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Ab Initio Study of Intriguing Coordination Complexes: A Metal Field Theory Picture[†]

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Two noninnocent ligands are theoretically studied using wave function based methods to demonstrate their ability to undergo singlet−triplet transition under the effect of an external charge mimicking the electrostatic role of a metal ion. It is shown that the singlet−triplet energy difference is very sensitive to the metal ion charge which tunes the HOMO−LUMO energy difference of these ligands. While the latter is reduced as the charge is enhanced in the glyoxal-bis-(2-mercaptoanil) (gma) ligand, it is increased in the bis(imino)pyridine diradical ligand. This result shows a strong analogy with the crystal field theory, interchanging the roles played by the metal ion and the ligand. As the metal ion is explicitly treated in the Fe(gma)CN complex, this analogy can be pushed further resulting in a "metal field theory" conceptualization.

1. Introduction

The intrinsic feature of noninnocent ligands to undergo multiple redox reactions results in fascinating observations which makes these compounds interesting magnetic targets. This puzzling behavior had already been suspected in biological systems[1] and extensively studied in the galactose oxidase system where a tyrosyl radical coordinated to a Cu(II) center represents the catalytically active species. Such highly unusual bonding situations have greatly inspired coordination chemists, who have subsequently characterized many model systems that contain coordinated radicals and that are catalytically active in oxidation chemistry. These studies have led to a revival of the field of the coordination chemistry of metals with noninnocent ligands.[2,3] Many of these ligands were originally introduced in order to stabilize high oxidation states of metal ions in biomimetic synthetic routes. High-spin Fe(IV) species are known to be reactive intermediates in catalytic cycles of nonheme enzymes, a feature example being the methane-hydroxylating intermediate.[4] While such a strategy has effectively led to spectacular oxidation states of the metal ion,[5−7] as for instance the Fe(VI)−nitrido complex,[7] it has also generated magnetic properties unexpectedly originating from oxidized ligands. In this respect, several "classic" systems have been subject to intense and controversial discussion in the literature for several decades.[8,9] For the extensively debated $Ni(C_6H_4(NH_2))_2$ complex,[10] it was first suggested,[8] and later refuted,[9] that its electronic ground-state should be understood as a diradical singlet rather than a combination of resonant limit forms. Regarding the metal centers, a similar controversy came up with speculated unusual formal oxidation states (e.g., +IV and +V for Fe),[5] an observation which is to be contrasted with experimental data favoring traditional oxidation states (+II and +III) on the metal in the environment of open-shell diradical dianions.[2] In the mean time, many theoretical studies have supported the presence of π radicals in a variety of noninnocent ligand based complexes in agreement with high precision X-Ray and magneto-optic experimental observations.[11,12] This important class of systems has been considered in the light of combined experimental and theoretical works.

Due to the strong similarity between noninnocent ligands and magnetic transition metal ions (i.e., presence of correlated electrons), the modelization of the complex ground-state relies on a Heisenberg Hamiltonian based on the local ground states of both partners. It is known from crystal field theory that the ground-state spin-multiplicity of a complex is directly controlled by the field created by the environment. Due to the strong atomic character of the magnetic orbitals, the local spin electronic configuration on the metal ion in a low-field is governed by Hund's first rule.

The major difference between the metal ion and the ligand stems from the multicentric nature of the latter. Indeed, the molecular orbitals (MOs) resulting from the intraligand delocalization usually favors a low-spin ground state. Nevertheless, there is both experimental and theoretical evidence for a high-spin state ligand in several iron complexes. Thus, the possibility to tune the nature of the ligand spin-multiplicity state in the complex has opened up new perspectives in coordination chemistry.

This paper presents an attempt to explore the analogies between open-shell metal ions and noninnocent ligands further through a simple, pictorial approach that is termed "metal-field theory" (MFT). We will point out how this approach connects to experimental observables. Furthermore, the purely electrostatic and delocalization effects are examined separately. In a first section, the electrostatic role on the glyoxal-bis-(2-mercaptoanil) (gma) and the bis(imino)pyridine diradical noninnocent ligands is studied by replacing the metal ion of the reported complexes[13,14] (see Figures 1 and 2) by a point charge. A model compound for the bis(imino)pyridine has been studied. Both the imine aryl-substituents and the backbone methyl groups were replaced by hydrogen atoms.

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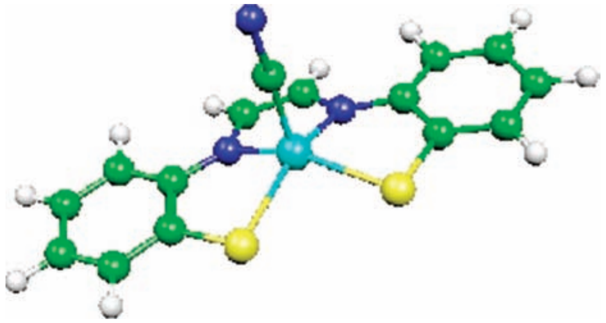

Figure 1. Fe(gma)CN complex.

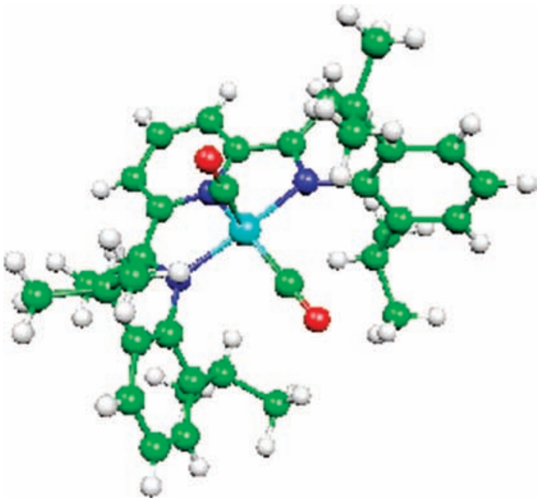

Figure 2. (^{i}PrPDI)Fe(CO)$_2$ complex (^{i}PrPDI = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N).

Its influence on the ligands spectrum of low-lying electronic states can be modeled by varying the value of this point charge. Then, the delocalization effects which require both metal-centered and ligand MOs are analyzed in the reported Fe(gma)CN complex. Finally, our results will strongly support the notion of an original MFT that is summarized in the final section of the paper in order to emphasize the singular role of noninnocent ligands in coordination chemistry.

2. Computational Information

Wave function based correlation methods were used to study both the Fe(gma) complex and the ligands alone. Concerning the ligands, active spaces containing the two highest occupied orbitals and two electrons CAS(2,2) were considered to get zeroth order complete active space self consistent field (CASSCF) wave functions of the lowest singlet and triplet states. These calculations were performed using the Molcas code.[15] In a second step, dynamic correlation was introduced using the variational difference dedicated configuration interaction (DDCI) method implemented in the CASDI code.[16] By varying the classes of excitations acting on the CAS references, one gives rise to the so-called DDCI-1, DDCI-2, and DDCI-3 levels of theory. While DDCI-1 is a CAS+single excitation, DDCI-2 and DDCI-3 involve configurations with up to 2 and 3-degrees of freedom respectively in the excitation space. A degree of freedom is defined as a hole in the internal space of the orbitals that are doubly occupied in all reference configurations or a particule in the external (virtual) space of orbitals that are unoccupied in all reference configurations. A more detailed description of the method and its underlying philosophy is given in ref 17.

TABLE 1: Energy Difference $\Delta\varepsilon$ (eV) between the SOMOs Labeled as a and a', Singlet-Triplet Gap ΔE_{ST} (cm^{-1}) and Occupation Numbers n_a, $n_{a'}$ of the a and a' MOs in the Singlet State of the Bis(imino)pyridine Diradical Ligand

q	0	+1	+2	+3	+4
$\Delta\varepsilon$	−0.07	0.53	0.97	1.37	1.73
ΔE_{ST} (DDCI-3)	1100	1870	−400	−2100	−4600
n_a	1.20	0.90	0.57	0.30	0.17
$n_{a'}$	0.80	1.10	1.43	1.70	1.83

TABLE 2: $\Delta\varepsilon$ (eV) between the SOMOs a' and a'', ΔE_{ST} (cm^{-1}) and Occupation Numbers $n_{a'}$, $n_{a''}$ of the a' and a'' MOs in the Singlet State of the gma Ligand

q	0	+1	+2	+3	+4
$\Delta\varepsilon$	1.37	1.09	0.843	0.704	0.419
ΔE_{ST} (DDCI-3)	−5100	−3700	−2550	−1970	+115
$n_{a'}$	0.04	0.03	0.06	0.16	0.37
$n_{a''}$	1.96	1.97	1.94	1.84	1.63

The energy differences $\Delta E_{ST} = E_S - E_T$ between the lowest singlet and triplet states of both ligands were estimated at the most correlated DDCI-3 level of calculation. As recommended for the study of magnetic systems, the triplet state orbitals set was used in the correlated calculations of both states. The energy difference between the singly occupied MOs (SOMOs) of the triplet state was computed using the open shell restricted Hartree−Fock (OSRHF) program of the MOLPRO code.[18]

Concerning the Fe(gma)CN complex, the zeroth order wave function was previously[19] determined in the CASSCF framework involving 5 electrons in 5 MOs (CAS(5,5)). Three active orbitals are located on the metal and 2 on the gma ligand. Dynamical correlation was then introduced by means of the iterative difference dedicated configuration interaction (IDDCI) method.[20] Along this scheme, natural orbitals were extracted from the mean density matrix of the correlated wave functions.

Calculations were performed using pseudopotentials to describe the core parts of Fe, S, O, N, and C atoms containing 12, 10, 2, 2, and 2 electrons, respectively. The corresponding optimized basis sets (3s3p4d) for Fe, (2s3p1d) for the metal ion nearest-neighbors S and N, (2s3p) on the other C atoms and minimal basis sets on H atoms were used for the Fe(gma)CN complex. In order to study the ligands alone at the DDCI level (which is computationally demanding), only double-ζ basis sets were considered. As shown in ref 19, the inclusion of another p orbital does not lead to qualitative changes in the results (the energy difference between the two lowest states of the Fe(gma)CN complex is affected by less than 10 cm^{-1}).

3. Role of the Electrostatic Effects

The electrostatic influence of the metal ion is examined by varying the value of a point charge q located at the crystallographic position of the metal ion in the complexes. For this purpose, the geometries of the bis(imino)pyridine and gma ligands have been taken from the crystallographic structures of (^{i}PrPDI)Fe(CO)$_2$ and Fe(gma)CN complexes. q is varied between 0 (i.e., no field) and +4 which are the expected oxidation numbers of iron in such systems. The energy differences between the SOMOs $\Delta\varepsilon$ in the triplet state and the singlet−triplet gap $\Delta E_{ST} = E_S - E_T$ as functions of q are summarized in Table 1 and Table 2. Let us stress that in the absence of any external electrostatic field, the bis(imino)pyridine diradical ligand exhibits a triplet ground-state whereas the gma ligand features a singlet ground state. As we shall see, already a point charge is likely to change this state of affairs.

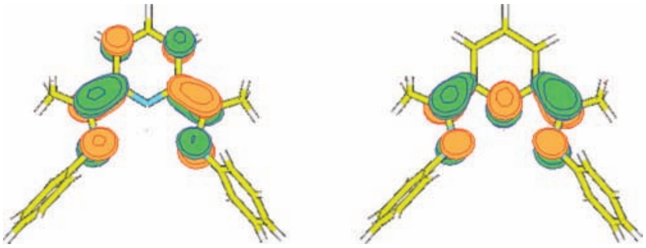

Figure 3. Delocalized active MOs *a* and *a*′ of the bis(imino)pyridine diradical ligand in zero field.

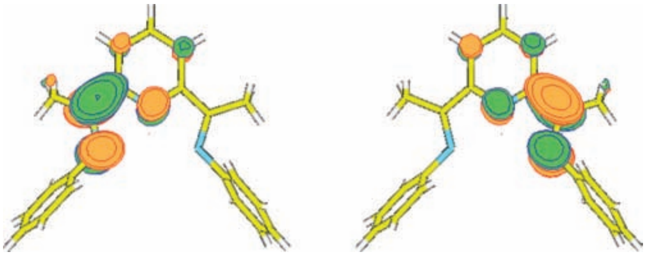

Figure 4. Relocalized MOs l and r of the bis(imino)pyridine diradical ligand in zero field.

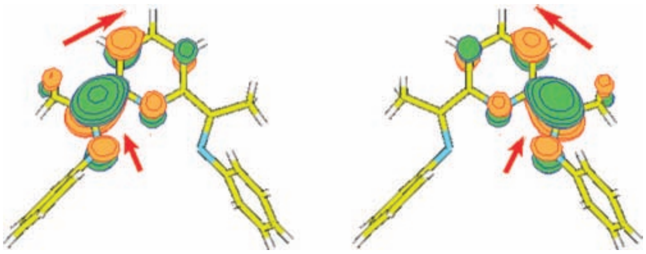

Figure 5. Relocalized MOs l and r of the bis(imino)pyridine diradical ligand in the presence of a charge $q = 4$. The arrows schematically indicate the electron flow.

Bis(imino)pyridine Diradical Ligand. Let us first concentrate on the bis(imino)pyridine diradical ligand. The SOMOs orbitals labeled a and a′ are represented in Figure 3. The analysis of their occupation numbers (see Table 1) reveals that the electric field induces a stabilization of the *a*′ orbital in comparison to the a one, a crossing occurs in the $0 < q < 1$ regime. One observes a monotonous behavior of both $\Delta\varepsilon$ and the singlet−triplet energy difference $\Delta E_{ST} = E_S - E_T$ in the $q > 1$ regime. The stronger the field, the larger the energy splitting of the ligand orbitals, and a low-spin ground-state finally results for the strongest considered fields (i.e., $q > 2$). This behavior is reminiscent of the well-known crystal field theory[21] for transition metal ions. As a matter a fact, in zero field the high-spin state is favored while an increasing metal field strength tends to stabilize the low-spin state.

In order to understand this result, the *a* and *a*′ MOs were relocalized for the $q = 0$ and $q = 4$ situations by an appropriate rotation that maximizes the weight of the relocalized orbitals on the left and right parts of the ligands. The so-obtained l and r orbitals are represented in Figures 4 and 5.

The diradical character of the two wave functions in low field may be understood from a localized picture of the two unpaired electrons in the left and right subspaces. The two delocalized MOs are now seen as the in-phase *a*′ and out-of-phase *a* linear combinations of the l and r orbitals. For larger fields, the in phase orbital *a*′ is lowered suggesting a stronger interaction between the l and r localized orbitals. Hence, the singlet is preferentially stabilized over the triplet state. As seen in Figure 5, the electronic density moves toward the pyridine moiety where the overlap between l and r is maximal. Interestingly, these electrons are repelled by the positive point charge, a rather counter-intuitive chemical picture.

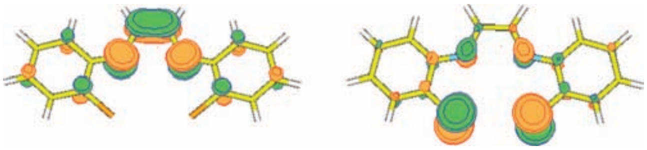

Figure 6. Delocalized active MOs *a*′ and *a*″ of the gma ligand in zero field.

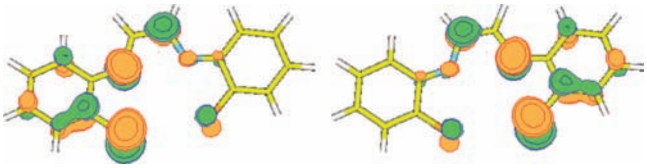

Figure 7. Relocalized active MOs l and r of the gma ligand in zero field.

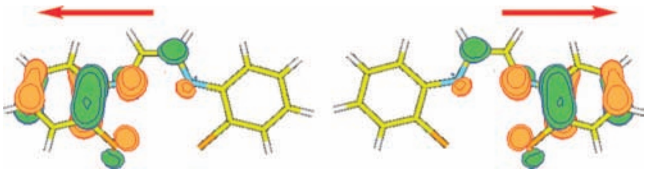

Figure 8. Relocalized active MOs l and r of the gma ligand in presence of a charge $q = 4$.

The orthogonal valence bond (OVB) analysis of the two wave functions confirms this result. While the physical nature of the triplet is strictly neutral ($\Psi^T_{CAS} = |l\bar{r}| - |r\bar{l}|$), the singlet also contains ionic configurations ($\Psi^S_{CAS} = \lambda(|l\bar{r}| + |r\bar{l}|) + \mu(|l\bar{l}| + |r\bar{r}|)$) in which both electrons are located on the same left or right subspace. The covalent/diradicalar character of the singlet, i.e., the nondynamical correlation contributions, can be appreciated by the ratio $\rho = \mu/\lambda$ as a function of q which varies from 0 for a pure diradical to 1 in a strongly covalent bond. While $\rho = 0.10$ in zero field, it reaches a covalent regime $\rho = 0.69$ for $q = 4$.

gma Ligand. Let us now concentrate on the gma ligand in order to see whether such a behavior can be expected for other noninnocent ligands as well. Since the ligand exhibits C_2 symmetry, the symmetry group labels for the MOs are used hereafter. As the field increases, $\Delta\varepsilon$ is reduced and a dramatic reduction of the singlet−triplet gap is observed (see Table 2) in contrast with our previous observations in the bis(imino)-pyridine diradical ligand. The delocalized MOs *a*′ and *a*″ in the absence of field (i.e., $q = 0$) are represented in Figure 6.

We performed similar orbital relocalization on the left and right parts of the ligand obtained in zero field (see Figure 7) and in presence of a $q = 4$ charge (see Figure 8) in order to clarify the role of the external field. The electronic density (brought by the two correlated electrons) tends to grow on the benzene-rings and to be depleted on the coordinating diamine-ethylene moiety. As already observed, the two correlated electrons “flee” the positive point charge.

Consequently, the overlap between the l and r orbitals is reduced and the singlet−triplet gap becomes much smaller. Here again the OVB analysis of the two wave functions confirms this assertion. The decrease of ρ from 0.75 in zero field to 0.36 for $q = 4$ shows that the diradical character (i.e., the weight of the neutral configurations) is enhanced as the external field increases, confirming the increasing mean separation of the two unpaired electrons.

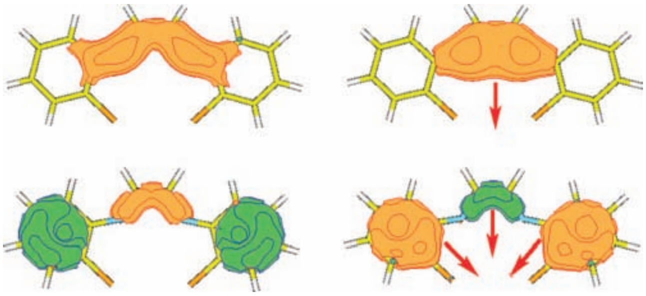

Figure 9. Field effect on the σ MOs of the gma ligand.

This nonintuitive result can be rationalized upon looking at the σ MOs. As seen in Figure 9, the electrons attraction exerted by the positive point charge is particularly effective in the σ subsystem. The resulting electron depletion is compensated by a flow in opposite direction of the two π unpaired electrons. This inductive effect is observed in both noninnocent ligands. Nevertheless, the identical response of the electrons results in a different effect on the singlet−triplet gap due to the different topologies of the systems. In the bis(imino)pyridine diradical ligand, the flow of the two unpaired electrons leads to a stronger interaction due to their closer mean distance, favoring a closed-shell ground state. This is to be contrasted with the gma ligand in which the two electrons are pushed in opposite directions thus enhancing the diradical character of the ligand.

4. Role of the Delocalization in the Fe(gma)CN Complex

The appearance of a gma triplet in the ground-state of the Fe(gma)CN complex[13,19] cannot be explained by electrostatic arguments only. As a matter of fact, the gma ligand turns out to be a singlet in the presence of a charge $q = 3$ and the ΔE_{ST} energy difference is quite important. In order to predict a triplet ground state, and to push further the analogy between the metal ion and the noninnocent ligand, the delocalization between the organic and metallic partners should be considered, suggesting a MFT picture.

A correlated ab initio study[19] of the Fe(gma)CN has shown that its low-energy spectrum is constituted of a doublet ground state $^2A'$ symmetry (in the C_2 symmetry point group), directly followed by a quartet state $^4A''$ lying close in energy (200 cm^{-1}) as well as an additional quartet $^4A'$ and a sextet $^6A'$ states. It was then shown that the three states of A′ symmetry may be understood as resulting from a strong spin coupling $J = -3500$ cm^{-1} between a triplet on the ligand and a quartet on the metal ion. Interestingly, the second state is of symmetry A″. The analysis of the physical content of its wave function reveals that the ligand has undergone a "spin transition" since its ground-state is singlet. Besides, the three unpaired electrons of the complex are essentially located on the metal ion. These results led to the interesting conclusion that the magnetic properties of the complex (actually the $^4A''$ is populated at room temperature) are due to a "spin transition" occurring on the ligand and not to the exchange coupling between the ligand and the metal ion. If the ligand had been singlet in the complex, the ground-state would have been the $^4A''$ state. The appearance of a doublet ground-state is attributable to the electronic delocalization between the ligand and the metal. Simple molecular diagrams (represented in Figures 10) rationalize the stability of the two almost degenerate states $^4A''$ and $^2A'$ observed in the Fe(gma)CN complex according to the ligand state either singlet (case a) or triplet (case b). The wave functions of the two considered states are multireference, thus these diagrams only provide the dominant reference of each state and the energy of the orbitals are of course different in the two states. Case (a) shows that for a large energy difference between the ligand orbitals which favors the closed-shell singlet state of the ligand the ground-state of the complex would be a quartet essentially localized on the metal. Case (b) illustrates the situation corresponding to a small energy difference between the orbitals of the ligand. The energetic proximity of these orbitals favors a strong metal−ligand delocalization which involves principally the a'_L, a''_L, a'_{M2}, and a''_{M1} MOs (where the indexes L and M stand for ligand and metal ion, respectively) and results in a large stabilization of the doublet ground-state of the complex in agreement with the strong antiferromagnetic exchange integral J. Actually the second a'_{M3} orbital of A′ symmetry which is considered as a nonbonding orbital is essentially localized on the metal ion. As a matter of fact, in a simple molecular orbital description of the complex, the participation of two orbitals of the ligand is invoked suggesting an important contribution of the open-shell states of the ligand. Of course, one may expect that the contribution of the local triplet is greater than the one of the open-shell singlet which is much higher in energy.

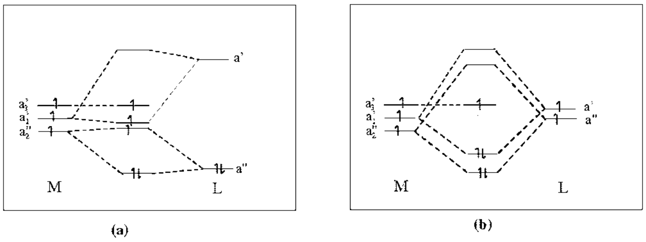

Figure 10. Qualitative energetic diagrams of the Fe(gma)CN complex. Case (a) the gma ligand is singlet, and case (b) the gma ligand is triplet.

TABLE 3: Percentages of Fe +II, +III, +IV, and Mean Oxidation Numbers in the Lowest States of the Fe(gma)CN Complex

	Fe(II)	Fe(III)	Fe(IV)	Fe	gma
$^2A'$	33	61	6	+2.73	−1.73
$^4A''$	20	73	7	+2.86	−1.86
$^4A'$	29	66	5	+2.58	−1.58

TABLE 4: Weights of the Dominant Local Spin States in the Low Energy States of the Fe(gma)CN Complex

	singlet (gma)	triplet (gma)	quartet (Fe)
$^2A'$	4	49	47
$^4A''$	66	7	66
$^4A'$	8	57	59

Thus, a quantitative estimate of the participation of each ligand spin state to the three lowest states of the complex has been performed from the wave functions analysis. In particular, we concentrated on (i) the mean oxidation numbers of both ligand and metal (i.e., relative proportions of Fe(II), Fe(III), and Fe(IV)) extracted from a relocalization orbitals procedure (see Table 3) and (ii) the local spin states contributions in the low-energy spectrum to investigate the "excited-state" coordinated nature of the noninnocent gma ligand (see Table 4).

At the CAS+DDCI2 level, the sum of the weights of the references ($c_{cas}^2 \approx 0.87$) indicates that the ground state $^2A'$ wave function is dominated by determinants involving the five mentioned orbitals. A similar conclusion holds for $^4A''$ and $^4A'$ ($c_{cas}^2 \approx 0.87$). Thus, all the contributions in the CI expansion were normalized using the c_{cas}^2 values considering that the other contributions were physically meaningless for the present purpose. The determinants corresponding to the Fe^{3+}-gma^{2-} charge configuration with one electron per active orbital represent ≈50−60% of the wave functions, a reflection of the correlation effects within this set of electrons. The other contributions account for the ligand-to-metal (i.e., Fe^{2+}-gma^{-}) and metal-to-ligand (i.e., Fe^{4+}-gma^{3-}) charge transfers. The mean oxidation numbers were estimated and are summarized in Table 3.

These theoretical data clearly rule out the existence of an +IV oxidation number for Fe, in agreement with the noninnocent nature of the gma ligand. Conversely, such occupancies strongly suggest the presence of two correlated electrons in the gma ligand giving rise to the local open-shell spin states singlet and triplet. From the Fe^{3+}-gma^{2-} configurations, these contributions can be extracted using basic spin algebra (see Table 4). On the metal center, three spin states are anticipated, namely two doublets and a quartet. Thus, a very similar treatment was performed in order to determine the contribution of the local quartet state of the metal to the CI wave function.

As seen in Table 4, the quartet configuration dominates in all three states, suggesting a rather unusual intermediate spin state on Fe in agreement with experimental conclusions. This is to be contrasted with the puzzling gma ligand spin nature which alternates as the state symmetry changes. In particular, the triplet contribution greatly dominates over the singlet one in the ground-state confirming the “excited state coordination chemistry” concept introduced earlier.[13]

5. Conclusion

The OVB analysis carried out on the ligand MOs in the “metal field” environment strongly suggests that noninnocent ligands behave in analogy to transition metal ions thus making them very attractive in the synthesis of magnetic materials. Our electrostatic study shows that the field (and therefore the oxidation number of the metal) is likely to tune the spin nature of the ligand ground-state when bound to a metal ion. Unexpectedly, the effects of the field at the metal site place induces a motion of the π electrons away from the positive charge. The topology of the ligand tells us wether these two electrons will lie closer or farther in space in the presence of a metal ion. Therefore, the energetic ordering of the ligand spin states in the presence of an electrostatic field generated by the metal ion is predictable. However, no entirely pictorial rules have yet emerged that would allow experimentalists to a priori predict the most likely behavior of a given ligand without recourse to detailed quantum chemical calculations. Nevertheless, the singlet−triplet energy difference can be related with the energy difference between the two ligand orbitals bearing the correlated electrons, in strong analogy with a metal ion in the crystal field theory.

Finally, it has been shown that the delocalization between the metal and the ligand should sometimes be considered in order to determine the main electronic interactions ruling the chemical physics of complexes as well as the nature of their low-energy states. The OVB reading of the correlated wave functions provides an analysis of the different electronic contributions in terms of oxidation numbers and spin configurations of the partners.

The benefit of combining delocalized MO pictures with localized valence bond concepts has been extensively practiced by Sason Shaik throughout his long and successful carreer.[22]

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