Density functional theory of spin-coupled models for diiron-oxo proteins: Effects of oxo and hydroxo bridging on geometry, electronic structure, and magnetism

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We have performed a comprehensive study of the electronic structure and magnetic properties of structurally characterized models for diiron-oxo proteins. Results from Kohn–Sham density functional theory show that two complexes, with formula Fe$_2$(μ-O)(μ-O$_2$CCH$_3$)$_2$(HBpz$_3$)$_2$ and [Fe$_2$(μ-OH)(μ-O$_2$CCH$_3$)$_2$(HBpz$_3$)$_2$]$^+$, are strongly and weakly antiferromagnetically coupled, respectively, in agreement with experiment. The physical origin of the stronger and weaker exchange typically measured for oxo- and hydroxo-bridged diiron complexes, respectively, has been elucidated. The main superexchange pathways giving rise to molecular antiferromagnetism in both complexes have been identified. The dominant pathway in the oxo-bridged complex, Fe$_1$(d$_{zx}$):μ-O(p$_1$):Fe$_2$(d$_{yz}$), was formed by π interactions whereas that of the hydroxo-bridged, Fe$_1$(d$_{zx}$):μ-OH(p$_1$):Fe$_2$(d$_{yz}$), was formed by σ interactions. We also found a pathway mediated by the bridging acetates, Fe$_1$(d$_{zx}$,...:bis(μ-acetato):Fe$_2$(d$_{yz}$)...), which induces weak antiferromagnetism in the oxo-bridged complex but is significantly more important in the hydroxo-bridged complex. The antiferromagnetic exchange constants that parameterize the Heisenberg Hamiltonian $H=J_S^1S^1+S^2$ have been predicted for both, strongly and weakly, coupled complexes. Overall, the signs, trends, and magnitudes of the theoretical values ($J_{\text{calc}}^{\text{oxo}}=+152.7\text{cm}^{-1}$, $J_{\text{calc}}^{\text{hydrox}}=+23.3\text{cm}^{-1}$) were in excellent agreement with experiment. The geometries of the complete molecular structures have been optimized in C$_{2v}$ symmetry and used to calculate molecular properties such as atomic charges and spin densities. The electronic configurations (Fe:4$s^2$3$d^{9.93}$, O:2$p^{1.92}2$p$^{4.99}$, Fe:4$s^{0.30}$3$d^{5.82}$, μ-OH:2$s^{1.82}2$p$^{5.25}$, H:1$s^{0.51}$) of the respective binuclear cores revealed relatively high occupancies for the nominally ferric ions, thus reflecting a donating character of their immediate N$_3$O$_3$ coordination. In addition, the diiron-oxo protein hemerythrin has been discussed. Theoretical and structural considerations indicated that the oxo-bridged diferrocen complex considered herein models extremely well the antiferromagnetic behavior of azidomet- and azidometmyo-hemerythrin. Finally, the magnetic behavior of closely related oxo-bridged diferrocen and hydroxo-bridged diferrocen complexes containing Me$_3$TACN capping ligands has been explained in light of the results presented in this work. © 2002 American Institute of Physics. [DOI: 10.1063/1.1461363]

I. INTRODUCTION

A number of homobinuclear$^1$–$^6$ and heterobinuclear$^5$–$^7$ first row transition metal complexes that display remarkable electronic and magnetic properties have been synthesized. A general characteristic of these complexes is the presence of two paramagnetic spin centers that interact via (μ-O)bis(μ-acetato) ligands and couple antiferromagnetically. Diiron complexes of this type are of particular biological relevance since their oxo-bis-oxo complexes constitute structural models for active sites in non-heme diiron-oxo$^1$–$^5$ proteins. Magnetic studies (e.g., susceptibility$^1$, $^2$, $^5$ Mossbauer$^{10,12}$) of diiron centers in model compounds and metalloproteins consistently show a strong dependence on the nature of their bridging ligands. Indeed, upon protonation of their oxo bridges, the strength of antiferromagnetic exchange, as quantified by the Heisenberg Hamiltonian $H_{\text{IB}}=J_S^1S^1+S^2$, generally drops by an order of magnitude:

$$J \approx 10^9 \text{ cm}^{-1}$$

Fe$^{4+}$(S$_1=\frac{3}{2}$):(μ-O)bis(μ-acetato)-Fe$^{3+}$(S$_2=\frac{3}{2}$)

Fe$^{4+}$(S$_1=\frac{3}{2}$):(μ-OH)bis(μ-acetato)-Fe$^{3+}$(S$_2=\frac{b}{2}$)

Heisenberg States

Scheme 1.

In oxo-bridged binuclear complexes, such as those studied in this work (Fig. 1), the magnetic $d$ orbitals (i.e., those hosting unpaired electrons) of the two metal sites can overlap via $p$ orbitals of their (nominally) diamagnetic bridging ligands. As a result of such indirect overlap, a number of

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superexchange (i.e., bridge-mediated) pathways can be formed which favor an antiparallel alignment of the electron spins. Such antiferromagnetic pathways can be represented as idealized electronic configurations of the form $\text{Fe}^1(d_{1}^{-1}); \mu-O(p^{1^{-1}}); \text{Fe}^2(d_{2}^{-1})$. Here, the atomic orbitals of the iron sites can have equal (i.e., $d_{1} = d_{2}$) or mixed (i.e., $d_{1} \neq d_{2}$) local symmetry. Depending on the oxidation and spin state of the cations involved, molecular symmetry, and geometry, there may be several pairs of interacting electrons.

Although detailed papers have given insight about the mechanisms of spin coupling in oxo-bridged diiron complexes, there remain fundamental questions to be answered. In particular: What are the physical origins and microscopic mechanisms giving rise to the dramatically weaker antiferromagnetism of hydroxo-bridged complexes relative to their oxo-bridged counterparts? What are the compositions of the dominant exchange pathways before and after protonation of the oxo bridge? What are the concurrent, but different, effects of geometric variations and proton addition that occur upon protonation of the oxo bridges? Furthermore, although calculations to elucidate several subtle, but fundamental, differences between the electronic and magnetic structures of oxo- and hydroxo-bridged model compounds. It has been our aim to perform such calculations to elucidate several subtle, but fundamental, differences between the electronic and magnetic structures of oxo- and hydroxo-bridged (bio)inorganic diiron complexes.

Despite significant computational efforts, many theoretical determinations of exchange constants ($J$) have only afforded the right order of magnitude for strongly coupled (e.g., oxo-bridged) diiron and dimanganese complexes. Greater accuracy has been obtained by Adamo et al. for bis (μ-azido) dicopper complexes. However, theoretical estimates of $J$ have generally been significantly less accurate and even qualitatively incorrect (i.e., predicting ground state ferromagnetism instead of antiferromagnetism or vice versa) for weakly coupled (e.g., hydroxo-bridged) complexes. The great difficulty encountered in the accurate prediction of exchange constants can be traced to several factors. These include: (i) the extremely small antiferromagnetic energy splittings to be calculated, about $10^{-6} - 10^{-7}$ smaller than the total molecular energies; (ii) the inadequacy of some electronic structure methods to account for inclusion of correlation or proper balance between exchange and correlation in spin-polarized metal complexes; and (iii) the oversimplification of molecular models and geometries used in the calculations.

In this work we apply gradient-corrected Kohn–Sham density functional theory to elucidate the electronic structure of two compounds synthesized by Armstrong and Lippard (Fig. 1), hereafter referred to as Fe$^{3+}$–O–Fe$^{3+}$(HBpz$_3$)$_2$ and Fe$^{3+}$–OH–Fe$^{3+}$(HBpz$_3$)$_2$. By studying the complete molecular structures and fully optimized geometries of these complexes we have obtained a detailed understanding of several important and related topics. In particular: (i) Which metallic and bridging orbitals are involved in the antiferromagnetism exhibited by these compounds; (ii) The detailed physical origin of strong and weak antiferromagnetism in the oxo- and hydroxo-bridged complexes, respectively; (iii) The specific and different roles of oxo, hydroxo, and acetato bridges; and (iv) The accurate prediction of Heisenberg exchange constants for both (i.e., strong and weak) antiferromagnetic coupling regimes. In addition, by studying a third structure, Fe$^{3+}$–O$^-$–Fe$^{3+}$(HBpz$_3$)$_2$, which corresponds to the deprotonated optimized geometry of Fe$^{3+}$–OH–Fe$^{3+}$(HBpz$_3$)$_2$, we have been able to differentiate the related, but distinct, effects of bridge protonation and concomitant Fe-μO distance variations. Finally, in light of the results presented in this work, we discuss the mechanisms of antiferromagnetic spin-coupling in (i) the diiron-
oxo proteins azidomet and azidometmyo-hemerythrin and (ii) two closely related model compounds hereafter referred to as Fe$^{3+}$–O–Fe$^{3+}$ ($\text{Me}_2\text{TACN}$)$_2$ and Fe$^{2+}$–OH–Fe$^{2+}$ ($\text{Me}_2\text{TACN}$)$_2$ ($\text{Me}_2\text{TACN}$=1,4,7-trimethyl-1,4,7-triazaacyclo-
nonane).

II. THEORETICAL BACKGROUND

Kohn–Sham density functional theory (KS-DFT)\textsuperscript{32–34} is a powerful method for studies of ground state electronic structure of large (e.g., 60–120 atoms) transition metal-containing complexes. The Kohn–Sham Hamiltonian\textsuperscript{32,33} takes into account exchange and correlation effects\textsuperscript{35–37} that are important for the description of many molecules and in particular\textsuperscript{38} of spin-polarized open-shell transition metal clusters.

To allow for spin polarization one can apply a spin unrestricted (U) formalism\textsuperscript{33,39} which allows $\alpha$ and $\beta$ electrons to occupy orbitals with different energy and spatial localization. The unrestricted Kohn–Sham (UKS) equations give rise to molecular orbitals $\phi_i^\text{UKS}(\mathbf{r})$ which have eigenvalues $\epsilon_i$ and $\alpha$ or $\beta$ spin index. Although Kohn–Sham orbitals have an auxiliary role\textsuperscript{33,34} recent studies have pointed out their properties. For example, Kohn, Becke, and Parr\textsuperscript{34} noticed that all $\phi_i^\text{KS}(\mathbf{r})$ and $\epsilon_i$ are of great semiempirical magnitude because they reflect correlation effects. Baerends and Gritsenko\textsuperscript{40,41} also recommended the Kohn–Sham orbitals and corresponding one-electron energies as tools in qualitative chemical considerations. They noticed that Kohn–Sham orbitals retain their expected bonding or antibonding character as well as their expected behavior under perturbations (e.g., geometrical distortions).

To obtain orbitals that mimic those of a pure open shell singlet, it is convenient to impose self-consistent-field (SCF) convergence to a singlet wave function ($\Psi_1^\text{UKS}$) of broken spatial and spin symmetry.\textsuperscript{42,43} Such wave functions have a symmetry lower than that of the geometric structure and impose fair localization of unpaired $\alpha$ electrons on one iron site and unpaired $\beta$ electrons on the other site. Kohn–Sham orbitals of broken symmetry are regarded\textsuperscript{40,43,44} as approximations to localized natural magnetic orbitals\textsuperscript{22,45,46} and, as such, their overlaps can provide a semiempirical measure of magnetic interactions in weakly coupled systems.

In general, unrestricted Kohn–Sham wave functions obtained from SCF calculations are eigenfunctions of $\mathbf{S}$, but are not eigenfunctions of the total spin operator $\mathbf{S}^2$. As a consequence, the singlet (i.e., antiferromagnetic) single determinant wave functions ($\Psi_1^\text{UKS}$) are, in general, spin contaminated and can have strong admixtures from higher spin states\textsuperscript{42} [i.e., ($S^2$)$^\text{UKS}$$>$S(S+1)]. However, the high spin (i.e., ferromagnetic) states of spin-coupled systems can be well represented\textsuperscript{21,22,47} by single Slater determinants ($\Psi_{11}^\text{UKS}$). Accordingly, spin unrestricted wave functions of ferromagnetic states are generally found pure [i.e., ($S^2$)$^\text{UKS}$$=$S(S+1)] in conventional ab initio (UHF and MP2)\textsuperscript{48,49} and also DFT\textsuperscript{38,47,50} calculations.

Heisenberg exchange interaction

Ground state antiferromagnetism in binuclear complexes arises from interactions between pairs of unpaired electrons, each member of the pair being localized on a different metal ion. Although the phenomenon of antiparallel spin coupling resembles a magnetic interaction between two spins, its physical origin is electrostatic in nature (Heisenberg\textsuperscript{51}) and a consequence of the antisymmetry requirement of the Pauli exclusion principle\textsuperscript{13,51} Dirac\textsuperscript{52,53} showed that this interaction, although electrostatic in origin, could be written as a scalar product of the spin operators of two electrons. Such formulation was readily extended and applied by Van Vleck\textsuperscript{54} to exchange interactions between atoms in molecules and solids. As such, the net spin coupling between two metal ions with single-ion operators $\mathbf{S}_1$ and $\mathbf{S}_2$ can be represented and quantified by the Heisenberg–Dirac–Van Vleck Hamiltonian

\begin{equation}
H_{\text{HB}} = J \mathbf{S}_1 \cdot \mathbf{S}_2. \tag{1}
\end{equation}

In general, the net spin coupling within a binuclear complex results from a complex admixture of antiferromagnetic and ferromagnetic interactions.\textsuperscript{15,20,21,55} Often, the former are dominant and the spin ground state corresponds to the lowest (i.e., $S_{\text{min}}=S_1-S_2$) eigenvalue of the total spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. In this case, the $J$ constant of Eq. (1) is positive and the binuclear complex is said to have an antiferromagnetic ground state.

The eigenstates of the Heisenberg Hamiltonian [Eq. (1)] have energies given by

\begin{equation}
E_{2S+1} = \frac{1}{2} J (S(S+1) - S_1(S_1+1) - S_2(S_2+1)). \tag{2}
\end{equation}

It follows from Eq. (2) that the exchange interaction partially removes the degeneracy of the various spin manifolds giving rise to the energy splittings shown in Scheme 1. To calculate the exchange constant from density functional calculations we can use Eq. (2) in conjunction with spin projections\textsuperscript{38,49,56} on the spin unrestricted wave functions. In a previous paper\textsuperscript{38} we presented expressions for the calculation of exchange constants in complexes where a $S=\frac{1}{2}$ cation is bound to a $S=\frac{1}{2}$ radical. Here, we followed Yamaguchi \textit{et al.}\textsuperscript{49,56} and used a general expression for symmetric or asymmetric binuclear complexes. As shown in the Appendix,\textsuperscript{57} we approximated the energies of the calculated (UKS) and pure (PUKS) Kohn–Sham wave functions for the high-spin state as being equal (i.e., $E_{2S_{\text{max}}+1}^{\text{UKS}} \approx E_{2S_{\text{max}}+1}^{\text{PUKS}}$). Such approximation is valid since high-spin (i.e., ferromagnetic) wave functions are essentially free from spin contamination (\textit{vide supra}). An important feature of Eq. (3) is that it is based on expectation values of energy and spin operators that can be evaluated directly from converged SCF wave functions. We notice, however, that our application of Eq. (3) is for Kohn–Sham wave functions from which the proper computation of $\langle S^2 \rangle$ is not straightforward.\textsuperscript{58}

III. MATERIALS AND METHODS

Several combinations of exchange and correlation functionals were used in the DFT calculations. The geometry
optimizations were performed with two different methods. The first is a combination of Becke\textsuperscript{59} gradient-corrected exchange and Perdew–Wang\textsuperscript{57,60} nonlocal correlation (U-BPW91). The second method uses the three parameter exchange of Becke\textsuperscript{55,59,61,62} in conjunction with Lee–Yang–Par\textsuperscript{70} correlation (U-B3LYP). This latter functional constitutes a hybrid approach that combines Hartree–Fock\textsuperscript{39,63–65} with Slater\textsuperscript{32,66,67} and gradient-corrected Becke\textsuperscript{55,59,61} exchange. The correlation in U-B3LYP is introduced by a combination of the local and nonlocal functionals of Vosko–Wilk–Nusair\textsuperscript{62} and Lee–Yang–Par\textsuperscript{70} respectively. Further single point calculations designed to study ground state electronic structures were performed with U-BPW91, U-B3LYP, and U-MPW1PW91.\textsuperscript{58} The Heisenberg exchange couplings were calculated with the latter functional and a 6-311G\textsuperscript{**} basis.

All electron basis sets were used during the course of the calculations, namely 6-31G\textsuperscript{66,70} and 6-311G\textsuperscript{*,70,71,72} For iron we used the basis optimized by Wachters\textsuperscript{73} and Hay\textsuperscript{74} calculations, namely 6-31G\textsuperscript{*} and 6-311G\textsuperscript{*}.\textsuperscript{39,71,72} For corrected Becke\textsuperscript{55,59,61} exchange. The correlation in low-spin (\(\Psi_{\text{UKS}}\)) states of \(\mbox{Fe}^{3+}-\mbox{O}–\mbox{Fe}^{3+}\) (\(\Psi_{\text{UKS}}\)) states are reported here since such states can be well represented by a single determinant Kohn–Sham wave function (Sec. II). The optimizations were carried out in \(C_{2v}\) symmetry and produced the structures shown in Fig. 1 with parameters given in Table I. The Cartesian coordinates of the optimized geometries are given as Supplementary tables. The bond lengths and angles optimized at the U-BPW91/6-31G* and U-B3LYP/6-31G* levels were fairly close. However, the U-B3LYP parameters were, in general, in closer agreement with the x-ray structures.\textsuperscript{1,2} In what follows we mainly refer to geometries obtained from this latter method.

1. \(\mbox{Fe}^{3+}\)–\(\mbox{Fe}^{3+}\) (\(\Psi_{\text{UKS}}\)) states of \(\mbox{Fe}^{3+}\)–\(\mbox{O}–\mbox{Fe}^{3+}\) (\(\Psi_{\text{UKS}}\)) states are reported here since such states can be well represented by a single determinant Kohn–Sham wave function (Sec. II). The optimizations were carried out in \(C_{2v}\) symmetry and produced the structures shown in Fig. 1 with parameters given in Table I. The Cartesian coordinates of the optimized geometries are given as Supplementary tables. The bond lengths and angles optimized at the U-BPW91/6-31G* and U-B3LYP/6-31G* levels were fairly close. However, the U-B3LYP parameters were, in general, in closer agreement with the x-ray structures.\textsuperscript{1,2} In what follows we mainly refer to geometries obtained from this latter method.

### IV. RESULTS

#### A. Geometry optimizations

An accurate knowledge of geometric parameters, in particular those related to the (\(\mu\)-O)bis(\(\mu\)-acetato) diiron cores, is important for understanding the magnetic properties of the spin-coupled complexes. For instance, it is known that Fe–\(\mu\)-O bond lengths correlate with the strength of antiferromagnetic coupling, the magnitude of that coupling decaying nearly exponentially with increasing distances.\textsuperscript{83} Some of the most reliable DFT functionals (e.g., U-BPW91, U-B3LYP) are known to predict high quality, yet slightly different, geometries for the same molecular structures.\textsuperscript{84} Therefore, to establish subtle, but fundamental differences between the magnetic properties of \(\mbox{Fe}^{3+}\)–\(\mbox{O}–\mbox{Fe}^{3+}\) (\(\Psi_{\text{UKS}}\)) states are reported here since such states can be well represented by a single determinant Kohn–Sham wave function (Sec. II). The optimizations were carried out in \(C_{2v}\) symmetry and produced the structures shown in Fig. 1 with parameters given in Table I. The Cartesian coordinates of the optimized geometries are given as Supplementary tables. The bond lengths and angles optimized at the U-BPW91/6-31G* and U-B3LYP/6-31G* levels were fairly close. However, the U-B3LYP parameters were, in general, in closer agreement with the x-ray structures.\textsuperscript{1,2} In what follows we mainly refer to geometries obtained from this latter method.

Distances between individual metal sites and their main bridge (i.e., \(\mu\)-O) are of special interest. The calculated (U-B3LYP) Fe–\(\mu\)-O (i.e., Fe1–O3 and Fe2–O3) bond lengths were 1.830 Å, whereas the average x-ray value is 1.786 Å.\textsuperscript{2} While the predicted Fe–\(\mu\)-O bonds were about 0.044 Å longer than the x-ray values, the agreement between theoretical and experimental values for other bonds (Table I) was much closer. In particular, for Fe1–O4 and Fe1–O5 the calculated values were only 0.01 Å longer whereas for Fe1–N8, Fe1–N9, and Fe1–N10 the calculated values were about 0.02 Å longer. Thus, the trends observed in the x-ray structure were generally well reproduced by the optimizations. For example, both optimized and x-ray structures displayed Fe1–N9 and Fe2–N15 bonds which were longer than the other Fe–N bonds.

In terms of magnetic properties, the Fe1–\(\mu\)-O–Fe2 angle is the most interesting since it largely determines which \(d\) orbitals localized on one iron site can interact, via bridging \(p\) orbitals, with \(d\) orbitals localized on the other iron site.\textsuperscript{13,15–19} To some approximation, the nature of the possible intermetallic \(d\) orbital interactions (i.e., antiferromagnetic or ferromagnetic) are given by the Goodenough–Kanamori\textsuperscript{16–19} rules as extended by Anderson and others.\textsuperscript{13,15} One rule predicts that when two ions have lobes of magnetic orbitals pointing toward each other in such a way that the orbitals would have a reasonable large overlap integral, the exchange is antiferromagnetic.\textsuperscript{15} However, such simple rules are often used to make qualitative predictions
for the limiting cases of linear (e.g., Fe1–O–Fe2=180°) or perpendicular (e.g., Fe1–O–Fe2=90°) geometries. The Fe1–O3–Fe2 angle (≈126°) was far from these limiting values. This underscored the need to perform the detailed study for the limiting cases of linear and perpendicular geometries. The distorted octahedral environment around the individual iron sites was illustrated by the somewhat different values of the various O–Fe–O angles. The calculated O3–Fe1–O4 and O3–Fe1–O5 angles were 2.1° larger than the calculated O4–Fe1–O5 angle. This latter trend was more pronounced in the x-ray structure, which shows O3–Fe1–O4 and O3–Fe1–O5 angles 4.7°–5.2° larger than O4–Fe1–O5.

2. **Fe**

The optimized (U-B3LYP) Fe1–O3 and Fe2–O3 bond lengths were 1.994 Å, only 0.01 Å shorter than the other (i.e., μ-acetato) Fe–O bonds. This was in sharp contrast to Fe3+–O–Fe3+ (HBpz)2 where the former bonds were 0.221 Å shorter than the latter. Therefore, contrary to Fe3+–O–Fe3+ (HBpz)2, the Fe1–O3 and Fe2–O3 bonds in Fe3+–OH–Fe3+ (HBpz)2 might not be expected to substantially dominate the electronic structure of its iron sites, the longer bonds giving rise to a more ionic character and also to a weaker antiferromagnetic interaction. The predicted Fe1–O3 and Fe2–O3 distances were 0.034 Å and 0.041 Å longer than the x-ray values, respectively. This discrepancy suggests that more accurate distances for the pseudo three-center-bond (Fe1–μO–Fe2) may be predicted by using larger basis sets. However, the other bond lengths given in Table I were in closer agreement with the experimental structure. For instance, for Fe1–O4 and Fe1–O5 the average calculated-experimental difference was only 0.001 Å whereas for Fe1–N8, Fe1–N9, and Fe1–N10 the calculated values were within experimental error.

The calculated Fe1–O3–Fe2 angle (123.5°) was fairly close to its x-ray value (123°) and slightly more acute than the corresponding angle of Fe3+–O–Fe3+ (HBpz)2 (126.2°). We note that for Fe3+–OH–Fe3+ (HBpz)2 all O–Fe–O angles had nearly identical values. This was in contrast to the results obtained for Fe3+–O–Fe3+ (HBpz)2 which showed O4–Fe1–O5 and O6–Fe2–O7 being somewhat more acute than the other O–Fe–O angles. This indicated that, in comparison to Fe3+–O–Fe3+ (HBpz)2, the iron sites of Fe3+–OH–Fe3+ (HBpz)2 had a less distorted octahedral environment.

In general, there was close agreement between the theoretical and experimental parameters of Fe3+–OH–Fe3+ (HBpz)2. However, there was a significant difference between optimized (0.970 Å) and reported experimental (0.702 Å) O3–H44 distances. We have also reported discrepancies in the hydrogen positions of another complex. Typically, hydrogen positions determined from x-ray diffraction data correspond to a minimization of residual densities and do not necessarily correspond to proton positions. By contrast, the calculated distance for the proton corresponded, within the accuracy of the method, to its true equilibrium position in a particular molecular electronic state. Knowledge of the proton position in Fe3+–OH–Fe3+ (HBpz)2 was important for the accurate prediction of the exchange constant of this weakly coupled complex.
B. Energies and composition of delocalized molecular orbitals

The coordinate systems of Fig. 2 have been used to describe all molecular and atomic orbitals. There were similarities but also significant differences between the electronic structures of Fe$^{3+}$−O−Fe$^{3+}$ (HBpz$_3$)$_2$, Fe$^{3+}$−O$^*$−Fe$^{3+}$ (HBpz$_3$)$_2$, and Fe$^{3+}$−OH−Fe$^{3+}$ (HBpz$_3$)$_2$. We now describe the energies and most salient features of some metal-rich frontier orbitals.

1. Fe$^{3+}$−O−Fe$^{3+}$ (HBpz$_3$)$_2$

Figure 3 and Supplementary Table I show the main composition and energies of MOs corresponding to the high-spin state ($\Psi_{11}^{\text{UKS}}$) of Fe$^{3+}$−O−Fe$^{3+}$ (HBpz$_3$)$_2$. The table also shows the labels corresponding to the C$_{2v}$ irreducible representations. The spin-unrestricted calculations allowed $\alpha$ and $\beta$ orbitals to have, in general, different energies and spatial localizations. Exchange interactions between majority ($\alpha$) electrons significantly stabilized their frontier MOs with respect to the corresponding unoccupied $\beta$ orbitals. Within the energy scale of Fig. 3 there were two groups of occupied $\alpha$ orbitals. The first included the five highest MOs (i.e., 173$\alpha$−177$\alpha$) which were mainly composed of Fe($d_{xz}$) with or without admixture from $\mu$−O($p_{\perp}$) orbitals. The second group comprised orbitals delocalized throughout the HBpz$_3$ ligands (i.e., 166$\alpha$−172$\alpha$). Some lower energy orbitals (not shown) had some metal character but also substantial contribution from the bridging or capping ligands.

The metal-rich molecular orbitals corresponded to symmetric (S) and antisymmetric (A) combinations of two $d$ orbitals of equal local symmetry, each localized on a different iron center (Fig. 3). The occupied $\alpha$ set included MOs with either dominant or relatively minor contributions from the metals. By contrast, the corresponding unoccupied $\beta$ set consisted entirely of MOs mainly centered on the iron sites. All of these (168$\beta$−177$\beta$) were grouped together significantly higher in energy than the two nearly degenerate, highest occupied, minority orbitals (166$\beta$,167$\beta$). For these reasons, we focused on the unoccupied $\beta$ set (Table II). The most relevant orbitals have been extensively described in the Supplementary material and are shown in Figs. 4−6.

2. Fe$^{3+}$−O$^*$−Fe$^{3+}$ (HBpz$_3$)$_2$

Figure 7 and Supplementary Table II show the main compositions and energies of MOs corresponding to the high-spin state ($\Psi_{11}^{\text{UKS}}$) of Fe$^{3+}$−O$^*$−Fe$^{3+}$ (HBpz$_3$)$_2$. The energy scheme of Fig. 7 resembled that of Fig. 3. The relative order of the frontier orbitals for both oxo-bridged structures was nearly the same. The exceptions were the MOs of Fe($d_{yz}$) and Fe($d_{xz}$) composition, which switched order between 169$\beta$ and 170$\beta$, and the MOs of $\mu$−O($p_{\perp}$) and $\mu$−O($p_{\perp}$) composition that were higher in energy for Fe$^{3+}$−O$^*$−Fe$^{3+}$ (HBpz$_3$)$_2$. A comparison of the energy splittings between symmetric and antisymmetric combinations of Fe($d_{l}$) orbitals, $\Delta^{\beta} = (\varepsilon_{S_{l}} - \varepsilon_{A_{l}})$, revealed some meaningful differences. In general, the splittings were larger for Fe$^{3+}$−O−Fe$^{3+}$ (HBpz$_3$)$_2$ than Fe$^{3+}$−O$^*$−Fe$^{3+}$ (HBpz$_3$)$_2$. The greatest changes between these two structures were seen for $\Delta^{\beta}_{11}$ (0.388 eV), $\Delta^{\beta}_{10}$ (0.342 eV) and, to a lesser extent, for $\Delta^{\beta}_{12}$ (0.111 eV). By contrast, $\Delta^{\beta}_{11}$ and $\Delta^{\beta}_{12}$ were only slightly smaller for the first structure.

Concurrent with variations in $\Delta^{\beta}$ splittings, some meaningful changes in orbital composition were also noted (Supplementary Tables I and II). The metal-rich orbitals (168$\beta$−177$\beta$) of Fe$^{3+}$−O$^*$−Fe$^{3+}$ (HBpz$_3$)$_2$ had, in general, greater metallic character than those of Fe$^{3+}$−O−Fe$^{3+}$ (HBpz$_3$)$_2$. Again, the main differences be-
between the two structures were noticed for MOs of \( d_{xz} \) and \( d_{yz} \) symmetry which were more metallic in the first case. By contrast, the orbitals of \( d_{xy} \) character \( \approx 174 \) and \( 175 \) had nearly equal composition in both structures and also nearly equal \( D_{xy} \) splittings. Supplementary Table II also revealed that although MOs \( 166 \) and \( 167 \) were mainly localized on the bridging oxygen, there was delocalization toward the iron centers.

### 3. \( \text{Fe}^{3+} – \text{O} – \text{Fe}^{3+}(\text{HBpz})_2 \)

Figure 8 and Supplementary Table III show the orbital energies of the hydroxo-bridged complex. The relative order of the one electron orbitals were somewhat different from those of the two oxo-bridged structures (Figs. 3 and 7). For instance, the \( \beta \) orbitals of \( t_{2g} \) parentage were more closely packed in the energy scale. Similarly, the orbitals of \( e_g \) parentage were more closely spaced.

A comparison with the energy scheme of Fig. 7 allowed us to distinguish the effects of bridge protonation from those of related geometric variations. Upon protonation, the splittings between symmetric and antisymmetric combinations of \( \text{Fe}(d) \) orbitals were, in general, very close to those of \( \text{Fe}^{3+} – \text{O}^* – \text{Fe}^{3+}(\text{HBpz})_2 \). However, there was an appreciable difference in the value of \( \Delta E_{yz} \): this splitting was 0.470 eV smaller for \( \text{Fe}^{3+} – \text{O} – \text{Fe}^{3+}(\text{HBpz})_2 \) due to the stabilization of MO 173. At the same time, the \( \text{Fe}(d_{xz}) \) contribution to MO 173 \( \approx (55\%) \) increased substantially relative to that of the two oxo-bridged geometries. Inversely, the contribution of \( \text{O}(p_x) \) to MO 173 \( \approx (8.8\%) \) was significantly lower for \( \text{Fe}^{3+} – \text{O} – \text{Fe}^{3+}(\text{HBpz})_2 \).

### C. Broken symmetry calculations on \( \text{Fe}^{3+} – \text{O} – \text{Fe}^{3+}(\text{HBpz})_2 \) and \( \text{Fe}^{3+} – \text{OH} – \text{Fe}^{3+}(\text{HBpz})_2 \)

The singlet wave functions of broken space and spin symmetry (\( \Psi_{\text{UKS}}^{\text{U-BPW91/6-311G*}} \)) were spin contaminated and corresponded to an admixture of states with various spin multiplicities. Accordingly, the U-BPW91/6-311G* expectation values of...
the total spin operator\(^{26,87}\) were \(\langle S^2 \rangle_1 = 4.35\) and \(\langle S^2 \rangle_2 = 4.84\) for \(\text{Fe}^{3+}-\text{O}^{2-}-(\text{HBpz})_2\) and \(\text{Fe}^{3+}-\text{OH}-(\text{HBpz})_2\), respectively.\(^{88}\)

The single determinants of broken symmetry were characterized by metal-rich MOs mainly localized on a single iron site. However, important features of some orbitals were their additional contributions from bridging ligands and delocalization tails toward the other iron site. Figures 9–11 show some \(d\)-type \(\alpha\) orbitals mainly localized on the left (Fe1) site of the oxo- and hydroxo-bridged complexes. The corresponding set of \(\beta\) orbitals (not shown) were mainly localized on the right (Fe2) site and, otherwise, had an equivalent description.

\[\begin{alignat}{2}
1. \text{Localized molecular orbitals of} & \quad \text{Fe}^{3+}-\text{O}^{2-}-(\text{HBpz})_2 \\
\text{Three occupied MOs involved bonding interactions} & \quad \text{of} \quad \text{Fe} \quad \text{atomic orbitals} \quad (d_{z^2}, d_{yz}, d_{xz}) & \quad \text{with} \quad \text{the} \quad \text{three} \quad \mu.\quad \text{O} (p_{\parallel}, p_{\perp}, p_z) \quad \text{orbitals}. \quad \text{Three additional occupied, higher} & \quad \text{energy MOs involved the corresponding antibonding} \quad \text{interactions}. \quad \text{The other two iron orbitals did not interact strongly} & \\
\quad \text{with} \quad \text{the} \quad \text{o xo} \quad \text{bridge}. \quad \text{Instead, MO} \quad 145\alpha & \quad \text{had} \quad \text{mainly} \quad d_{z^2} - y^2 \quad \text{composition} \quad \text{and}, \quad \text{although} \quad \text{nominally nonbonding}, \quad \text{was delocalized} & \\
\text{toward} \quad \text{the} \quad \text{acetato} \quad \text{bridges}. \quad \text{MOs} \quad 139\alpha \quad \text{and} \quad 171\alpha & \quad \text{had} \quad d_{xy} \quad \text{character} \quad \text{and} \quad \text{included} \quad \text{bonding} \quad \text{and} \quad \text{antibonding interactions}, \quad \text{respectively,} & \\
\text{with} \quad \text{the} \quad \text{nitrogen} \quad \text{and} \quad \mu-\text{acetato} \quad \text{ligands} \quad \text{in} \quad \text{the} \quad \text{local} \quad \text{axial} \quad (i.e., \quad xy) & \quad \text{planes}. \quad \text{The} \quad \text{occupied} \quad \alpha \quad \text{orbitals} & \\
\text{involved} \quad \text{in} \quad \text{molecular magnetism} \quad \text{are} \quad \text{shown} \quad \text{in} \quad \text{Figs.} \quad 9–12 & \quad \text{and} \quad \text{have} \quad \text{been} \quad \text{extensively} \quad \text{described} \quad \text{in} \quad \text{the} \quad \text{Supplementary} & \\
\text{material}. & \\
\end{alignat}\]

\[\begin{alignat}{2}
2. \text{Localized molecular orbitals of} & \quad \text{Fe}^{3+}-\text{OH}^{2-}-(\text{HBpz})_2 \\
\text{There were similarities but also significant differences} & \quad \text{between} \quad \text{interactions} \quad \text{of} \quad \text{Fe} (d) \quad \text{and} \quad \text{bridging} \quad \text{orbitals} \quad \text{in} \quad \text{the} \quad \text{oxo-} & \\
\text{and} \quad \text{hydroxo-bridged} \quad \text{complexes}. \quad \text{In both cases, metal-} & \quad \text{rich} \quad \text{MOs involved bonding} \quad \text{and} \quad \text{antibonding} \quad \text{interactions} \quad \text{of} \quad \text{Fe} (d_{z^2}) \quad \text{and} \quad \text{Fe} (d_{xz}) \quad \text{with} & \\
\text{bridging} \quad \text{O3} (p) \quad \text{orbitals}. \quad \text{However,} & \quad \text{in} \quad \text{sharp} \quad \text{contrast} \quad \text{to} \quad \text{Fe}^{3+}-\text{O}^{2-}-(\text{HBpz})_2 & \\
\text{the} \quad \text{other} \quad \text{two} \quad \text{orbitals} \quad \text{of} \quad \text{each} \quad \text{iron} \quad \text{were} \quad \text{essentially} & \quad \text{isolated} \quad \text{from} \quad \text{the} \quad \text{hydroxo} \quad \text{bridge} \quad \text{and} \quad \text{their} \quad \text{MOs} \quad \text{had} \quad \text{similar} & \\
\text{compositions} \quad \text{to} \quad \text{those} \quad \text{corresponding} \quad \text{to} \quad \text{Fe}^{3+}-\text{OH}^{2-}-(\text{HBpz})_2 & \quad \text{MO} \quad 145\alpha \quad \text{had} \quad \text{substantial} \quad d_{z^2} - y^2 \quad \text{character} \quad \text{and} \quad \text{was} \quad \text{delocalized} & \\
\text{toward} \quad \text{the} \quad \text{acetato} \quad \text{bridges}, \quad \text{whereas} \quad \text{MOs} \quad 127\alpha \quad \text{and} & \quad \text{172\alpha} \quad \text{had} \quad d_{xy} \quad \text{character} \quad \text{and} \quad \text{revealed} \quad \text{bonding} \quad \text{and} \quad \text{antibonding} & \\
\text{interactions}, \quad \text{respectively,} \quad \text{with} \quad \text{nitrogen} \quad \text{and} \quad \mu-\text{acetato} \quad \text{oxygens} \quad \text{in} \quad \text{the} \quad (xy) \quad \text{planes}. \quad \text{The} \quad \text{magnetic} \quad \text{orbitals} \quad \text{have} & \\
\text{been} \quad \text{described} \quad \text{in} \quad \text{the} \quad \text{Supplementary} \quad \text{material}. & \\
\end{alignat}\]
D. Atomic charges and spin densities

The distributions of molecular charge are shown in Table III. We found fairly close agreement between results derived from U-BPW91, U-B3LYP, and U-MPW1PW91 wave functions. The latter two (i.e., hybrid) methods produced a slightly greater charge polarization; however, all functionals yielded similar trends.

The molecular (C2v) symmetry imposed charge equivalence between the two iron cations of each complex. For the high-spin (Ψ11KS) states the positive charge was mainly assigned to the Fe ions. Carbons from μ-acetato bridges were also found to be positively charged. By contrast, all six atoms coordinated to the cations exhibited negative charges. Oxygens corresponding to μ-oxo and μ-hydroxo groups also found to be positively charged. By contrast, all six atoms coordinated to the cations exhibited negative charges. Oxygens corresponding to μ-oxo and μ-hydroxo groups.

FIG. 8. Energies and main composition of frontier molecular orbitals corresponding to the high-spin (Ψ11KS, U-BPW91/6-311G*) wave function of Fe3+-OH–Fe3+(HBpz3)2. Orbital energies and C2v labels are given in Supplementary Table III. S and A indicate symmetric and antisymmetric combinations of metal d orbitals.

TABLE III. NPA atomic charge and spin densities calculated from broken symmetry (Φ1KS) and high-spin (Φ11KS) wave functions at the U-BPW91/6-311G* level.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Φ1KS</th>
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<th>Φ1KS</th>
<th>Φ11KS</th>
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<th>Φ11KS</th>
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<td>Spin</td>
<td>Charge</td>
<td>Spin</td>
<td>Charge</td>
<td>Spin</td>
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<td>-0.427</td>
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<td>-0.401</td>
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<td>+0.823</td>
<td>0.000</td>
</tr>
</tbody>
</table>
were the most negative whereas those corresponding to \(\mu\)-acetatos had lesser negative charges. The nitrogens of the HBpz\(_3\) ligands were the least negative. Similar trends were found for both complexes, Fe\(^{3+}\)-OH–Fe\(^{3+}\) (HBpz\(_3\))\(_2\) being slightly more polarized in the Fe1–O3–Fe2 plane. This was consistent with the longer Fe–O3 bond lengths and, therefore, more ionic nature of the hydroxo-bridged complex. Remarkably, consistent with molecular geometries, the NPA\(^{82}\) charge analysis made a slight distinction between N9,15 and

the other nitrogens bound to iron. Charge distributions corresponding to low-spin broken-symmetry (\(\Psi\)\(^{1KS}\), U-BPW91/6-311G\(^*\)) states were qualitatively similar to those of high-spin states but, in the case of Fe\(^{3+}\)-O–Fe\(^{3+}\) (HBpz\(_3\))\(_2\), somewhat less polarized. This was only slightly noticeable for the low-spin state of Fe\(^{3+}\)-OH–Fe\(^{3+}\) (HBpz\(_3\))\(_2\) which had a distribution of charge fairly close to that of the high-spin state.

The polarization of molecular charge was also reflected in the occupancy of the s, p, and d shells of each binuclear core. Electronic configurations were calculated within the natural population (NPA) framework.\(^{82}\) The results obtained for Fe\(^{3+}\)-O–Fe\(^{3+}\) (HBpz\(_3\))\(_2\) (Fe1:2.4s\(^{0.29}\)s\(^{2}\)d\(^{5.9}\), O: 2s\(^{1.82}\)p\(^{4.99}\)) and those of Fe\(^{3+}\)-OH–Fe\(^{3+}\) (HBpz\(_3\))\(_2\) (Fe1:2.4s\(^{0.30}\)d\(^{5.82}\), O:H:1s\(^{1.05}\)) showed subtle, but meaningful, differences. However, the configurations of both complexes revealed relatively high occupancies for their nominally ferric ions. This reflected the donating character of the N\(_3\)O\(_3\) coordination.

Table III also shows the distribution of molecular spin. All atoms in the table displayed positive (\(\alpha\)) spin density for the high-spin (\(\Psi\)\(^{1KS}\)) states. Most of this density was localized on each of the two equivalent iron ions: +4.103 and +4.150 units for Fe\(^{3+}\)-O–Fe\(^{3+}\) (HBpz\(_3\))\(_2\) and Fe\(^{3+}\)-OH–Fe\(^{3+}\) (HBpz\(_3\))\(_2\), respectively. The bridging O3 had significant density localized in the first complex (+0.797) but a lesser amount in the second (+0.276). The spin associated with the other atoms bound to iron was rela-
spin wave functions (\(C_i\)) to the pairwise contributions to the antiferromagnetic symmetry. In particular, such wave functions can be dependent and complementary model that can provide additional information. In particular, such wave functions can reveal intermetallic interactions between atomic orbitals of different local symmetry (i.e., mixed-symmetry pathways). Metal-rich broken-symmetry orbitals of different spin index (i.e., \(\alpha\) or \(\beta\)) are not, in general, orthogonal to each other and are mainly localized on Fe1 (\(\phi_{\alpha_1}^i\)) or Fe2 (\(\phi_{\beta_1}^i\)). Thus broken-symmetry orbitals constitute an approximation to the natural magnetic orbitals (NMO) defined by Girerd and Kahn\(^{22,46}\) and, to this extent, can be analyzed in terms of their overlaps \(S_{ij} = \langle \phi_{\alpha_i}^i | \phi_{\beta_j}^j \rangle\). Within the NMO framework, the overlaps \(S_{ij}\) are intimately related to the strength of antiferromagnetic spin coupling.\(^{46}\)

1. \(\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+} (\text{HBpz}_3)^2\)

The \(\Delta_j^\beta\) splittings calculated for the oxo-bridged complex (Fig. 3) and the Hay–Hoffman model\(^{21}\) indicated the presence of four main antiferromagnetic same-symmetry superexchange pathways. The main three involved intermetallic interactions via the oxo bridge and contributed to the molecular antiferromagnetism in the following order: Fe1(d\(_4\))–\(\mu\cdot\text{O}(p_x)\cdot\text{Fe2}(d_{2z})\), Fe1(d\(_y\))–\(\mu\cdot\text{O}(p_y)\cdot\text{Fe2}(d_{2x})\), and Fe1(d\(_z\))–\(\mu\cdot\text{O}(p_z)\cdot\text{Fe2}(d_{2z})\). According to the \(\Delta_j^\beta\) values, the first pathway was clearly dominant. The latter two, however, were more comparable and made fairly similar contributions to the antiferromagnetic ordering. In addition, a fourth pathway had a lesser but noticeable contribution and involved the other bridging ligands: Fe1(d\(_x\)–\(\mu\cdot\text{acetato})\cdot\text{Fe2}(d_{2z})\). The main antiferromagnetic orbital interactions of \(\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+} (\text{HBpz}_3)^2\) were also inferred from overlaps calculated from the broken-symmetry wave function (Table IV). The broken-symmetry results were consistent with those inferred from the full-symmetry wave function since the former also included the four pathways of equal local symmetry. Significantly, the broken-symmetry results indicated that the relative importance of the four same-symmetry pathways followed, in general, the same trends indicated above.

By applying the \((\epsilon_{Si} - \epsilon_{Ai})^2\) model to high-spin fully symmetric wave functions we identified the main interactions between Fe1(d\(_i\)) and Fe2(d\(_j\)) orbitals of equal local symmetry (i.e., same-symmetry pathways). The analysis of low-spin broken-symmetry wave functions constitutes an independent and complementary model that can provide additional information. In particular, such wave functions can reveal intermetallic interactions between atomic orbitals of different local symmetry (i.e., mixed-symmetry pathways). Metal-rich broken-symmetry orbitals of different spin index (i.e., \(\alpha\) or \(\beta\)) are not, in general, orthogonal to each other and are mainly localized on Fe1 (\(\phi_{\alpha_1}^i\)) or Fe2 (\(\phi_{\beta_1}^i\)). Thus broken-symmetry orbitals constitute an approximation to the natural magnetic orbitals (NMO) defined by Girerd and Kahn\(^{22,46}\) and, to this extent, can be analyzed in terms of their overlaps \(S_{ij} = \langle \phi_{\alpha_i}^i | \phi_{\beta_j}^j \rangle\). Within the NMO framework, the overlaps \(S_{ij}\) are intimately related to the strength of antiferromagnetic spin coupling.\(^{46}\)

### Table IV. Absolute values of overlaps calculated from broken symmetry molecular orbitals of \(\Psi_{1}^{\text{UKS}}\)

<table>
<thead>
<tr>
<th>Main character of MOs</th>
<th>(\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+} (\text{HBpz}_3)^2)</th>
</tr>
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<td>(\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+} (\text{HBpz}_3)^2)</td>
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</tr>
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<td>(\text{Fe}^{3+} - \text{OH} - \text{Fe}^{3+} (\text{HBpz}_3)^2)</td>
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<tr>
<td>(\text{Fe}^{3+} - \text{OH} - \text{Fe}^{3+} (\text{HBpz}_3)^2)</td>
<td>0.2114</td>
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</table>

V. DISCUSSION

### A. Microscopic mechanisms of spin coupling

To identify some main atomic orbital interactions involved in antiferromagnetic superexchange we first considered delocalized MOs of the fully symmetric (\(C_{2v}\)) high-spin wave functions (\(\Psi_{1}^{\text{UKS}}\)). In particular, we focused on the differences in energy, \(\Delta_i = (\epsilon_{Si} - \epsilon_{Ai})\), of MOs corresponding to symmetric (\(S\)) and antisymmetric (\(A\)) combinations of Fe(d\(_i\)) orbitals. According to a model presented by Hay, Hoffman et al.,\(^{21}\) such energy differences are particularly sensitive to geometric distortions and substituent effects in bimetallic molecules.\(^{21}\) These authors also showed\(^{21}\) that the squares of these parameters, \((\epsilon_{Si} - \epsilon_{Ai})^2\) are directly proportional to the pairwise contributions to the antiferromagnetic component (\(J_{AA}\)) of the Heisenberg exchange constant (Sec. II).\(^{21,22}\) Here, the subscripts \(i\) represent the local (i.e., monomeric) symmetry of the atomic orbitals.

By applying the \((\epsilon_{Si} - \epsilon_{Ai})^2\) model to high-spin fully symmetric wave functions we identified the main interactions between Fe1(d\(_i\)) and Fe2(d\(_j\)) orbitals of equal local symmetry (i.e., same-symmetry pathways). The analysis of low-spin broken-symmetry wave functions constitutes an independent and complementary model that can provide additional information. In particular, such wave functions can reveal intermetallic interactions between atomic orbitals of different local symmetry (i.e., mixed-symmetry pathways). Metal-rich broken-symmetry orbitals of different spin index (i.e., \(\alpha\) or \(\beta\)) are not, in general, orthogonal to each other and are mainly localized on Fe1 (\(\phi_{\alpha_1}^i\)) or Fe2 (\(\phi_{\beta_1}^i\)). Thus broken-symmetry orbitals constitute an approximation to the natural magnetic orbitals (NMO) defined by Girerd and Kahn\(^{22,46}\) and, to this extent, can be analyzed in terms of their overlaps \(S_{ij} = \langle \phi_{\alpha_i}^i | \phi_{\beta_j}^j \rangle\). Within the NMO framework, the overlaps \(S_{ij}\) are intimately related to the strength of antiferromagnetic spin coupling.\(^{46}\)
mixed-symmetry pathways were equal and their magnitude suggested that their efficiencies were slightly greater than three out of four same-symmetry interactions.

In summary, orbital interactions inferred from both full-symmetry and broken-symmetry models were fairly consistent with each other. Based on the combined results of high-spin and low-spin calculations we have identified six main antiferromagnetic superexchange (i.e., bridge-mediated) pathways. Four of these corresponded to interactions between Fe(d) orbitals of equal local symmetry and two to interactions between Fe(d) orbitals of different local symmetry. Furthermore, five out of six pathways originated from intermetallic interactions via the oxo bridge and one via the bridging acetates. For Fe^3+–O–Fe^3+ (HBpz)_2, both models indicated that the main agent of antiferromagnetism was the same-symmetry pathway Fe1(d_xz):μ-O(p_y):Fe2(d_yz).

Overlaps derived from broken-symmetry calculations also provided insight about interactions between μ-O(p) and Fe(d) electrons of opposite spin. For Fe^3+–O–Fe^3+ (HBpz)_2 the larger overlaps corresponded to interactions with the following approximate symmetries: μ-O(p^a_y):Fe2(d^β_y) ((143α|172β)), μ-O(p^a_x):Fe2(d^β_z) ((168α|144β)), and μ-O(p^a_y):Fe2(d^β_z) ((125α|172β)). All of these were visualized as bonding interactions between the bridging oxygens and minor contributions from Fe2 in MOs of these were visualized as bonding interactions between the interacting pathways. This latter pathway, however, was of greater relative importance for the antiferromagnetic ordering of Fe^3+–O–Fe^3+ (HBpz)_2 since Δ^β_d was comparable to splittings corresponding to other (i.e., oxo-bridged) intermetallic interactions.

3. Fe^3+–OH–Fe^3+ (HBpz)_2

The Δ^β_d splittings calculated for the hydroxo-bridged complex (Fig. 8) indicated the presence of four main same-symmetry superexchange pathways. Three of these involved intermetallic interactions via the hydroxo bridge and one through the μ-acetato groups. In terms of the antiferromagnetic ordering, the relative importance of these same-symmetry pathways was as follows: Fe1(d_yz):μ-OH(p_y):Fe2(d_yz), Fe1(d_yz):μ-OH(p_y):Fe2(d_yz), Fe1(d_yz):μ-OH(p_y):Fe2(d_yz), and Fe1(d_yz):μ-OH(p_y):Fe2(d_yz). The first interaction was dominant, whereas the latter two had more comparable contributions. Quite remarkably, the main trends derived from the broken-symmetry model were the same. In fact, for Fe^3+–OH–Fe^3+ (HBpz)_2, the overlaps (Table IV) between broken-symmetry orbitals also indicated that, out of four same-symmetry interactions, Fe1(d_yz):μ-OH(p_y):Fe2(d_yz) was the strongest, whereas Fe1(d_yz):μ-OH(p_y):Fe2(d_yz) was the weakest.

To distinguish the effects of the presence of a proton on the oxo bridge from those of concomitant geometric variations that occur upon protonation (i.e., second structural variable), we compared results obtained for Fe^3+–OH–Fe^3+ (HBpz)_2 and Fe^3+–O–Fe^3+ (HBpz)_2. The isolated effects of this second variable were clearly assessed by comparing the Δ^β_d splittings of Figs. 7 and 8. Such a comparison showed that a main effect was to significantly stabilize MO 173β, thus reducing Δ^β_d. This effect was related to a noticeable localization of MO 173β on the metals and, correspondingly, a smaller contribution from the bridging μ-OH (Supplementary Tables II and III). Therefore, within the framework of the (ε_Si−ε_Ai)^2 model, the sole presence of the proton (i.e., not including geometric variations) was accompanied by a significantly less efficient Fe1(d_yz):μ-OH(p_y):Fe2(d_yz) pathway and, consequently, a weaker molecular antiferromagnetism. This appears to be the dominant effect as we noted only a minor variation in the Δ^β_d splittings of the other same-symmetry pathways. Further insight was given by the composition of broken-symmetry

tings of these two structures we identified significant variations in the efficiency of three exchange pathways. The main effects were seen for Fe1(d_yz):μ-O(p_y):Fe2(d_yz) and Fe1(d_yz):μ-O(p_y):Fe2(d_yz) whose Δ^β_d splittings decreased with increasing Fe–μO distances. A similar but less pronounced effect was found for Fe1(d_yz):μ-O(p_y):Fe2(d_yz). Therefore, these three pathways, in that order, became less efficient via of molecular antiferromagnetism as the geometric parameters of Fe^3+–O–Fe^3+ (HBpz)_2 were imposed. By contrast, there was only a slight increment in Δ^β_d indicating that the intermetallic interaction corresponding to Fe1(d_yz):μ-O(acetato):Fe2(d_yz) was not significantly affected by the same geometric variations. This latter pathway, however, was of greater relative importance for the antiferromagnetic ordering of Fe^3+–O–Fe^3+ (HBpz)_2 since Δ^β_d was comparable to splittings corresponding to other (i.e., oxo-bridged) intermetallic interactions.

2. Fe^3+–O–Fe^3+ (HBpz)_2

Conversion from oxo- to hydroxo-bridging is associated with variations of two intimately related, but different, structural variables: (i) geometric parameters (e.g., Fe–μO distances and Fe1–μO–Fe2 angles) and (ii) the presence of the proton. One main objective of our study was to probe the distinct effects of these two variables. Toward this end, we performed calculations on the oxo-bridged structure Fe^3+–O–Fe^3+ (HBpz)_2 which corresponded to the optimized geometry of Fe^3+–OH–Fe^3+ (HBpz)_2 with the proton on the bridge being absent. By focusing on the absolute values of Δ^β_d for the three structures studied in this work we obtained a semiquantitative measure of the isolated effects of the two structural variables. The effects of the first variable (i.e., geometry) on the delocalized orbitals were clearly observed by comparing Figs. 3 and 7. As inferred below (Sec. V C), these effects were essentially related to the different Fe–μO bond lengths of Fe^3+–O–Fe^3+ (HBpz)_2 and Fe^3+–O–Fe^3+ (HBpz)_2. Based on the different Δ^β_d split-
MO 135α of Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$ (Supplementary material) which, in contrast to MO 144α of Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$, also showed some delocalization toward the HBpz groups and, consequently, a smaller overlap of Fe1 with the other iron site.

The combined effects of geometry and protonation were visualized by comparison of results obtained for Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$ and Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$. Both models, that is (ε$_{\text{Si}}$ – ε$_{\text{Ai}}$)$^2$ (Figs. 3 and 8) and broken-symmetry (Table IV), revealed some significant differences between the antiferromagnetic interactions of the two complexes. Although both molecules displayed similar same-symmetry interactions, the absolute and/or relative contributions to their antiferromagnetic couplings were markedly different. The main difference lied in the same-symmetry interactions involving Fe1($d_{xy}$) orbitals. At a qualitative level, this was seen in the broken-symmetry MOs of Fig. 11 which provided a pictorial and intuitive representation of the π interactions between Fe1($d_{xy}$) and μ-O(p$_{z}$). The figure shows how MO 135α of Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$ was more localized on the metals than MO 144α of Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$. In addition to qualitative insight about bridge-mediated intermetallic interactions, the two models also provided a semiquantitative measure of their importance. For example, the strongest interaction in Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$, Fe1($d_{xy}$):μ-O(p$_{z}$):Fe2($d_{xy}$), was associated with a Δ$_{\text{B}}^2$ value of 1.104 eV and a broken-symmetry overlap of 0.476. By contrast, the strongest interaction in Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$, Fe1($d_{xy}$):μ-OH(p$_{z}$):Fe2($d_{xy}$), was associated with a Δ$_{\text{B}}^2$ value of 0.469 eV and a broken-symmetry overlap of 0.275.

Important differences were also noted in the mixed-symmetry pathways of Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$ and Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$. We did not find, by simple inspection of the Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$ orbitals, an occupied mixed-symmetry pathway with composition Fe1($d_{xy}$):μ-OH(p$_{z}$):Fe2($d_{xy}$) and which was mainly centered on Fe1. Instead, Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$ displayed the highly stabilized MO 107α (Fig. 10), an orbital that was mainly localized on the bridging hydroxide. Such stabilization and bridge localization were clearly due to a strong bonding interaction between μ-OH(p$_{z}$) and H(s) orbitals. At the same time, protonation resulted in a fair localization of MO 144α (Fig. 10) which had main Fe1($d_{xy}$) character and only a very minor contribution from the bridging μ-OH.

Therefore, the composition of MOs 107α and 144α strongly suggested that two vias of antiferromagnetism (i.e., the mixed-symmetry pathways) which were very important, although not dominant, in Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$, were significantly less efficient in Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$. This view derived from simple inspection of the molecular orbitals was consistent with the more quantitative insight provided by overlaps calculated between MOs of mainly Fe1,2($d_{xy}$) and Fe2,1($d_{xy}$) composition. These overlaps showed significantly lower values for Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$ (Table IV). It should be emphasized that the previous comparisons were made between broken-symmetry wavefunctions calculated at exactly the same level of theory for both complexes. Such comparisons should provide reliable trends of atomic orbital interactions in the two closely related molecules.

The one-electron energies (Figs. 3 and 8) strongly suggested a different ordering for the atomic orbitals of $t_{2g}$ parentage in Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$ and Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$. The main antiferromagnetic superexchange pathways, which were consistent with (ε$_{\text{Si}}$ – ε$_{\text{Ai}}$)$^2$ splittings and (φ$_{i,l}$|$d_{j}^\alpha$) overlaps, are summarized in Scheme 2 (not drawn to scale). Here, μO and μAcet. represent the specific intervening bridges and the dashed boxes identify the dominant interaction in each complex. A more detailed estimate of the relative importance of the various pathways can be inferred from Figs. 3 and 8 and Table IV as discussed above.

### B. Atomic spin densities

The distinct spatial localization of spin density on each of their paramagnetic fragments (e.g., metal cations, organic radicals) is an important characteristic of spin coupled complexes. In particular, in ferromagnetic states the individual fragments have parallel and, at the same time, significant net spin density. Thus, for Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$ and Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$, the positive signs and magnitudes of the spin densities in the $\Psi_{\text{UKS}}$ states (Table III) were consistent with ferromagnetic spin coupling between two high-spin ferric ions. The nominal high-spin configuration of oxo-bridged diferric cores (in units of unpaired spins) is Fe1($S_1 = 5$)–O–Fe2($S_2 = 5$). This useful, but simple, description idealizes a system having five unpaired electrons localized on each metal ion and no unpaired electrons on the diamagnetic bridging ligand. By contrast, results derived from density functional calculations allowed us to describe the high-spin states with significantly greater detail, namely Fe1($S_1 = 4.10 \pm 0.43$)–O–Fe2($S_2 = 4.10 \pm 0.43$) for Fe$^{3+}$–O–Fe$^{3+}$(HBpz)$_2$ and Fe1($S_1 = 4.15 \pm 0.43$)–OH–Fe2($S_2 = 4.15 \pm 0.43$) for Fe$^{3+}$–OH–Fe$^{3+}$(HBpz)$_2$. Here, the numbers to the left (U-BPW91) and right (U-MPW1PW91) of the arrows represent a range determined from two highly representative exchange-correlation density functionals.

As discussed in Sec. II, the spin distribution of the singlet states (\$\Psi_{\text{UKS}}^\text{S}\$) mimicked the open-shell singlet structure of the antiferromagnetically coupled binuclear complexes. The net $\alpha$ and $\beta$ spin localized on the otherwise identical iron ions was consistent with the experimentally established antiferromagnetism of the complexes. The magnitude of the local densities (Table III)
allowed us to describe the antiferromagnetic core of Fe$_{3}^{3+}$–O–Fe$_{3}^{3+}$ (HBpz)$_{2}$ as Fe$_{1}(S_{1} = \pm 3.83 \pm 4.28)$ –O(S = 0)–Fe$_{2}(S_{2} = \pm 3.83 \pm 4.28)$ and that of Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$ as Fe$_{1}(S_{1} = \pm 4.08 \pm 4.39)$ –OH(S = 0)–Fe$_{2}(S_{2} = \pm 4.08 \pm 4.39)$. The ± signs of Fe1 and Fe2, respectively, represented the two possible solutions of broken symmetry. There was a meaningful increment in the absolute values of metallic spin density upon protonation (=0.25 units for each ion). This reflected the more ionic character of Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$ relative to Fe$_{3}^{3+}$–O–Fe$_{3}^{3+}$ (HBpz)$_{2}$ and was consistent with the longer Fe–O3 bond lengths (Table I) and slightly greater metallic charge of the former (Table III).

In this regard, two points should be mentioned: (i) The total calculated molecular spin was +10 units for $\Psi_{11}^{\text{UKS}}$ and 0 units for $\Psi_{11}^{\text{SKS}}$. These were necessary and exact results for our calculations since they imposed convergence to high-spin and low-spin states, respectively. The spatial distribution of spin, however, was not known a priori and corresponded to the net molecular spin density, $\rho^{s}(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) - \rho^{\beta}(\mathbf{r})$, of each complex. A useful and highly informative idealization of $\rho^{s}(\mathbf{r})$ is given by atomic densities derived from partitioning analyses such as NPA.

(iii) Spin-unrestricted density functional theory is capable of yielding nearly fully spin-polarized descriptions for spin-coupled complexes with fairly localized unpaired electrons. For such complexes, the calculated densities of each individual paramagnetic fragment are very close to their nominal spin state. Therefore, we view as significant the fact that densities calculated for individual iron ions in Fe$_{3}^{3+}$–O–Fe$_{3}^{3+}$ (HBpz)$_{2}$ and Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$ were somewhat lower than their nominal ($S = 5$) values. This reflected the fair degree of delocalization of some valence Fe($d$) and $\mu$-O($p$) electrons, particularly in the former complex.

### C. Heisenberg exchange constants and magnetostructural correlations

The exchange couplings calculated from Eq. (3) are given in Table V. The predicted values had positive signs indicating that both complexes had antiferromagnetic ground states. This was in agreement with the experimentally established antiferromagnetism of the complexes. The predicted values for Fe$_{3}^{3+}$–O–Fe$_{3}^{3+}$ (HBpz)$_{2}$ and Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$ were +122 cm$^{-1}$ and +23.3 cm$^{-1}$, respectively ($J_{\mu \cdot \mu} = 0.15$). These values can be compared with those determined from susceptibility experiments, namely +242 cm$^{-1}$ and +34 cm$^{-1}$, respectively ($J_{\mu \cdot \mu} / J_{\mu \cdot \mu} = 0.14$). Therefore, the theoretical values reproduced extremely well the trends observed in the two complexes. Similar trends have been observed experimentally in a variety of binuclear complexes and diiron-oxo proteins where the exchange constant drops by an order of magnitude upon protonation of the $\mu$-oxo bridge.

The predicted $J$ values for the oxo- and hydroxo-bridged complexes differed by 37% and 27%, respectively, from their experimental values. These differences between theoretical and experimental values, the former being lower, were mainly attributed to the slightly longer calculated Fe–$\mu$O distances (Table I). Accordingly, the theoretical-experimental discrepancy was lower for Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$ for which closer agreement was obtained between calculated and x-ray Fe–$\mu$O distances. In spite of these differences, theoretical and experimental $J$ values were remarkably close. The fact that fairly close theoretical-experimental agreement was obtained with the same methodology for two different coupling regimes (i.e., strong and weak antiferromagnetism) was particularly striking. This may be further appreciated if one considers that for Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$ the absolute value of the total molecular (SCF-DFT) energy was 98.0 $\times 10^{7}$ cm$^{-1}$ whereas $J$ was only 23.3 cm$^{-1}$. Consequently, the parameters of Table V involved the prediction of energies that, in comparison to the total molecular energies, were very small.

The prediction of Heisenberg exchange constants for binuclear metal complexes has traditionally been a challenging theoretical problem. While fairly accurate parameters have been obtained from experiment (e.g., magnetic susceptibility), theoretical values have mostly been an approximation, often giving only the right order of magnitude. This has been particularly true for weakly coupled $\mu$-hydroxo-bridged complexes, such as Fe$_{3}^{3+}$–OH–Fe$_{3}^{3+}$ (HBpz)$_{2}$, for which even prediction of the correct sign of $J$ was not generally achieved. Thus the values presented in this work (Table V) represented significant progress toward the accurate prediction of signs, trends, and magnitudes of Heisenberg exchange constants. To our knowledge, the combined accuracy of our predictions for ($\mu$-O)bis($\mu$-acetato) and ($\mu$-OH)bis($\mu$-acetato) diiron complexes is unprecedented. This suggests that the exchange-correlation and spin projection schemes described in Sec. II constitute a robust methodology with wide applicability.

The optimized U-BPW91 geometries (Table I) displayed a Fe–O3 bond 0.164 Å longer and an Fe1–O3–Fe2 angle...
3.4° more acute for the protonated complex. Further calculations on simple three (Fe$^{3+}$-O-Fe$^{3+}$) and four (Fe$^{3+}$-OH-Fe$^{3+}$) atom models, with varying geometric parameters, revealed that a Fe-$\mu$O increment of 0.164 Å has a large effect on the strength of spin coupling (i.e., decreasing $J$ by 85.4%), whereas the corresponding angular variation of $-3.4°$ had only a minor effect (i.e., increasing $J$ by 1.6%).

The calculated $J$ values for the actual complexes and simplified three and four atom models followed similar trends. Thus in analogy to the distance and angular dependence of Fe$^{3+}$-O-Fe$^{3+}$, we could attribute the effects of geometry on the antiferromagnetism of Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$ and Fe$^{3+}$-OH-Fe$^{3+}$ (HBpz$_3$)$_2$ to be almost entirely related to variations in Fe-$\mu$O distances and not to small Fe1-$\mu$O-Fe2 angular variations.

D. The magnetism of diiron-oxo proteins: Azidomet-hemerythrin

While part of our previous discussion should apply to the physiologically important oxy-Hr and deoxy-Hr, one should notice that these forms have some differences in comparison to Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$ and Fe$^{3+}$-OH-Fe$^{3+}$ (HBpz$_3$)$_2$, respectively. In oxy-Hr, one of its iron sites is bound to a terminal hydroperoxide which, being a fairly strong-field ligand, should perturb the electronic structure of that iron. Deoxy-Hr is in the diferrous state and one of its iron sites is only five coordinate. For these reasons, we shall focus on the azido forms of hemerythrin which, in comparison to Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$, have similar (i.e., $N_5O_4$) coordination around the immediate environment of their iron sites.

Azidomet-Hr and azidometmyo-Hr contain an azide anion bonded to the iron site which is otherwise occupied by hydroperoxide in oxy-Hr. Recent theoretical studies have shown that, in comparison to stronger-field ligands such as NO or O$_2$, the azido anions behave as weak-field ligands that do not significantly perturb the electronic structure of the iron sites. This is consistent with observed Mössbauer isomer shifts and quadrupole splittings which are the same for the two iron sites of azidomet-Hr. Thus a fairly similar electronic structure is expected for the diferrous cores of azidomet-Hr, azidometmyo-Hr, and Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$, all of their iron sites having $N_5O_4$ coordination. This fact, in conjunction with the similarity in geometric and susceptibility parameters among these three structures, implied that the same essential antiferromagnetic mechanisms outlined above (Scheme 2-a) for Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$ are also at work in the two biological systems. Therefore, our results allowed us to conclude that six main superexchange pathways are present in azidomet-Hr and azidometmyo-Hr. The five main interactions should occur via the oxo bridge and one via the $\mu$-carboxylato groups. In particular, the strongest and weakest interactions should be Fe1($d_{z^2}$):$\mu$-O(1):Fe2($d_{z^2}$) and Fe1($d_{z^2}$-2,$g$):bis($\mu$-carboxylato):Fe2($d_{z^2}$-2,$g$), respectively.

E. The magnetism of Fe$^{3+}$-O-Fe$^{3+}$ (Me$_3$TACN)$_2$ and Fe$^{2+}$-OH-Fe$^{2+}$ (Me$_3$TACN)$_2$

Oxo-bis(acetato)-bridged diferrous and diferrous complexes containing facially coordinating Me$_3$TACN ligands have been synthesized and characterized by Hartman et al. Both complexes display a distorted biocathedal structure with all iron sites having $N_5O_4$ coordination. Thus the binuclear cores of the compounds containing Me$_3$TACN capping ligands are structural analogs of the HBpz$_3$-ligated complexes studied in this work. We note that identical experimental Fe-$\mu$O average distances (1.785 Å) and nearly identical exchange constants ($J = +238$ cm$^{-1}$ and +242 cm$^{-1}$) have been reported for Fe$^{3+}$-O-Fe$^{3+}$ (Me$_3$TACN)$_2$, and Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$, respectively. It followed from theoretical, geometric, and experimental considerations, similar to those made above for azidomet-Hr, that the same six antiferromagnetic interactions of Fe$^{3+}$-O-Fe$^{3+}$ (HBpz$_3$)$_2$ were also present in Fe$^{3+}$-O-Fe$^{3+}$ (Me$_3$TACN)$_2$. These interactions are displayed in Scheme 3-a in which Fe1($d_{z^2}$):$\mu$-O($p_g$):Fe2($d_{z^2}$) and Fe1($d_{z^2}$-2,$g$):bis($\mu$-acetato):Fe2($d_{z^2}$-2,$g$) are the dominant and weakest, respectively.

Scheme 3.

Fe$^{2+}$-OH–Fe$^{2+}$ (Me$_3$TACN)$_2$ has an average x-ray Fe-$\mu$O$^H$ distance of 2.065 Å and an experimental exchange constant $J = +26$ cm$^{-1}$. By comparison, Fe$^{3+}$-OH–Fe$^{3+}$ (HBpz$_3$)$_2$ has an average Fe-$\mu$O$^H$ distance of 1.956 Å and an exchange constant of $J = +34$ cm$^{-1}$. Thus the somewhat longer Fe-$\mu$O$^H$ distance of the former is qualitatively consistent with its somewhat lower exchange constant. Nevertheless, considering that one complex is high-spin diferrous whereas the other is high-spin diferrite, it is at first surprising that their exchange constants are not markedly different. High-spin Fe$^{2+}$ has four unpaired electrons whereas high-spin Fe$^{3+}$ has five. Thus, one may initially expect that the former will form binuclear cores with a lesser number of exchange pathways and, consequently, substantially weaker antiferromagnetism than the latter. However, this is not observed experimentally.

The magnetic behavior of Fe$^{2+}$-OH–Fe$^{2+}$ (Me$_3$TACN)$_2$ and Fe$^{3+}$-OH–Fe$^{3+}$ (HBpz$_3$)$_2$ is consistent with and can be explained by the mechanism proposed by Rodriguez et al. These authors pointed out that large differences in coupling strength between oxo- and hydroxo-bridged diiron centers are mainly related to the type of bridging ligand and not to the iron oxidation state. More specifically, they stated that a change in oxidation state (i.e., from Fe$^{3+}$ to Fe$^{2+}$) should not drastically alter the magnitude of $J$ as long as the main bridging ligand and exchange pathways remain the same. With the added insight provided by the present calculations, their argument can be applied here as follows. The main pathway in Fe$^{3+}$-OH–Fe$^{3+}$ (HBpz$_3$)$_2$ is formed by Fe($d_{z^2}$) orbitals...
which, as dictated by the local ligand fields, have substantially higher energy than the ground-state Fe(d) orbitals (10Dq ≈ 10^3 cm⁻¹). Upon reduction, at low temperatures, the extra (i.e., sixth) electron of each high-spin Fe²⁺ will populate the ligand field ground state and pair with another electron. This will in turn give rise to a nonmagnetic orbital Fe(d) and, consequently, to the disappearance of the corresponding antiferromagnetic pathway(s). Assuming that the ordering of the d orbitals is the same in Fe³⁺–OH–Fe³⁺(HBpz₂) and Fe⁴⁺–OH–Fe³⁺(Me₃TACN)₂, Fe(dₓ) will become the nonmagnetic orbital upon reduction to the diferrous state. Since for Fe³⁺–OH–Fe³⁺(HBpz₂) the same-symmetry and mixed-symmetry pathways formed by Fe(dₓ) orbitals were not dominant contributors, their disappearance in Fe²⁺–OH–Fe²⁺(Me₃TACN)₂ should not drastically alter the strength of antiferromagnetic coupling. Thus the main antiferromagnetic interactions of Fe²⁺–OH–Fe²⁺(Me₃TACN)₂ can be represented by Scheme 3-b in which Fe₁(dₓz):μ-OH(pₓ):Fe₂(dₓz) is dominant.

VI. CONCLUSION

We have performed a comprehensive study of the electronic structures of Fe³⁺–O–Fe³⁺(HBpz₂), Fe³⁺–O–Fe²⁺(HBpz₂), and Fe³⁺–OH–Fe³⁺(HBpz₂). The first gradient-corrected density functional calculations on the complete molecular structures of these complexes are reported here. The optimized geometries, energies, frontier orbital compositions, atomic charges, and spin densities that emerged from these calculations provided a detailed description of the electronic configurations and magnetic properties of the compounds. We have gained novel insight about the specific and different roles of oxo, hydroxo, and acetato bridges on the molecular magnetism of these diiron complexes. The understanding obtained from this work also helped to explain much of the electronic structure and magnetism of biological diiron centers, in particular, those present in the diiron-oxo proteins azidomet- and azidometmyo-hemerythrin. In addition, our results also explained the different antiferromagnetic behavior of the strongly and weakly coupled Fe³⁺–O–Fe³⁺(Me₃TACN)₂ and Fe²⁺–OH–Fe²⁺(Me₃TACN)₂ complexes, respectively. Signs and magnitudes of Heisenberg exchange constants of oxo- and hydroxo-bis(acetato)-bridged diiron complexes have been predicted with an unprecedented degree accuracy for both strong- and weak-coupling regimes. In what follows, we summarize some of our findings and conclusions:

(i) The strong antiferromagnetism of Fe³⁺–O–Fe³⁺(HBpz₂) arises from the presence of six main superexchange pathways. Four of these correspond to interactions between atomic orbitals of equal local symmetry whereas two arise from interactions between orbitals of different local symmetry. Furthermore, five out of these six intermetallic interactions are mediated by the oxo bridge whereas one is mediated by the acetato groups. The dominant pathway was Fe₁(dₓz):μ-O(pₓ):Fe₂(dₓz) whereas Fe₁(dₓz):μ-O(acetato):Fe₂(dₓz) was the weakest.

(ii) The weak antiferromagnetism of Fe³⁺–OH–Fe³⁺(HBpz₂) originates in six main superexchange pathways that are qualitatively similar to those present in Fe³⁺–O–Fe³⁺(HBpz₂). However, the absolute contributions and/or relative importance of the pathways in these two complexes are significantly different. In Fe³⁺–OH–Fe³⁺(HBpz₂), the contributions to antiferromagnetic ordering from all six pathways are more comparable. Nevertheless, Fe₁(dₓz):μ-OH(pₓ):Fe₂(dₓz) can be considered the dominant pathway whereas those of same-symmetry and mixed-symmetry involving Fe(dₓ) orbitals are weakest. The relative importance of Fe₁(dₓz):μ-O(acetato):Fe₂(dₓz) in Fe³⁺–OH–Fe³⁺(HBpz₂) is approximately the same as that of Fe₁(dₓz):μ-OH(pₓ):Fe₂(dₓz).

(iii) Superexchange interactions mediated by mixed-symmetry pathways contribute significantly to the antiferromagnetism of Fe³⁺–O–Fe³⁺(HBpz₂) but are appreciably less important for Fe³⁺–OH–Fe³⁺(HBpz₂). To the extent that the in-plane dₓz orbitals become nonmagnetic (i.e., doubly occupied) in some biocatalytic diferrous complexes, such as Fe²⁺–OH–Fe²⁺(Me₃TACN)₂, the mixed-symmetry pathways vanish.

(iv) Significantly, magneto-structural correlations derived from the two semiquantitative methods used in this work [i.e., based on (Δg₀ − Δgₐ)² energy differences and ⟨φ₁(1)φ₂(2)⟩ overlaps] are in very close agreement. The latter method also provided an estimate of antiferromagnetic contributions from mixed-symmetry pathways.

(v) In most cases, the bonding and antibonding MOs of broken symmetry follow traditional trends of MO theory, the former being of main ligand character and the latter of metal character. One notable exception are the π-bonding interactions between Fe(dₓz) and μ-O(pₓ) (Fig. 11) which are mainly localized on the metals.

(vi) A variety of geometric parameters and physical quantities, such as Fe–μ-OH bond lengths, atomic charges, and spin densities, reflect a more ionic nature of the Fe³⁺ ions in Fe³⁺–OH–Fe³⁺(HBpz₂) relative to those in Fe³⁺–O–Fe³⁺(HBpz₂).

(vii) Optimized Fe–μ-O and Fe–μ-OH distances as well as the overall electronic structures (e.g., atomic charges) indicate that μ-O behaves as a strong-field ligand whereas μ-OH is a relatively weak-field ligand. The one-electron energies (Figs. 3 and 8) strongly suggest a different ordering for the ligand-field (d) orbitals of t₂g parentage in Fe³⁺–O–Fe³⁺(HBpz₂) and Fe³⁺–OH–Fe³⁺(HBpz₂) (Scheme 2).

(viii) Considerations based on electronic and geometric structures, as well as magnetic susceptibility data, indicate that Fe³⁺–O–Fe³⁺(HBpz₂) models extremely well the microscopic interactions leading to the strong antiferromagnetism of azidomet-Hr and azidometmyo-Hr.

(ix) Schemes 2 and 3 constitute a general guideline for understanding, qualitatively and semiquantitatively, the antiferromagnetism in a variety of (fairly) symmetric biocatalytic diferrous and diferrous centers. Scheme 2a, in particular, models not only the interactions of (μ-O)(μ-acetato) diferrous proteins but, by removing the corresponding pathway, those of (μ-O) biological units that may not have bridging carboxylato. A judicious application of the results presented...
in this work should provide insight into the electronic structure and magnetism of a variety of (bio)inorganic diiron complexes.

(x) The accurate determination of Heisenberg exchange ($J$) in molecular antiferromagnets has traditionally been the realm of experimental techniques. We have performed calculations that allow the prediction of antiferromagnetic strengths with an accuracy that approaches that of the best experimental methods (e.g., SQUID susceptibility). These results suggest that the density functional and spin projection methods described in this work constitute an alternative method for the accurate determination of exchange constants. The results for weakly and strongly coupled diiron complexes also suggest that our methods are robust and may have wide applicability for studies of (bio)molecular magnetism.

Supplementary material is available for four tables containing the optimized Cartesian coordinates of Fe$^{3+}-$O–Fe$^{3+}$ (HBpz)$_2$ and Fe$^{3+}$–OH–Fe$^{3+}$ (HBpz)$_2$. Extensive descriptions of molecular orbitals involved in molecular magnetism.

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APPENDIX: CALCULATION OF HEISENBERG EXCHANGE CONSTANTS

To calculate Heisenberg exchange constants we first assumed that the spin-contaminated $\Psi_{UKS}^{\text{min}+1}$ wave function was a linear combination of the pure (projected) and normalized wave functions of all accessible spin states:

$$\Phi_{UKS}^{\text{min}+1} = \sum_{2S_{\text{min}}+1}^{2S_{\text{max}}+1} C_{2S+1} \Phi_{UKS}^{2S+1}.$$  

(A1)

Second, we made use of the normalization condition that follows from Eq. (A1):

$$\sum_{2S_{\text{min}}+1}^{2S_{\text{max}}+1} C_{2S+1}^2 = 1.$$  

(A2)

Third, the energy and spin expectation values of the contaminated low-spin (e.g., singlet) states were expanded in terms of the corresponding quantities of the projected states:

$$E_{2S_{\text{min}}+1}^{\text{UKS}} = \langle \Phi_{2S_{\text{min}}+1}^{\text{UKS}} | H_{\text{UKS}} | \Phi_{2S_{\text{min}}+1}^{\text{UKS}} \rangle.$$  

(A3)

$$\langle S^2 \rangle_{2S_{\text{min}}+1}^{\text{UKS}} = \langle \Phi_{2S_{\text{min}}+1}^{\text{UKS}} | S^2 | \Phi_{2S_{\text{min}}+1}^{\text{UKS}} \rangle.$$  

(A4)

$$E_{2S_{\text{min}}+1}^{\text{UKS}} = \sum_{2S_{\text{min}}+1}^{2S_{\text{max}}+1} C_{2S+1}^2 E_{2S+1}^{\text{UKS}}.$$  

(A5)

Finally, from Eqs. (A5) and (A6) we determined $E_{2S_{\text{min}}+1}^{\text{UKS}} - E_{2S_{\text{min}}+1}^{\text{UKS}}$. Then, assuming $E_{2S_{\text{min}}+1}^{\text{max}+1} - E_{2S_{\text{min}}+1}^{\text{UKS}}$ (Sec. II) and using Eq. (A2), we arrived at Eq. (3):

$$J = 2 \frac{E_{2S_{\text{min}}+1}^{\text{UKS}} - E_{2S_{\text{min}}+1}^{\text{UKS}}}{\langle S^2 \rangle_{2S_{\text{min}}+1}^{\text{UKS}} - \langle S^2 \rangle_{2S_{\text{min}}+1}^{\text{UKS}}}.$$  

(A6)

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