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Article

Electronic Structure of Bispidine Iron(IV) Oxo Complexes

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The electronic structure, based on DFT calculations, of a range of $Fe^{IV}{=}O$ complexes with two tetra- (L^1 and L^2) and two isomeric pentadentate bispidine ligands (L^3 and L^4) is discussed with special emphasis on the relative stability of the two possible spin states ($S = 1$, triplet, intermediate-spin, and $S = 2$, quintet, high-spin; bispidines are very rigid diazaadamantane-derived 3,7-diazabicyclo[3.3.1]nonane ligands with two tertiary amine and two or three pyridine donors, leading to *cis*-octahedral $[(X)(L)Fe^{IV}{=}O]^{2+}$ complexes, where X = $NCCH_3$, OH_2, OH^-, and pyridine, and where X = pyridine is tethered to the bispidine backbone in L^3, L^4). The two main structural effects are a strong trans influence, exerted by the oxo group in both the triplet and the quintet spin states, and a Jahn–Teller-type distortion in the plane perpendicular to the oxo group in the quintet state. Due to the ligand architecture the two sites for substrate coordination in complexes with the tetradentate ligands L^1 and L^2 are electronically very different, and with the pentadentate ligands L^3 and L^4, a single isomer is enforced in each case. Because of the rigidity of the bispidine ligands and the orientation of the "Jahn–Teller axis", which is controlled by the sixth donor X, the Jahn–Teller-type distortion in the high-spin state of the two isomers is quite different. It is shown how this can be used as a design principle to tune the relative stability of the two spin states.

Introduction

High-valent iron–oxo species have long been of interest in bioinorganic chemistry, largely because of their importance in biological oxidation processes.[1] The cytochrome P450 enzymes are perhaps the best known example, where the iron–oxo group, in conjunction with a porphyrin radical, provides the oxidizing power necessary to hydroxylate hydrocarbons and arenes.[2] Iron–oxo intermediates have also been proposed in a number of other iron biosystems, notably in the antimalarial drug artemisinin[3] and the anticancer drug bleomycine.[4–6] In P450, the iron center has a triplet ground state (intermediate-spin), as do the majority of non-heme iron model complexes.[1,2] This is perhaps unsurprising, as the strong donor ligands required to stabilize the high oxidation state also favor intermediate- rather than high-spin states. Two crystal structures of non-heme $Fe^{IV}{=}O$ complexes have been reported so far, and Mössbauer spectroscopy indicates that both have $S = 1$ ground states, along with all other spectroscopically characterized non-heme $Fe^{IV}{=}O$ complexes.[7–12]

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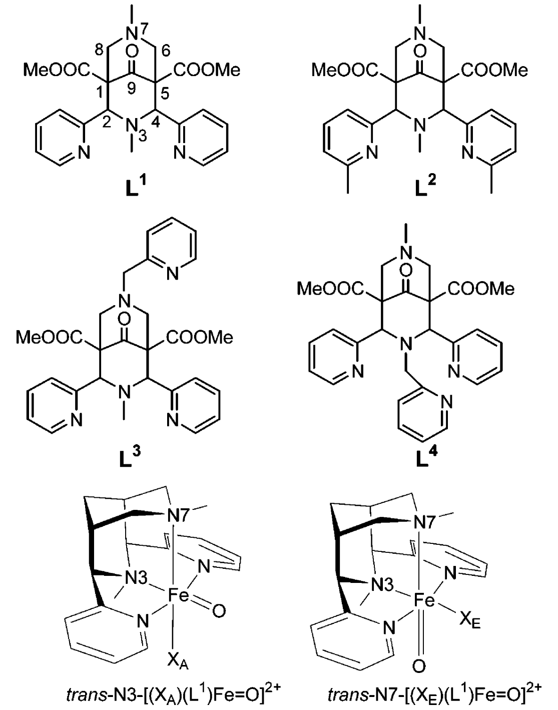
The Fe−O distances in the two known crystal structures are 1.646(3) and 1.639(5) Å, very similar to each other and comparable to the Fe−O bond distances deduced from EXAFS studies of oxoiron(IV) units in synthetic porphyrin (1.65/1.66 Å)[13] and heme peroxidase compounds (1.60−1.69 Å).[14,15] For comparison, the terminal Fe−O distance in the only characterized Fe(III)−oxo complex is 1.813(3) Å.[16]

In view of the dominance of the triplet ground state in model chemistry, the identification of a high-spin ($S = 2$) $Fe^{IV}{=}O$ intermediate in the non-heme iron enzyme TauD was a remarkable result[17] and one that has resulted in a concerted effort to explore the properties of high-spin model complexes. Previous examples of biologically relevant high-spin $Fe^{IV}{=}O$ species have been limited to the dinuclear diamond-shaped $[Fe^{IV}_2O_2]$ cores in intermediate Q of MMO, which oxidizes methane to methanol.[18,19] The only example of a structurally characterized synthetic high-spin Fe^{IV} complex is a distorted square pyramidal complex with a tetraamido-N macrocyclic ligand and a chloride in the axial site. The high-spin ($S = 2$) ground state of this complex was assigned on the basis of Mössbauer and EPR spectroscopy.[8,20] A large number of DFT- and ab initio-based studies have been conducted on the structure and reactivity of high-valent iron complexes, the majority of which have focused on the properties of the intermediate-spin triplet state.[21−30] In contrast, the properties of the quintet state have received comparatively little attention.[31]

In recent years we have developed the coordination chemistry of a series of very rigid diazaadamantane-derived ligands.[32] The basic architecture of the tetra- and pentadentate bispidine ligands discussed here features two tertiary amine and two or three pyridine donor groups (see Scheme 1). The rigid backbone constrains the four donors in the tetradentate ligands L^1 and L^2 to an octahedral coordination geometry with two cis-disposed vacant sites. In the two isomeric pentadentate ligands L^3 and L^4, one of these two sites for substrate coordination (X_E and X_A in Scheme 1) is blocked by an additional pyridine group tethered to the bispidine backbone. The iron(II) complexes of a number of tetra- and pentadentate bispidine ligands are among the most active catalysts of their class for the epoxidation and dihydroxylation of alkenes in the presence of H_2O_2, comparable in activity to the tpa-based complexes (tpa = tris(2-methylpyridyl)amine).[11,33] Of particular interest are the two bispidine ligands L^1 and L^3 (Scheme 1): both have similar activities for the iron-catalyzed epoxidation and dihydroxylation of cyclooctene with H_2O_2, but the product distributions are very different. We have been able to show that the $Fe^{IV}{=}O$ complexes of L^3 and L^4 are the catalytically active species, that they can be formed in aqueous solution, and that their spectroscopic properties are consistent with the presence of an intermediate-spin ground state.[11,12] So far, we have been unable to spectroscopically characterize any high-valent iron intermediate of L^1 and L^2. The combination of experimental and computational data for the catalytic oxidation of cyclooctene do, however, indicate that high-valent L^1-based iron complexes formed in this reaction have rather different properties than those formed when the pentadentate ligands are involved in the oxidation process.[33,34]

Scheme 1



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In the present communication we concentrate on the geometry and electronic structure of the possible $\mathrm{Fe^{IV}{=}O}$ complexes of L^{1-4}, specifically on how the relative stability of the triplet and quintet spin states can be tuned. There are four fundamental principles that influence the structure and energetics of these complexes: (i) The oxo group exerts a strong trans influence, leading, independent of the spin state, to a long bond trans to the $\mathrm{Fe^{IV}{=}O}$ unit. (ii) The quintet state (high spin, $S = 2$) is Jahn–Teller active,[35] leading to an elongation of some or all of the bonds that lie perpendicular to the strong $\mathrm{Fe^{IV}{=}O}$ bond. (iii) The two sites for substrate coordination in any metal complex of L^1-type tetradentate bispidine ligands, which are either perpendicular to or in the average plane defined by the pyridine nitrogen donors and N3, are sterically and electronically distinct (see Scheme 1). (iv) The metal–amine bonds to N3 and N7 in bispidine complexes generally are distinct. The difference is due to the bispidine architecture and ligand-induced stresses, which enforce relatively short metal–N3 and relatively long metal–N7 distances (see Scheme 1). For all four ligands, we distinguish the two isomers by specifying the orientation of the oxo group, i.e., trans-N7 and trans-N3 for the isomers with $\mathrm{Fe^{IV}{=}O}$ perpendicular to or in the plane of Fe/Npy1/Npy2/N3, respectively. The strength of the Fe–X and Fe═O bonds depends on the particular site that they occupy, and this leads in general to isomers that differ in stability and reactivity.[36−38] A number of reasons for these differences have been discussed,[39−41] and a full theoretical analysis of this for bispidine coordination chemistry central feature is in progress.[42] The basic point for the present study is that the orientation of the $\mathrm{Fe^{IV}{=}O}$ bond (trans-N3 or trans-N7), and hence, its strength is enforced by the bispidine ligand architecture. This, together with the trans influence of the $\mathrm{Fe^{IV}{=}O}$ group (see (i) above) and the Jahn–Teller-type activity of the $S = 2$ state (see (ii) above), is the design principle for the spin-state tuning discussed here.

Computational Methods

All calculations were performed with spin-unrestricted DFT methods within the Gaussian03 package.[43] Geometries were fully optimized in the gas phase using the B3LYP functional[44,45] and a 6-31G(d) basis set.[46] The suitability of B3LYP to predict structures and energetics is well documented. In particular for $\mathrm{Fe^{IV}{=}O}$ complexes in various spin states, the B3LYP results generally agree well with data obtained from CCSD(T) calculations.[21−24,30,49−52] Frequency calculations were performed to verify the status of all stationary points as minima on the potential energy surface. A simplified model system was used in all calculations, in which the ester groups at C1 and C5 on the ligand backbone (see Scheme 1) are replaced by hydrogen atoms; a ketone (C═O) was always used at C9, although this is known to be hydrolyzed ($\mathrm{C(OH)_2}$) in many structures.[32] Although the simplified ligand and some of the complexes have C_S symmetry, symmetry restraints were not used in the final optimizations.

Results and Discussion

Electronic Structure of the Five-Coordinate Complexes $[(L^1)\mathrm{Fe^{IV}{=}O}]^{2+}$ and $[(L^2)\mathrm{Fe^{IV}{=}O}]^{2+}$. For the two tetradentate ligands L^1 and L^2, there are two possible isomers of each $[(L)\mathrm{Fe^{IV}{=}O}]^{2+}$ complex, i.e., trans-N3 and trans-N7. Although computational studies of the iron-catalyst cycle $\mathrm{Fe^{II}}$-$(L^1)X_2/H_2O_2$[47] and combined experimental and computational studies of the iron-catalyzed oxidation of cyclooctene[33] indicate that the relevant $[(L^1)\mathrm{Fe^{IV}{=}O}]^{2+}$ and $[(L^2)\mathrm{Fe^{IV}{=}O}]^{2+}$ complexes are six- and not five-coordinate, with a donor derived from the solvent ($\mathrm{NCCH_3}$, $\mathrm{OH_2}$, or $\mathrm{OH^-}$) completing the coordination sphere, we briefly present here the structural data and energetics of the five-coordinate complexes (see Figure 1, Table 1) to establish a framework for understanding the six-coordinate species. For the $[(L^1)\mathrm{Fe^{IV}{=}O}]^{2+}$ complex we have only been able to locate a single minimum for each spin state. The Fe–O bond length in the triplet state (1.579 Å) is significantly shorter than in the quintet (1.614 Å), in

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(35) Throughout this paper, we use the term ‘Jahn–Teller distortion’ to describe the elongation of a pair of mutually trans-disposed bonds that arises from the presence of a single electron in the Fe–L σ^* d_{z^2} or $d_{x^2-y^2}$ orbitals. These orbitals form the degenerate e_g set in octahedral symmetry. All complexes described have at most C_s point symmetry, and in a strict sense, there is no Jahn–Teller distortion. However, the elongation of metal–ligand bonds has exactly the same physical origin as in higher-symmetry cases, leading to an elongation of some or all of the bonds that lie perpendicular to the strong $\mathrm{Fe^{IV}{=}O}$ bond (the singly occupied orbital is $d_{x^2-y^2}$, where the z axis lies along the Fe–O bond).

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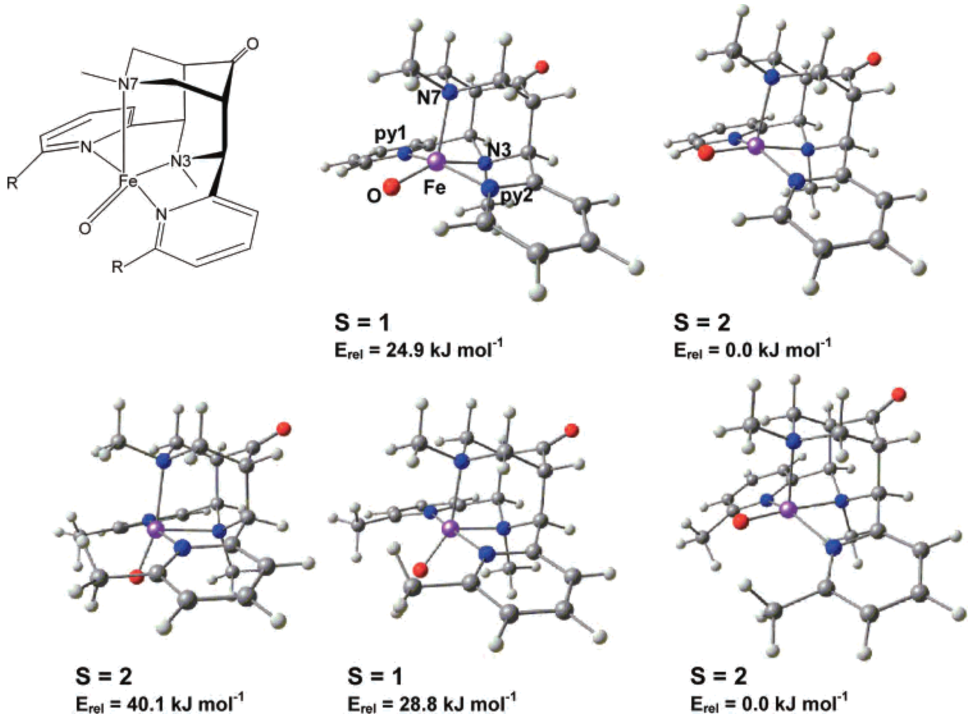


S = 1 E_{rel} = 24.9 kJ mol^{-1}

S = 2 E_{rel} = 0.0 kJ mol^{-1}

S = 2 E_{rel} = 40.1 kJ mol^{-1}

S = 1 E_{rel} = 28.8 kJ mol^{-1}

S = 2 E_{rel} = 0.0 kJ mol^{-1}

Figure 1. Optimized geometries of the $S = 1$ and 2 states of $[(L^1)Fe^{IV}{=}O]^{2+}$ (top) and $[(L^2)Fe^{IV}{=}O]^{2+}$ (bottom); bond distances (Å) and angles (deg) (L^1, $S = 1$; L^1, $S = 2$; L^2, $S = 2$; L^2, $S = 1$; L^2 (trans-N3), $S = 2$): Fe−O: 1.579; 1.614; 1.579; 1.616; 1.613; Fe−N7: 2.040, 2.184; 2.146; 2.168; 2.179; Fe−N3: 2.030, 2.056, 1.952, 2.129, 2.047; Fe−Npy: 2.000, 2.002, 2.022, 2.042, 2.054; O−Fe−N3/O−Fe−N7: 152/112, 169/101, 128/143, 122/149, 168/100.

Table 1. Bond Lengths, Relative Energies, and Triplet−Quintet Splittings for the Bispidine $Fe^{IV}{=}O$ Complexes[a]

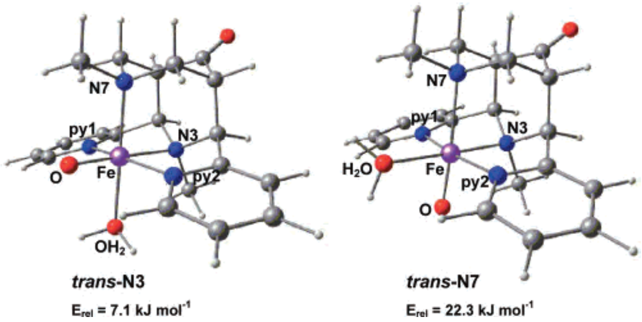
			bond lengths/Å						
	Fe=O	*S*	Fe−O	Fe−N7	Fe−N3	Fe−Npy	Fe−X	E_{rel} (kJ mol^{-1})	$\Delta E_{T\to Q}$ (kJ mol^{-1})
			Five−Coordinate Complexes, $[(L^{1,2})Fe^{IV}{=}O]^{2+}$						
$[(L^1)\,Fe^{IV}{=}O]^{2+}$	trans-N3	1	1.579	2.040	2.030	2.000	−	+24.9	−24.9
		2	1.614	2.184	2.056	2.002	−	0.0	
$[(L^2)\,Fe^{IV}{=}O]^{2+}$	trans-N7	1	1.579	2.146	1.952	2.022	−	+28.8	
		2	1.616	2.168	2.129	2.042	−	+40.1	+11.3
	trans-N3	2	1.613	2.179	2.047	2.054	−	0.0	
			Six-Coordinate Complexes, $[(X)(L^{1,2})\,Fe^{IV}{=}O]^{2+}$						
$[(OH_2)(L^1)\,Fe^{IV}{=}O]^{2+}$	trans-N3	1	1.617	2.099	2.100	1.987	2.069	+7.1	−7.1
		2	1.615	2.281	2.082	2.030	2.335	0.0	
	trans-N7	1	1.612	2.270	1.970	2.000	2.084	+22.3	+9.4
		2	1.612	2.230	2.167	2.090	2.177	+31.8	
$[(NCCH_3)(L^1)\,Fe^{IV}{=}O]^{2+}$	trans-N3	1	1.621	2.137	2.096	1.985	1.991	0.0	+4.2
		2	1.613	2.321	2.097	2.036	2.302	+4.2	
	trans-N7	1	1.617	2.309	1.992	2.000	1.991	+13.4	+22.1
		2	1.611	2.257	2.181	2.107	2.165	+35.5	
$[(pyridine)(L^1)\,Fe^{IV}{=}O]^{2+}$	trans-N3	1	1.616	2.200	2.124	1.990	2.088	0.0	+3.4
		2	1.610	2.360	2.113	2.063	2.307	+3.4	
	trans-N7	1	1.609	2.451	2.021	2.015	2.065	+15.8	+12.3
		2	1.609	2.287	2.180	2.185	2.152	+28.1	
$[(OH)(L^1)\,Fe^{IV}{=}O]^{+}$	trans-N3	1	1.616	2.275	2.122	1.982	1.852	+18.6	−18.1
		2	1.615	2.332	2.188	2.207	1.809	+0.5	
	trans-N7	1	1.615	2.067	2.364	1.981	1.852	+22.6	−22.6
		2	1.608	2.303	2.211	2.221	1.803	0.0	
$[(NCCH_3)(L^2)Fe^{IV}{=}O]^{2+}$	trans-N3	1	1.618	2.144	2.088	2.048	1.988	+7.4	−7.4
		2	1.611	2.263	2.080	2.118	2.298	0.0	
			Six-Coordinate Complexes, $[(L^{3,4})\,Fe^{IV}{=}O]^{2+}$						
$[(L^4)\,Fe^{IV}{=}O]^{2+}$	trans-N3	1	1.619	2.143	2.069	1.988	1.980	0.0	+26.5
		2	1.610	2.236	2.093	2.125	2.089	+26.6	
$[(L^3)\,Fe^{IV}{=}O]^{2+}$	trans-N7	1	1.616	2.225	2.004	2.004	1.988	+9.7	+22.6
		2	1.610	2.206	2.189	2.189	2.059	+32.4	

[a] Relative energies are given with respect to the most stable spin state of a particular complex, regardless of geometry. Triplet−quintet splittings are given for each isomer (see Supporting Information for Mulliken spin densities and absolute energies).

contrast to the computed Fe−O distances published for $[(X)(tpa)Fe^{IV}{=}O]^{2+}$, where the corresponding bonds are longer and invariant to the spin state (1.65 Å in both $S = 1$ and 2).[31] The computed Fe=O bond lengths in the six-coordinate bispidine complexes discussed below are also invariant to spin state, in agreement with the computational data discussed above and with experimental data of tpa-based iron complexes (1.646(3) and 1.639(5) Å).[7,8,53] The trends in Fe−O bond length can be related to the distortions away from square pyramidal geometry, which are possible in $[(L^1)Fe^{IV}=O]^{2+}$ due to the vacant coordination site cis to the oxo group. In the triplet, the O−Fe−N3 and O−Fe−N7 angles of 152° and 112°, respectively (cf. square pyramidal: 180°, 90°; trigonal bipyramidal: 120°, 120°) allow the mixing of significant Fe−O π^* character into the vacant Fe−N7 σ^* orbital, thereby strengthening the Fe−O bond. In the quintet, this orbital is singly occupied and the much reduced driving force for a trigonal bipyramidal distortion is clearly reflected in the O−Fe−N angles (O−Fe−N3 = 169°, O−Fe−N7 = 101°).

For the five-coordinate complex with the methylated ligand $[(L^2)Fe^{IV}=O]^{2+}$, we have again only been able to locate a single minimum on the potential energy surface in the triplet spin state. In this case the complex adopts a distorted square pyramidal geometry, with the oxo ligand approximately trans to N7 (O−Fe−N3 = 122°, O−Fe−N7 = 149°). The methyl groups on the pyridyl donors effectively block the coordination site trans to N3 and force the oxo ligand to occupy the less electronically favored position trans to N7. For the quintet state, in contrast, we have been able to locate distinct minima corresponding to the trans-N3 and trans-N7 isomers (Figure 1). Of these, the trans-N3 structure is, as expected, the more stable by 40.1 kJ mol^{-1} and has a very similar structure to the quintet state of $[(L^1)Fe^{IV}=O]^{2+}$, the only exception being the Fe−Npy bonds which are some 0.05 Å longer, probably due to the steric repulsion of the two methyl groups. In contrast to the tpa-based systems, there is no destabilization of the intermediate-spin state as a result of the increased steric crowding ($\Delta E_{T\rightarrow Q}$ = 24.9 kJ mol^{-1} in $[(L^1)Fe^{IV}=O)]^{2+}$ vs 28.8 kJ mol^{-1} in $[(L^2)Fe^{IV}=O]^{2+}$). This is a consequence of the ability of the oxo ligand to avoid the increased steric crowding at the trans-N3 position by moving to the vacant trans-N7 site. We will return to the effects of steric bulk in the subsequent discussion of $[(X)(L^1)Fe^{IV}=O]^{2+}$, where a similar reorganization is blocked by the presence of the sixth ligand X.

Influence of a Sixth Ligand in the Coordination Sphere: Electronic Structure of $[(X)(L^1)Fe^{IV}=O]^{2+}$, X = OH^-, OH_2, $NCCH_3$, pyridine. In this section we explore the influence of a sixth ligand on the balance between the different spin states. Specifically, we consider H_2O and CH_3CN as potential solvent donors and also OH^- which may arise from deprotonation of coordinated H_2O. We also consider the effects of coordination of a pyridine as an unconstrained model for the complexes of the pentadentate ligands L^3 and L^4 to be discussed in the next section. In these pseudo-octahedral complexes, the motion of the oxo ligand emphasized in the previous section is blocked by the sixth ligand. As a result, we have been able to locate distinct minima for the trans-N3 and trans-N7 isomers, for both triplet and quintet states of $[(X)(L^1)Fe^{IV}=O]^{2+}$ with X = pyridine, $NCCH_3$, OH_2, and OH^-. The optimized geometries of the S = 1 states of the two isomeric aqua complexes are shown in Figure 2, and selected bond distances and relative energies for all species are collected in Table 1.



***trans*-N3**
E_{rel} = 7.1 kJ mol^{-1}

***trans*-N7**
E_{rel} = 22.3 kJ mol^{-1}

Figure 2. Optimized geometries of the S = 1 states of the trans-N3 and trans-N7 isomers of $[(OH_2)(L^1)Fe^{IV}=O]^{2+}$; bond distances (Å) (trans-N3; trans-N7): Fe−O: 1.617; 1.612; Fe−N7: 2.099; 2.270; Fe−N3: 2.100; 1.970; Fe−Npy: 1.987; 2.000; Fe−OH_2: 2.069; 2.084.

In all cases, the trans-N3 isomer is the more stable, consistent with the known tendency for strong donor ligands to coordinate in this position (see Introduction), and the stabilization of the trans-N3 isomer is of the same order of magnitude as observed for other bispidine complexes.[40,54] A comparison of the relative energies of the more stable trans-N3 isomers with the five-coordinate complexes discussed in the previous section confirms that the addition of a neutral ligand (OH_2, $NCCH_3$, pyridine) stabilizes the triplet relative to the quintet state, and in the case of the N-donor ligands, this is sufficient to cause a reversal of the order of spin states. The stronger ligand field in the octahedral complexes naturally reduces the relative stability of the high-spin state, but the difference between π-acceptor ($NCCH_3$, pyridine) and π-donor (OH_2) ligands is also clearly reflected in the relative stability of the quintet in the latter complex. The strong trans influence of the oxo ligand ensures that the Fe−O σ^* orbital is the highest lying member of the Fe 3d manifold, and so the HOMO of the quintet state (the LUMO of the triplet) will always lie orthogonal to the Fe−O axis. For the more stable trans-N3 isomer discussed here, this places it in the plane defined by N7, the two pyridyl groups, and the sixth ligand X. As a result, the change in spin state has almost no effect on the Fe−O bond lengths, regardless of the identity of X, and the changes in the spin density on the $Fe^{IV}=O$ unit associated with the triplet−quintet transition are also independent of the sixth ligand (see Supporting Information).

In contrast, the sixth ligand does play a significant role in determining the relative energies of the two spin states because it controls the orientation of the Jahn−Teller axis in the quintet state. As we have noted above, the trans influence of the oxo ligand orients the HOMO of the quintet in the plane defined by N7, the two pyridyl groups, and X. For the neutral donor ligands ($NCCH_3$, pyridine, OH_2), the HOMO is further localized along the N7−Fe−X axis (see Figure 3), and as a result, the Jahn−Teller distortion takes

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(53) Decker, A.; Rohde, J. U.; Que, L., Jr.; Solomon, E. I. *J. Am. Chem. Soc.* **2004**, *126*, 5378.

(54) Comba, P.; Merz, M.; Pritzkow, H. *Eur. J. Inorg. Chem.* **2003**, 1711.

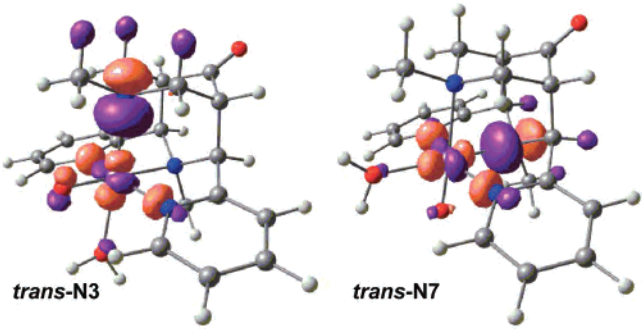

Figure 3. Contour plots of the HOMO of the $S = 2$ state for the trans-N3 and trans-N7 isomers of $[(OH_2)(L^1)Fe^{IV}{=}O]^{2+}$.

the form of a strong elongation along this axis. In the hydroxo complex, in contrast, the stronger trans influence of the X ligand reorients the Jahn−Teller axis such that it is now more strongly localized along the two Fe−Npy bonds, which are significantly elongated in the quintet while Fe−N7 and Fe−OH remain largely unaffected (see Table 1).

The discussion in the preceding two paragraphs illustrates that the structure of any given complex is determined by two distinct factors, the trans influence of the oxo ligand and, in the quintets, the Jahn−Teller distortion, both of which tend to elongate one or more bonds. We can, however, separate the two factors by noting that they are approximately orthogonal: as a result of the orientation of the quintet HOMO, bonds elongated by the trans influence of the oxo ligand are unaffected by the Jahn−Teller distortion and vice versa. This allows us to define a 'natural' length for the $Fe^{IV}-N3$ and $Fe^{IV}-N7$ bonds as the bond length, when affected by neither the trans influence nor the Jahn−Teller distortion. Taking the aqua complexes as a representative case, we estimate these 'natural' lengths to be 2.10 Å for Fe−N7 and 1.97 Å for Fe−N3 (i.e., the bonds trans to X in the two triplet states). The elongation due to the trans influence of the oxo group is then given by the difference in Fe−Nx bond lengths between the two isomers in the triplet state: $(2.27 - 2.10) = 0.17$ Å for Fe−N7 and $(2.10 - 1.97) = 0.13$ Å for Fe−N3. This analysis reveals the important principle that the Fe−N7 bond is easier to elongate than Fe−N3 (see Introduction). This proves to have important consequences for the stability of the spin states of the pentadentate ligands (vide infra). The Jahn−Teller distortion in the quintet superimposes a further elongation of ~0.18 Å of the Fe−N bond cis to Fe═O.

In terms of energetics, similar trends to those noted for the trans-N3 isomers emerge for the less-stable trans-N7 complexes, with the triplet−quintet separation increasing in the order pyridine < $NCCH_3$ < OH_2 < OH^-. However, the triplet−quintet gap for the neutral OH_2 and $NCCH_3$ ligands is increased by ~18 kJ mol^{-1} compared to the trans-N3 isomer, and this is sufficient to make the triplet the ground state in each case. The remarkably constant destabilization of the quintet state in the trans-N7 isomers suggests that the energetics of the spin-state equilibrium are intimately linked to the architecture of the bispidine ligand. The structural changes associated with the spin-state change offer a possible explanation. As in the trans-N3 isomers, the Fe−O bonds are almost identical in the triplet and quintet structures, confirming that the Jahn−Teller axis again lies in the orthogonal plane, defined in this case by N3, the two pyridyl groups, and X. However, unlike the trans-N3 isomer where the Jahn−Teller distortion is largely localized along a single axis (N7−Fe−X), the distortion in the trans-N7 structure is more evenly distributed over all four bonds. The difference between the trans-N3 and trans-N7 isomers ultimately lies in the bispidine architecture, which enforces relatively short bonds to the N3 and relatively long bonds to the N7 donor atom (see Introduction). The intrinsic Jahn−Teller instability of the quintet state can therefore be much more effectively accommodated in the trans-N3 isomer. The relative destabilization of the quintet state in the trans-N7 isomer is also apparent in $[(pyridine)(L^1)Fe^{IV}{=}O]^{2+}$ ($\Delta\Delta E = 9$ kJ mol^{-1}), although it is less extreme than in the OH_2 and $NCCH_3$ analogues. The unfavorable alignment of the Jahn−Teller axis in the high-spin trans-N7 state is, in this case, largely offset by the destabilization of the triplet state due to repulsion between the bulky pyridine ligand and the methyl substituent on N3. Finally, we note that the hydroxo complex is of specific interest for two reasons. First, the triplet−quintet separation in $[(OH)(L^1)Fe^{IV}{=}O]^+$ is largely independent of the isomer ($\Delta\Delta E = 4$ kJ mol^{-1}). This is because the Jahn−Teller axis is localized along the Fe−Npy bonds in both the trans-N3 and trans-N7 isomers. As a result, the ability of the complex to accommodate the Jahn−Teller distortion is not affected, to a first approximation, by the difference between the Fe−N3 and Fe−N7 bonds. Second, the energy separation between the trans-N3 and trans-N7 isomers in both spin states is very small. That is, the two isomers of $[(OH)(L^1)Fe^{IV}{=}O]^+$ may coexist in solution, and this could have an influence on the reactivity.

Finally, before considering the pentadentate ligands, we return to the influence on the spin-state equilibrium of the steric bulk of ortho substituents on the pyridyl arms. In the discussion of $[(L^2)Fe^{IV}{=}O]^{2+}$, we noted that the expected destabilization of the intermediate-spin state was not manifested because the oxo ligand was able to avoid the sterically hindered trans-N3 position by moving to the trans-N7 site. This rearrangement is clearly blocked in the six-coordinate systems, allowing us to estimate the true effect of the ortho methyl substituents on the spin-state equilibrium. Optimized structural parameters and relative energies of the two spin states of $[(NCCH_3)(L^2)Fe^{IV}{=}O]^{2+}$ are collected in Table 1. The bond lengths show the expected elongation of the Fe−Npy bond in each state relative to those in $[(NCCH_3)(L^1)Fe^{IV}{=}O]^{2+}$ and also confirm that the Jahn−Teller axis in the $S = 2$ state remains oriented along the N7−Fe−X bonds. The quintet now lies 7.4 kJ mol^{-1} below the triplet, compared to an energy difference of 4.2 kJ mol^{-1} in favor of the triplet for $[(NCCH_3)(L^1)Fe^{IV}{=}O]^{2+}$, indicating that steric bulk stabilizes the high-spin state by ~12 kJ mol^{-1}.

Hexa-coordination with Pentadentate Bispidine Ligands: $[(L^3)Fe^{IV}{=}O]^{2+}$ and $[(L^4)Fe^{IV}{=}O]^{2+}$. In the L^3-based $Fe^{IV}{=}O$ complex, the fifth donor is tethered to the bispidine backbone in such a way that only a trans-N7 structure is possible, while L^4 enforces the trans-N3 arrange-

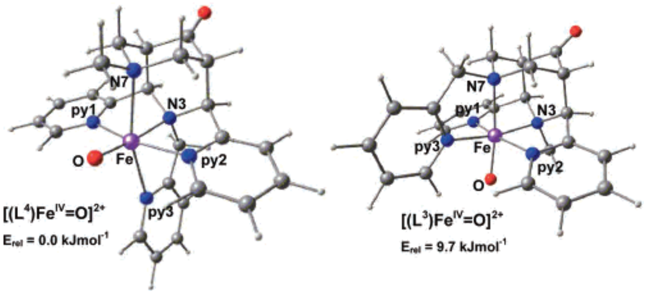

Figure 4. Optimized geometries of the $S = 1$ ground states of the two isomers $[(L^3)Fe^{IV}{=}O]^{2+}$ and $[(L^4)Fe^{IV}{=}O]^{2+}$; bond distances (Å) (L^3; L^4): Fe−O: 1.619; 1.616; Fe−N7: 2.143; 2.225; Fe−N3: 2.069; 2.004; Fe−Npy1,2: 1.988; 2.004; Fe−Npy3: 1.980; 1.988.

ment (Scheme 1). A comparison of the structural properties of the L^3- and L^4-based $Fe^{IV}{=}O$ complexes (Figure 4) with their L^1/pyridine analogues (trans-N3 and trans-N7 isomers, respectively) can therefore offer important insights into the structural and electronic impact of constraining the movement of the pyridine unit. The most striking feature of the comparison between $[(L^4)Fe^{IV}{=}O]^{2+}$ and the trans-N3 isomer of $[(pyridine)(L^1)Fe^{IV}{=}O]^{2+}$ is the relative destabilization of the quintet in the former ($\Delta E_{T\rightarrow Q} = 26.5$ vs 3.4 kJ mol^{-1}). We have emphasized the importance of the relatively soft X−Fe−N7 distortion axis in accommodating the Jahn−Teller distortion in the quintet state of trans-N3-$[(pyridine)(L^1)Fe^{IV}{=}O]^{2+}$ ($\Delta Fe{-}N7_{T\rightarrow Q} = 0.140$ Å, $\Delta Fe{-}X_{T\rightarrow Q} = 0.219$ Å). The distortion along the same axis in $[(L^4)Fe^{IV}{=}O]^{2+}$ is severely constrained by the covalent link between the pyridyl arm and the ligand backbone, which limits the span of the L^4 ligand. As a result, the elongation along the X−Fe−N7 axis is decreased ($\Delta Fe{-}N7_{T\rightarrow Q} = 0.093$ Å, $\Delta Fe{-}X_{T\rightarrow Q} = 0.109$ Å), causing the pronounced relative destabilization of the quintet state.

In the trans-N7 isomer of $[(pyridine)(L^1)Fe^{IV}{=}O]^{2+}$, the Jahn−Teller axis in the quintet was strongly localized along the Npy−Fe−Npy axis, rather than X−Fe−N3, and on that basis, we might anticipate that constraining the geometry of the X ligand trans to N3 in $[(L^3)Fe^{IV}{=}O]^{2+}$ would have a smaller effect. The comparison of the triplet−quintet separations in $[(pyridine)(L^1)Fe^{IV}{=}O]^{2+}$ and $[(L^3)Fe^{IV}{=}O]^{2+}$ is complicated by the fact that the destabilizing steric interaction between the pyridine and the N7−Me group in the former is replaced by a covalent CH_2 linker in the latter, but the anticipated trend is nevertheless clearly present: $\Delta E_{T\rightarrow Q} = 22.6$ vs 12.3 kJ mol^{-1}. The structural trends confirm the relatively minor impact of tethering the pyridyl ligand: ($\Delta Fe{-}py_{T\rightarrow Q} = 0.170$ Å, $\Delta Fe{-}N3_{T\rightarrow Q} = 0.159$ Å, $\Delta Fe{-}X_{T\rightarrow Q} = 0.087$ Å in the trans-N7 isomer of $[(pyridine)(L^1)Fe^{IV}{=}O]^{2+}$ and $\Delta Fe{-}py_{T\rightarrow Q} = 0.185$Å, $\Delta Fe{-}N3_{T\rightarrow Q} = 0.185$ Å, $\Delta Fe{-}X_{T\rightarrow Q} = 0.071$ Å in $[(L^3)Fe^{IV}{=}O]^{2+}$).

Summary

In summary, we have explored the energetics and structural consequences of the triplet−quintet transition in a range of complexes containing the bispidine architecture and shown that the equilibrium position is highly dependent on the nature and position of the sixth ligand in the coordination sphere. The addition of a sixth ligand stabilizes the triplet in all cases, but the extent of this stabilization depends on the orientation of the oxo ligand with respect to the bispidine backbone. The quintet state is intrinsically Jahn−Teller active, and the strong trans influence of the oxo ligand localizes the distortion axis into the plane orthogonal to the Fe−O axis. The stability of the quintet state is therefore largely determined by the ability of the donors in this orthogonal plane to accommodate the Jahn−Teller distortion without imposing undue strain on the ligand backbone. In the trans-N3 isomers, the orthogonal plane contains X, the two pyridyl arms, and N7, while in the trans-N7 isomers the corresponding plane contains X, the two pyridyl arms, and N3. The structure of the bispidine backbone prefers relatively long Fe−N7 and relatively short Fe−N3 bonds and therefore allows the Jahn−Teller axis in the quintet to orient in different ways in the two isomers: along the N7−Fe−X axis in the trans-N3 isomers and along the Npyr−Fe−Npyr axis in their trans-N7 counterparts. When a pyridyl arm is tethered to the bispidine framework, as in L^3 and L^4, the major effect is to limit the span of the two mutually trans-disposed ligands, N7 and pyridine L^4 or N3 and pyridine L^3. Because the Jahn−Teller axis is localized along the N7−Fe−N_{pyr} bonds in $[(L^4)Fe^{IV}{=}O]^{2+}$, tethering the pyridine group severely compromises the ability of the complex to accommodate the Jahn−Teller distortion in the quintet. In contrast, tethering the pyridine in $[(L^3)Fe^{IV}{=}O]^{2+}$ has only a limited impact because in this case the Jahn−Teller distortion is not oriented along the N3−Fe−X axis. In the search for a stable $S = 2$ $Fe^{IV}{=}O$ complex with a pentadentate bispidine ligand, it therefore will be necessary to carefully tune the nature (see OH^- vs pyridine in the L^1-based systems) and position (restriction of the methyl linker in $L^{3,4}$) of the fifth bispidine donor.

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Supporting Information Available: Extended Table 1 which in addition has Mulliken spin densities and absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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