Inorg. Chem. **2006**, *45*, 3212–3216

Inorganic Chemistry
Article

Correlated ab Initio Study of the Excited State of the Iron-Coordinated-Mode Noninnocent Glyoxalbis(mercaptoanil) Ligand

Sabri Messaoudi,[†] Vincent Robert,[*,†] Nathalie Guihéry,[‡] and Daniel Maynau[‡]

Laboratoire de Chimie, UMR 5182, Ecole normale supérieure de Lyon, 46 allée d'Italie, 69364
Lyon Cedex 07, France, and Laboratoire de Physique Quantique, UMR 5626, IRSAMC, Université
Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France

Received September 7, 2005

The intriguing and theoretically unresolved magnetic coupling in the Fe(gma)CN (**1**) compound [gma = glyoxalbis(mercaptoanil)] has been investigated by means of first-principle correlated ab initio calculations. The low-energy spectrum of the complex has been studied using the difference dedicated configuration interaction method, which is a dynamically correlated multiconfigurational method. In agreement with available spectroscopic information, we found that the ground-state doublet is dominated by the coupling between an iron-centered quartet and the first excited triplet on the gma ligand. The open-shell character of the electronic structure of the ligand clarifies its noninnocent nature. The low-energy spectrum reveals the presence of a first excited quartet of different symmetry lying 200 cm^{-1} above. The lowest excitation energy in the ground-state symmetry is found at 4790 cm^{-1}, thus ruling out the simple description of the system based on a Heisenberg Hamiltonian.

Introduction

A variety of intriguing ligands that may display different oxidation states when coordinated to metallic centers has been under intense investigation over the past decade. As prototypes of such, 1,2-bis(2-pyridinecarboxamido)benzene [H_2(bpb)], 1,2,4,5-tetrakis(2-pyridinecarboxamido)benzene [H_4(tpb)], and 1,2,4,5-tetrakis(4-*tert*-butyl-2-2-pyridinecarboxamido)benzene [H_4(tbpb)] have been reported in the literature.[1−3] It was initially suggested that transition-metal complexes with coordinating carboxamido N atoms were very sensitive to oxidation at both the metal and ligand centers.[4] Originally, experimentalists put much effort into the design of macrocyclic ligands to stabilize unusually high valences of transition metals such as Co^{IV} and Fe^{IV}.[5,6] However, the use of carboxamido-derived ligands led to rather different conclusions when, for instance, photolysis of Fe^{III}(bpb)(N_3)$_2$ was performed.[4] The noninnocent term was thus suggested to emphasize the fact that such treatment might result in ligand oxidation. Indeed, some ligands may not necessarily possess a closed-shell configuration and the traditional definition of the formal oxidation state may not be appropriate for this class of compounds. Therefore, the possibility of generating radical ligands in coordination compounds has given rise to intense investigation because interesting magnetic materials can be anticipated. Mononuclear as well as dinuclear complexes of Co and Fe were synthesized and characterized.[1,3] On the basis of electrochemical and spectroscopic experiments, the noninnocent character was fully established. The comparison between the Mössbauer spectra of the oxidized compound Fe(bpb)(CN)$_2$ and its parent Na[Fe^{III}(bpb)(CN)$_2$] clearly demonstrated that the oxidation is essentially ligand-centered.[1,2] A similar conclusion was drawn for the dinuclear cyano complexes [N(n-Bu)$_4$]$_2$[Fe$^{III}_2$(tpb)(CN)$_4$] and [N(n-Bu)$_4$]$_2$[Co$^{III}_2$(tbpb)(CN)$_4$].[3]

From both experimental and theoretical points of view, other classes of ligands, namely, aminophenolate and aminothiophenolate, have also attracted a lot of attention.[7−10]

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[*] To whom correspondence should be addressed. E-mail: vrobert@ens-lyon.fr. Tel: 33 4 72 72 88 42. Fax: 33 4 72 72 88 60.

[†] Ecole normale supérieure de Lyon.

[‡] Université Paul Sabatier.

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10.1021/ic051526t CCC: $33.50

Indeed, the electronic structure of related compounds ML_2 (L being a noninnocent ligand) has been controversially discussed for several decades.[11,12] Even though the coordination chemistry of the aminophenolate ligands was characterized as noninnocent, aminothiophenolates were first believed to be redox-innocent.[13] However, recent experimental data have strongly supported their noninnocent character.[14] In particular, the shortening of the C−N bonds by roughly ≈0.04 Å and the appearance of C−C bond alternation in the six-membered rings were clear experimental evidence of the presence of open-shell ligand forms in $[M^{II}L^{ISQ}{}_2]$ (M = Ni, Pd, and Pt, and $[L^{ISQ}]^-$ stands for the *o*-iminothionebenzosemiquinonate[7] or *o*-iminobenzosemiquinonate[8,10,14] radicals). In agreement with these observations, density functional theory (DFT) calculations have supported the presence of such π radicals in Ni^{II},[8,9] Pd^{II}, and Pt^{II} [10] planar complexes. One important result is the rationalization of the singlet diradical character by the occurrence of an instability in the restricted DFT solution,[9] in agreement with elaborate multireference post-Hartree−Fock ab initio calculations.[8] Even more interesting, the prevalence of a radical form in these particular noninnocent ligands has revived important issues in the electronic structure determination.

Even though much effort has been devoted to the theoretical description of electronic structures of noninnocent ligand-based compounds, the comparison between experimental and calculated exchange-coupling constants and the analysis of the magnetic interactions still deserve clarification. Besides, most investigations rely on DFT calculations, which do not provide as much information as multireference post-Hartree−Fock ones.

The aim of this paper is to look into the electronic structure of one particularly intriguing system containing a noninnocent ligand, namely, glyoxalbis(mercaptoanil) (gma). Even though the noninnocent character of the gma ligand (i.e., sensitivity to oxidation with a resulting open-shell configuration) has been clearly identified based on experimental and theoretical analysis,[15] DFT calculations turned out to be partially successful in the electronic structure determination of Fe(gma)CN (**1**) compound (see Figure 1).

From the experimental point of view, zero-field Mössbauer experiments, IR, and magnetic susceptibility measurements were carried out on both **1** and its reduced parent $[Fe(gma)CN]^-$ (**2**). Along the one-electron oxidation of **2**, the Mössbauer parameters as well as the ν(CN) stretching-mode frequency do not evolve significantly. Therefore, the authors concluded that the one-electron oxidation of **2** is not a metal-centered process. Besides, for the analogue $[Fe(gma)(py)]^+$, the combination of Mössbauer data and theoretical investigations favored the presence of an intermediate spin $S_{Fe} = {}^3/_2$ coupled to a gma ligand in its first excited triplet state $S_{gma} = 1$. Thus, this study laid out the important concept of "excited-state coordination" as a novel coordination mode in which a ligand coordinates in an excited electronic state to a metal center. It was speculated that a similar ground-state picture should hold for **1**. From magnetic susceptibility measurements, the ground state was found to be a doublet. However, DFT calculations did not provide any clear evidence of such an electronic structure. Indeed, the $M_S = {}^1/_2$ solution exhibited a low-spin Fe^{III} ($S_{Fe} = {}^1/_2$) coupled to a closed-shell gma ligand ($S_{gma} = 0$).[15] It was simultaneously confirmed from Mössbauer parameter calculations that this electronic picture should not be appropriate and that correlated ab initio calculations should be performed. Indeed, one may argue that for such open-shell systems state-of-the-art ab initio calculations might be desirable. A very similar issue was encountered for the iodine analogue Fe(gma)I, which makes such a noninnocent ligand a particularly challenging system. Another critical issue for these systems is the lack of crystallographic structures, while it is known that the geometries directly control the magnitude of the magnetic interactions.[16,17]

Figure 1. Structure of **1**.

Thus, our strategy was to first optimize the complex geometry using a DFT approach. Then, we performed correlated ab initio calculations to elucidate the electronic structures of Fe^{III} complexes including the gma ligand. In this paper, our goal is to propose an appropriate theoretical method to investigate this extensively studied class of compounds. In particular, we will show that the importance of charge transfers may not allow one to depict such magnetic systems on the basis of a simple Heisenberg Hamiltonian.

Theoretical Calculations

Because exchange calculations are very sensitive to the geometries,[16,17] theoretical investigations should first reproduce reliable structures. However, from experimental data, such information is not accessible for the Fe(gma)CN compound. Thus, geometrical details are to be found in full-geometry DFT optimization. Let us mention that the sensitivity of the spin state strongly depends on the nature of the functional.[18] Still, we performed geometry optimization within this framework, otherwise out of reach with correlated approaches. Therefore, the geometry of **1** was optimized

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by means of the *Gaussian 98*[19] suite of programs in an unrestricted all-electron UB3LYP[20,21] DFT scheme with basis sets including polarization orbitals (6-31G*).[22−26] Such a combination of correlation and hybrid-exchange functionals is known to produce very good geometries.[9,27] On the basis of the experimental suggestions, we performed with $M_S = {}^5/_2$ a full-geometry optimization in an unrestricted UB3LYP framework. This spin projection is likely to take into account the five active electrons of the system and is free from spin-contamination problems. Let us notice that a full-geometry optimization of the $M_S = {}^1/_2$ state using the same hybrid functional provides very close distances and bond angles. To consolidate our strategy, we also calculated the C−N stretching-mode frequency, which has been reported from IR spectroscopy measurements.

In a second step, ab initio correlated calculations were carried out to clarify the low-energy spectroscopy of **1**. Even though these post-Hartree−Fock methods can be very demanding, the presence of near degeneracy (i.e., nondynamical correlation) may require a multiconfigurational treatment. Thus, we first performed complete active space self-consistent-field (CASSCF) calculations using the Molcas[30] package, optimizing simultaneously the orbitals and the wave-function coefficients for a five electron−five molecular orbital (MO) active space CAS(5,5). At this level, the polarization and correlation effects in the active space are taken into account in a variational procedure. The so-obtained active space is stable. Indeed, a larger active space CAS(5,7) that contains seven orbitals and five electrons, i.e., including the five d orbitals of the Fe ion, has also been considered. The so-optimized orbitals are very similar to those obtained at the CAS(5,5) SCF level and the occupation numbers of the two additional d orbitals are close to zero, showing that these orbitals can be removed from the active space. This result confirms the prediction of ref 15, according to which only three d orbitals should be partially occupied in the ground-state electronic structure of this complex. Extended basis sets and pseudopotentials[31] on the Fe atom (9s6p6d)/[3s3p4d] and nearest-neighbor atoms (5s5p1d)/[2s3p1d] for N, (7s6p1d)/[2s3p1d] for S, and (5s5p1d)/[2s3p1d] for C were used, whereas the rest of the molecule was described with smaller basis sets ((6s3p)/[3s2p] for C and (3s)/[1s] for H).[32] Because our goal was to investigate the low-energy spectrum, the crucial dynamical correlation effects were also estimated by including excitations on the top of the CASSCF wave function. The difference dedicated configuration interaction (DDCI) method[33] allows one to treat such contributions. We used the implementation of the method available in the CASDI code.[34] The method relies on a multireference configuration interaction (CI) expansion of the wave function, which focuses on energy differences rather than on absolute values for states belonging to a given CAS. In particular, the CI expansion does not include all of the double excitations from occupied inactive MOs to virtual ones. Indeed, at second order of perturbation theory, it can be shown that they do not contribute to the energy difference. The suppression of these excitations, which are by far the most numerous, significantly reduces the computational cost. The DDCI method has proven to be the most accurate approach in the evaluation of magnetic exchange-coupling constants in molecular as well as solid-state materials.[35−37]

Let us mention that one important issue along this framework is the use of a single MO basis set to construct the different excitations. To reproduce at best the energy difference between the two lowest states of the system, natural orbitals have been determined in an average way between the lowest doublet and quartet states. The orbital optimization has been performed using the iterated DDCI[38] procedure, which provides natural orbitals extracted from the mean density matrix of the correlated wave functions. As a result of the use of relatively large basis sets (264 atomic orbitals), our calculations were limited to the DDCI-2 level, allowing up to 2 degrees of freedom in the excitation space.[33,34] To our knowledge, a few studies using the DDCI method have been called for to rationalize the magnetic interactions in open-shell ligand-based complexes.[8,39,40] Clearly, the exchange mechanism between noninnocent ligands and metallic centers such as the Fe^{III} ion still deserves interpretation.

Results and Discussion

As mentioned before, the geometry optimization was performed in the sextet state, which is readily accessible in the DFT framework. Even though the calculation was done in an unrestricted scheme, we did not notice any particular spin contamination ($\langle S^2 \rangle = 8.81$ as compared to the pure spin state value 8.75). The geometry of the doublet state is very similar to the sextet one. The relative changes in bond lengths and angles are smaller than 3%. Regarding the geometry of the sextet state, the calculated bond distances Fe−S = 2.228 Å and Fe−N = 1.966 Å are close to the ones determined previously (2.167 and 1.921 Å).[15] However, the Fe−CN distance is 2.047 Å, i.e., 0.182 Å longer than

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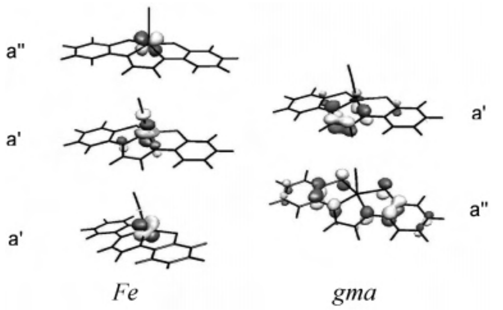

Figure 2. Optimized active average MOs for the lowest doublet $D_{A'}$ and quartet $Q_{A''}$ states for **1**. The symmetry labels in the C_s point group are given.

that in ref 15. This difference can be attributed to the use of a different functional and basis set exclusively because the Fe−CN distance is 1.995 Å in our doublet state. Because experimental data on very similar compounds exhibiting low spin states agree on ≈1.98-Å Fe−CN distances,[3] we believe that our value for an intermediate spin system should be acceptable. Using this particular geometry, the calculation of the cyano group stretching-mode frequency gave 2225 cm^{-1}. The satisfactory agreement with the experimental value (2111 cm^{-1}) is another element to support the optimized geometry that we found. DFT calculations generally lead to overestimations of the frequencies, and an error lower than 5% is commonly admitted. Even though the geometry was optimized without imposing any constraint, the complex reflects almost a C_s symmetry. To reduce the computational cost of the forthcoming calculations, we explicitly introduced this particular symmetry by means of slight distortions. The latter are less than 0.1% and 0.5% for the bond distances and valence or dihedral angles, respectively. Because ref 15 concluded in a shorter Fe−CN distance, we also performed exactly the same calculations using the reported 1.86-Å value. As will be shown in the following, results obtained using both geometries agree on the same electronic description of the ground state.

At the CAS(5,5)SCF level, the lowest doublet state $D_{A'}$ is of A' symmetry in the C_s point group. Conversely, the lowest state in A'' symmetry, $Q_{A''}$, is a quartet and lies lower in energy than $D_{A'}$. However, it is known that dynamical correlation is likely to modify this state of affairs. The I-DDCI2-optimized MOs are shown in Figure 2. For analytical purposes, these orbitals have been relocalized either on the metal or on the ligand using an a posteriori relocalization procedure, which only proceeds to rotations between active orbitals. It should be noted that, because of rotational invariance of the DDCI spaces, the here-calculated wave functions are identical in the delocalized and localized orbital sets. Interestingly, the active orbitals consist of three metal-centered and two ligand-centered MOs. This particular active space was strongly supported by experimental and calculated Mössbauer parameters (see ref 15). The singly occupied ligand orbitals are of A' and A'' symmetries (see Figure 2) and mainly of N π and S π character, respectively.

The energetic ordering of the states at the DDCI-2 level of treatment is modified under the dynamical correlation effects. $D_{A'}$ is now the ground state and consists mainly of a quartet localized on the metal ($S_{Fe} = {}^3/_2$, in agreement with the Mössbauer experiments) and a ligand-based triplet ($S_{gma} = 1$; see Figure 3a). Let us mention that other contributions accounting for the ligand-to-metal charge transfer (LMCT) also participate in the ground-state doublet description (see Figure 3b). The coefficients in the correlated wave function of the determinant with a closed-shell gma ligand (see Figure 3c) are smaller, namely, 0.18.

The nearest quartet $Q_{A''}$ is now found to be 200 cm^{-1} less stable than the ground state and is of A'' symmetry. On the basis of DFT calculations, a very similar observation was made for the parent compound [Fe(gma)(py)]$^+$.[15] From the DDCI-2 wave function analysis, $Q_{A''}$ is largely dominated by a closed-shell local singlet on the gma ligand ($S_{gma} = 0$; see Figure 3d), which is a rather different charge distribution as compared to the ground state $D_{A'}$. The first quartet and sextet of A' symmetry, $Q_{A'}$ and $S_{A'}$, lie 4790 and 14 140 cm^{-1} higher in energy, respectively. Let us mention that, using a Heisenberg Hamiltonian $\mathbf{H} = J\mathbf{S}_{Fe}\mathbf{S}_{gma}$, this spectrum is compatible with a very strong antiferromagnetic coupling $J \sim 3540-3740$ cm^{-1}. Such a large value shows the partially covalent character of the interaction between the metal and ligand and probably explains why DFT calculations, which are single-reference calculations, converge on a one-unpaired-electron electronic structure. From the ground-state wave-function coefficients, it is possible to define an index of covalency by the ratio between ionic and neutral determinants. A neutral determinant corresponds to an Fe^{3+}gma^{2-} electronic configuration, while in an ionic determinant, an electron is transferred between the metal and ligand, resulting in Fe^{2+}gma^{3-} or Fe^{4+}gma^{-} electronic configurations. Ideal values of the covalency index are respectively 1 in pure covalent bonds and 0 in pure magnetic bonds (for instance, in a triplet). In the present case, the covalency index (only calculated in the reference space) is 0.49, confirming both the intermediate magnetic/covalent character of the metal−ligand interaction and its rather strongly correlated nature.

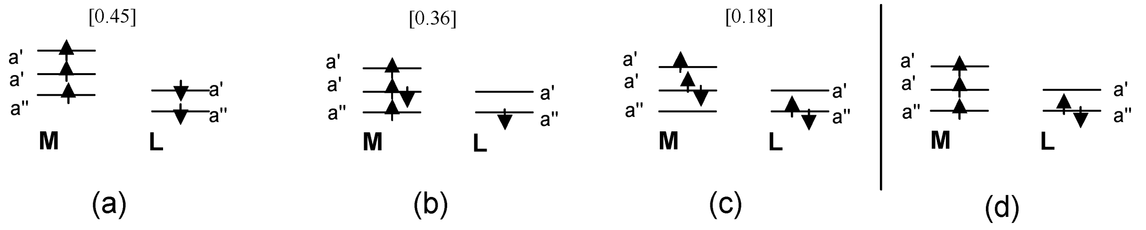

Figure 3. Main determinants participating in the different spin states: (a−c) on the doublet ground state $D_{A'}$; (d) on the first excited quartet $Q_{A''}$. The symmetry labels of the MOs are given in correspondence with those of Figure 2. The different determinant coefficients are given in brackets.

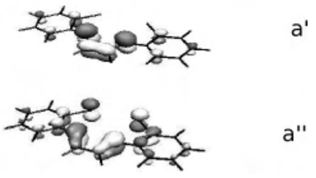

Figure 4. Optimized active MOs of the lowest triplet state of the isolated closed-shell gma^{2-} ligand.

Contrary to what was expected, the $Q_{A'}$ state therefore does not account for the temperature-dependent observed magnetic properties. Nevertheless, the lowest excitation energy corresponding to the $D_{A'}-Q_{A''}$ splitting (200 cm^{-1}) is in complete agreement with experimental evidence. The energy difference between the doublet ground state and the first quartet excited state should, of course, not be rationalized by an antiferromagnetic coupling constant because the spatial configurations of the states under consideration differ. Let us mention that the use of a modified geometry with a Fe−CN distance of 1.86 Å, as found in ref 15, led to a similar low-energy spectrum, exhibiting a doublet ground state of A' symmetry. The energy difference between the doublet ground state and the first quartet excited state, $Q_{A''}$, is 140 cm^{-1} for this particular Fe−CN distance.

Considering the rather versatile character of the gma ligand, we felt that similar calculations for the isolated ligand should be carried out to estimate its ability to undergo singlet−triplet transition. Thus, we started by computing the triplet MOs (see Figure 4) at a CASSCF level using two electrons in two orbitals as the active space. This set of orbitals was then used to estimate the singlet−triplet energy difference following the DDCI logics.[33,34] At the same level of calculations (i.e., DDCI-2), the lowest singlet A'−triplet A'' excitation energy is ≈14 000 cm^{-1}, a reflection of the deep electron reorganization in the ligand when interaction with the metal center is turned on.

From these calculations on the complex and ligand, we can conclude that the ground state is indeed a doublet spin state, featuring an "excited-state coordination" mode of the gma ligand. Therefore, one can think of the ligand as undergoing a spin transition when coordination occurs. This puzzling observation can be understood as follows. As indicated in parts a and b of Figure 3, the ground-state doublet $D_{A'}$ consists mainly of a combination of two electronic configurations with almost equal coefficients (0.45 and 0.36). Consequently, these electronic configurations must be barely degenerated. The leading one is a metal quartet spin state and ligand triplet distribution, whereas the second corresponds to a LMCT. In view of these wave-function coefficients, the resonance energy stabilization arising from the mixing of these two configurations must override the energy cost of the gma ligand singlet−triplet excitation. Evidently, in the ligand closed-shell distribution (see Figure 3c), such a resonant interaction is not possible. Furthermore, from our ab initio calculations, the metal-to-ligand charge-transfer amplitude is negligible, in agreement with the absence of Fe^{IV} in the ground state.

Finally, one can argue that the suggested resonance energy stabilization mechanism favorably competes with the singlet−triplet energy cost (≈14 000 cm^{-1}) in the ligand when coordination occurs. The dependence of the spin state with respect to the coordination number is well-known in biological systems. As a matter of fact, five-coordinate iron(II) porphyrins are high-spin, whereas the six-coordinate porphyrin complexes are low-spin.[41] Thus, there is a strong similarity between the studied system and the behavior of biological heme systems,[42] although the roles of the ligand and metal are exchanged.

Conclusion

Our correlated ab initio calculations on the Fe(gma)CN complex showed that the low-energy spectrum exhibits a 200-cm^{-1} $Q_{A'}-D_{A''}$ gap, in agreement with different experimental observations. Because the spatial configurations of the two lowest states are different, this excitation should not be rationalized using a Heisenberg Hamiltonian. On the contrary, the energy differences between the doublet $D_{A'}$, the quartet $Q_{A'}$, and the sextet $S_{A'}$ states of the same spatial configuration obey a Heisenberg logic. The strong antiferromagnetic coupling (≈3600 cm^{-1}) is due to important LMCT contributions. The resulting ground-state wave function exhibits an intermediate magnetic/covalent character and is rather strongly correlated. Moreover, it is dominated by local ($S_{\mathrm{Fe}} = {}^{3}/_{2}$ and $S_{\mathrm{gma}} = 1$) electronic configurations. From our calculations, the gma ligand is likely to be a triplet when coordinated to the iron center, whereas it is clearly a closed-shell singlet when considered alone. The present work can be considered as an original advancement in the study of intriguing systems that may display unusual electronic distributions. The multiconfigurational nature of the wave function has been clearly identified and makes this class of compounds very challenging for theoreticians. A detailed inspection of the ligand excitation mechanism in this particular compound is currently being carried out.

Acknowledgment. Dr. L. Chibotaru was very helpful in the understanding of the magnetic interaction interpretations.

IC051526T

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