox-Ph-NN.[3,26] Thus, long-range ferromagnetic exchange between the localized organic radicals in **Vdz** results from an excited state double-exchange mechanism,[3] which is effectively turned on by mixing an excited state configuration with mixed-valent $Ru(diox)_2$ character into the ground state via the *pJT* effect. This *pJT* distortion is revealed in the nature of the $D_{2h} \rightarrow C_{2h}$ ligand fold distortion observed in the X-ray structure of **Vdz** and **tBu₂**. A vibronic *pJT* mechanism has been shown to result in a long-range electron correlation between verdazyl spins that are separated by ~13 Å via a *diamagnetic* $[Ru(diox)_2]^0$ core in the **Vdz** ground state.[3] These initial results highlight how a novel excited state mediated exchange mechanism can be employed to spin polarize ground state radical pairs that are separated by very long distances and isolated from each other by a diamagnetic, electroactive bridge fragment.

## SUPPLEMENTARY MATERIAL

See the supplementary material for synthesis and characterization of **Vdz**.

## ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DE SC0020199 (M.L.K. and D.A.S. synthetic, spectroscopic, computational, and theoretical studies), and by the National Science Foundation (NSF) under Award CHE-1058077 (D.J.R.B. ligand synthesis studies).

## REFERENCES

[1] C. R. Tichnell, D. R. Daley, B. W. Stein, D. A. Shultz, M. L. Kirk, and E. O. Danilov, “Wave function control of charge-separated excited-state lifetimes,” J. Am. Chem. Soc. **141**(9), 3986–3992 (2019).

[2] B. W. Stein, C. R. Tichnell, J. Chen, D. A. Shultz, and M. L. Kirk, “Excited state magnetic exchange interactions enable large spin polarization effects,” J. Am. Chem. Soc. **140**(6), 2221–2228 (2018).

[3] M. L. Kirk, D. A. Shultz, R. D. Schmidt, D. Habel-Rodriguez, H. Lee, and J. Lee, “Ferromagnetic nanoscale electron correlation promoted by organic spin-dependent delocalization,” J. Am. Chem. Soc. **131**(51), 18304–18313 (2009).

[4] D. A. Shultz and M. L. Kirk, “Molecular spintronics: A web themed issue,” Chem. Commun. **50**(56), 7401–7402 (2014).

[5] C. Herrmann and J. Elmisz, "Electronic communication through molecular bridges," Chem. Commun. **49**(89), 10456–10458 (2013).

[6] S. Sanvito, "Molecular spintronics," Chem. Soc. Rev. **40**(6), 3336–3355 (2011).

[7] E. Z. Liu, Y. He, and J. Z. Jiang, "Ferromagnetism induced by defect complex in Co-doped ZnO," Appl. Phys. Lett. **93**(13), 132506 (2008).

[8] K. R. Kittilstved and D. R. Gamelin, "Manipulating polar ferromagnetism in transition-metal-doped ZnO: Why manganese is different from cobalt (invited)," J. Appl. Phys. **99**(8), 08M112 (2006).

[9] A. Soncini, T. Mallah, and L. F. Chibotaru, "Molecular spintronics in mixed-valence magnetic dimers: The double-exchange blockade mechanism," J. Am. Chem. Soc. **132**(23), 8106–8114 (2010).

[10] J. H. Olshansky, M. D. Krzyaniak, R. M. Young, and M. R. Wasielewski, "Photogenerated spin-entangled qubit (radical) pairs in DNA hairpins: Observation of spin delocalization and coherence," J. Am. Chem. Soc. **141**(5), 2152–2160 (2019).

[11] M. S. Fataftah and D. E. Freedman, "Progress towards creating optically addressable molecular qubits," Chem. Commun. **54**(98), 13773–13781 (2018).

[12] K. R. Kittilstved, W. K. Liu, and D. R. Gamelin, "Electronic structure origins of polarity-dependent high-T-C ferromagnetismin oxide-diluted magnetic semiconductors," Nat. Mater. **5**(4), 291–297 (2006).

[13] S. A. Chambers, T. C. Droubay, C. M. Wang, K. M. Rosso, S. M. Heald, D. A. SchwartZ, K. R. Kittilstved, and D. R. Gamelin, "Ferromagnetism in oxide semiconductors," Mater. Today **9**(11), 28–35 (2006).

[14] V. P. Coropceanu, V. G. Bordian, and V. I. Gamurari, "Double exchange in mixed-valence polynuclear cluster: The contribution of multicentre interaction," Mol. Phys. **90**(3), 465–474 (1997).

[15] D. R. Gamelin, E. L. Bominaar, M. L. Kirk, K. Wieghardt, and E. I. Solomon, "Excited-state contributions to ground-state properties of mixed-valence dimers: Spectral and electronic-structural studies of $[\mathrm{Fe}\text{-}_2(\mathrm{OH})_3(\mathrm{tmtacn})_2]^{2+}$ related to the $[\mathrm{Fe}_2\mathrm{S}_2]^+$ active sites of plant-type ferredoxins," J. Am. Chem. Soc. **118**(34), 8085–8097 (1996).

[16] S. A. Borshch, E. L. Bominaar, G. Blondin, and J. J. Girerd, "Double exchange and vibronic coupling in mixed-valence systems. Origin of the broken-symmetry ground-state of $[\mathrm{Fe}_3\mathrm{S}_4]^0$ cores in proteins and models," J. Am. Chem. Soc. **115**(12), 5155–5168 (1993).

[17] P. W. Anderson and H. Hasegawa, "Considerations on double exchange," Phys. Rev. **100**, 675–681 (1955).

[18] M. I. Belinsky, "The spin-coupling model of zero-field splitting for trimeric [3Fe–4S] and mixed-metal [3FeZn–4S] clusters of ferredoxins from Pyrococcus furiosus," Chem. Phys. **263**(2-3), 279–300 (2001).

[19] E. I. Solomon, D. W. Randall, and T. Glaser, "Electronic structures of active sites in electron transfer metalloproteins: contributions to reactivity," Coord. Chem. Rev. **200**, 595–632 (2000).

[20] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii, and B. S. Tsukerblat, "Anisotropic double exchange in orbitally degenerate mixed valence systems," Chem. Phys. **254**(2-3), 275–285 (2000).

[21] T. Glaser, F. Kesting, T. Beissel, E. Bill, T. Weyhermuller, W. Meyer-Klaucke, and K. Wieghardt, "Spin-dependent delocalization in three isostructural complexes $[\mathrm{LFeNiFeL}]^{2+/3+/4+}$ (L = 1,4,7-(4-tert-butyl-2- mercaptobenzyl)-1,4,7-triazacyclononane)," Inorg. Chem. **38**(4), 722–732 (1999).

[22] M. I. Belinsky, "Double exchange in distorted trimeric mixed-valence clusters," Chem. Phys. **215**(1), 7–22 (1997).

[23] M. L. Kirk, D. A. Shultz, E. C. Depperman, D. Habel-Rodriguez, and R. D. Schmidt, "Spectroscopic studies of bridge contributions to electronic coupling in a donor-bridge-acceptor biradical system," J. Am. Chem. Soc. **134**(18), 7812–7819 (2012).

[24] M. L. Kirk, D. A. Shultz, E. C. Depperman, and C. L. Brannen, "Donor-acceptor biradicals as ground state analogues of photoinduced charge separated states," J. Am. Chem. Soc. **129**(7), 1937–1943 (2007).

[25] M. L. Kirk, D. A. Shultz, and E. C. Depperman, "Beyond the active-electron approximation: Origin of ferromagnetic exchange in donor-acceptor heterospin biradicals," Polyhedron **24**(16-17), 2880–2884 (2005).

[26] P. R. Auburn, E. S. Dodsworth, M. Haga, W. Liu, W. A. Nevin, and A. B. P. Lever, "Bis(dioxolene)bis(pyridine)ruthenium redox series," Inorg. Chem. **30**(18), 3502–3512 (1991).

[27] S. S. Eaton, K. M. More, B. M. Sawant, and G. R. Eaton, "Use of the EPR half-field transition to determine the interspin distance and the orientation of the interspin vector in systems with two unpaired electrons," J. Am. Chem. Soc. **105**(22), 6560–6567 (1983).

[28] S. Stoll and A. Schweiger, "EasySpin, a comprehensive software package for spectral simulation and analysis in EPR," J. Magn. Reson. **178**(1), 42–55 (2006).

[29] F. Neese and E. I. Solomon, "MCD *C*-term signs, saturation behavior, and determination of band polarizations in randomly oriented systems with spin $S \geq 1/2$. Applicationis to $S = 1/2$ and $S = 5/2$," Inorg. Chem. **38**, 1847–1865 (1999).

[30] M. L. Kirk, "Magnetic circular dichroism spectroscopy of pyranopterin molybdenum enzymes," Paramagn. Reson. Metallobiomol. **858**, 340 (2003).

[31] J. F. Keana and R. J. Dinerstein, "A new highly anisotropic dinitroxide ketone spin label. A sensitive probe for membrane structure," J. Am. Chem. Soc. **93**, 2808 (1971).

[32] I. B. Bersuker, *The Jahn-Teller Effect* (Cambridge University Press, Cambridge, UK, 2006).

[33] I. B. Bersuker, "Pseudo-Jahn-Teller effect: A two-state paradigm in formation, deformation, and transformation of molecular systems and solids," Chem. Rev. **113**(3), 1351–1390 (2013).

[34] B. W. Stein, J. Yang, R. Mtei, N. J. Wiebelhaus, D. K. Kersi, J. LePluart, D. L. Lichtenberger, J. H. Enemark, and M. L. Kirk, "Vibrational control of covalency effects related to the active sites of molybdenum enzymes," J. Am. Chem. Soc. **140**(44), 14777–14788 (2018).

[35] N. N. Gorinchoy, I. I. Balan, and I. B. Bersuker, "Jahn-Teller, pseudo Jahn-Teller, and Renner-Teller effects in systems with fractional charges," Comput. Theor. Chem. **976**(1-3), 113–119 (2011).

[36] J. Yang, B. Mogesa, P. Basu, and M. L. Kirk, "Large Ligand folding distortion in an oxomolybdenum donor acceptor complex," Inorg. Chem. **55**(2), 785–793 (2016).

[37] I. B. Bersuker and S. A. Borshch, "Vibronic interactions in polynuclear mixed-valence clusters," Adv. Chem. Phys. **81**, 703–782 (1991).