A Combined Experimental and Theoretical Study of Carboxylate Coordination Modes: A Structural Probe

Vincent Robert* and Gilles Lemercier

Contribution from the Laboratoire de Chimie, UMR 5182 Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France

Received July 28, 2005; E-mail: vrobert@ens-lyon.fr

Abstract: The variations of the frequency differences of symmetric and asymmetric stretching vibrations in a series of carboxylato Fe(II) complexes have been theoretically studied. It is shown that structural information can be obtained from a direct comparison between the difference ($\Delta = \nu_{as} - \nu_s$) in the asymmetric ($\nu_{as}$) and symmetric ($\nu_s$) carboxylate vibrations of the free anion and that of the coordinated species. The coordination mode approaches C_{2v} symmetry as Δ decreases with respect to its value for the noncoordinated carboxylate. The use of IR spectroscopy in the resolution of speculated crystallographic structures is suggested.

1. Introduction

In the understanding of transition metal complexes, various experimental techniques have been called for to elucidate the intriguing metal−ligand interactions. By varying the nature of the coordination sphere as well as the metal and its oxidation state, a wide variety of properties can be tuned, ranging from UV electronic absorption characteristics to specific magnetic behavior. In particular, the possibility to use open-shell ligands in order to enhance the magnetic properties has been considerably investigated and debated in the literature.[1−3]

A standard way to rationalize the metal−ligand interactions is to compare the strength of the ligand field and the electron−electron repulsion (i.e., crystal field theory). However, such a picture assumes a given charge distribution (i.e., formal oxidation state) over the metal center and the surrounding ligands. Thus, the concept of a spectroscopic oxidation state opposed to a formal oxidation number has been introduced in order to bridge the gap between experimental measurements and theoretical analysis.[4,5] The electronic structure of ligands is a crucial issue which is currently being reconsidered in the field of organometallic materials, both from experimental and theoretical points of view. Spectroscopic oxidation numbers are a means to rationalize the importance of charge reorganization when coordination occurs. Nevertheless, discrepancies between the traditional formal oxidation number definition and this rather new concept arise when organic radicals with open shells are coordinated to a transition metal ion. The latter reflects the actual nature of the charge distribution, whereas the former has an arbitrary misleading character. From the experimental point of view, infrared (IR) spectroscopy is very sensitive to the charge distribution. Thus, it is well-adapted to clarify this particular kind of issue. Indeed, one can trace the frequency changes of a given stretching mode with respect to external perturbations (e.g., redox reaction) to probe the metal electronic structure. Such strategy has been extensively used in the field of heterogeneous catalysis, where small molecules such as carbon monoxide are used to probe active surfaces.[6] The combination of experimental measurements and ab initio calculations has been reported to clarify the nature of the active sites.[7] Since the stretching mode frequencies are a reflection of the bond strength, IR spectroscopy can be directly used to investigate the hapticity of the coordination mode. A major breakthrough in this field was achieved in 1980 in the milestone paper of Deacon and Phillips.[8] The authors clearly evidenced a strong relationship between the carbon−oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination.[9] The difference between the asymmetric (ν_{as}) and symmetric (ν_s) CO_2^- absorption frequencies observed in carboxylates of different complexes (the so-called Δ parameter in the following) may be compared to the values obtained for the noncoordinated ionic species (Δ_{ionic}) to obtain information on the coordination mode. It was suggested that $\Delta > \Delta_{ionic}$ may be correlated with a unidentate carboxylate coordination mode, involving two nonequivalent carbon−oxygen bonds. Nevertheless, the authors concluded that the factors which control the Δ value are not limited to geometrical characteristics, such as the carbon−oxygen bond length differences or the amplitude of the valence angle O−C−O. More recently, the diversity of bidentate coordination modes of carboxylates was illustrated in a series of high-spin Fe(II) complexes [Fe(TIM)(HCO$_2$)$_2$] (**1** = H,

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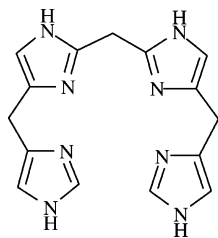(9) Costes, J.-P.; Dahan, F.; Laurent, J.-P. *Inorg. Chem.* **1985**, *24*, 1018.

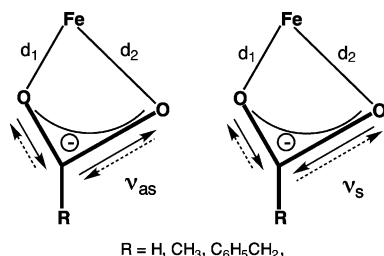**Figure 1.** Schematic representation of the TIM ligand.

Figure 2. Schematic representation of the asymmetric and symmetric stretching modes.

Table 1. Experimental Δ and Δ_{ionic} Values (cm^{-1}) of the Studied Fe(II) Complexes[10] (Fe−O distances, d_1 and d_2 (Å), are given for the resolved crystallographic structures **2** and **3**)

	Δ	Δ_{ionic}	d_1	d_2
1	254	240		
2a	150	165	2.108(2)	2.435(3)
2b	100	165	2.227(2)	2.263(2)
3	152	190	2.164(2)	2.328(2)

formiate), [Fe(TIM)(CH$_3$CO$_2$)](ClO$_4$) (**2** = Ac), Fe(TIM)(C$_6$H$_5$-CH$_2$CO$_2$)](ClO$_4$) (**3** = PhAc), Fe(TIM)(CH$_3$CO$_2$)$_2$, and Fe$_2$-(TIM)$_2$(TIM)$_2$C$_2$O$_4$)$_2$][10] involving the TIM ligand (TIM = bis[(imidazol-4-methyl)-4′-imidazol-2′-yl]methane; see Figure 1).[11] On the basis of the crystallographic data and IR measurements ran as CsBr pellets, it is rather tempting to specify the symmetry of the coordination mode by measuring the deviation of the local carboxylate symmetry from a strictly C_{2v} symmetry around the metal center (i.e., $d_1 = d_2$; see Figure 2). Interestingly, the coordination symmetry of the carboxylate seems to directly control the Δ parameter; Δ and Δ_{ionic} collected in the literature are summarized in Table 1. One should note that the unit cell of the crystal structure of **2** (see Figure 3) consists of two complexes (referred to as **2a** and **2b** in the following) which exhibit different geometrical and spectroscopic characteristics. The comparison between the crystal structures of **2** and **3** shows that both carboxylates are bidentate. However, the experimental Δ values differ and can be correlated to the coordination mode symmetry. While the bidentate coordination mode of the acetate anion can be either strongly asymmetrical in site *a* or symmetrical in site *b* of complex **2**, the bidentate coordination mode of the phenylacetate anion is symmetrical in complex **3**. Even though the crystal structure of **1** has not been resolved, the experimental Δ value strongly supports a monodentate coordination mode, reflecting the largest asymmetry. The fact that IR spectroscopy has the ability to differentiate symmetrical and asymmetrical bidentate coordination modes clearly indicates the importance of structural and electronic effects of this apparently tenuous difference.
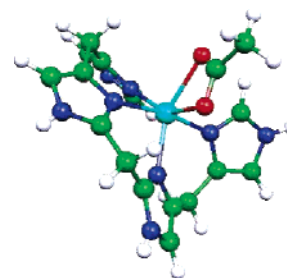
Figure 3. Crystal structure of **2b**. **1**, **2a**, and **3** differ in the Fe−O distances, d_1 and d_2.

From the coordination chemistry point of view, the versatility of carboxylates has been stressed in numerous complexes, many of which had played a key role in the conceptual development of modern inorganic chemistry or in the bioinorganic field. Among the relatively few ligands involved in metalloproteins, carboxylate groups of glutamate and the aspartate side chain form an important class.[12] Hemerythrin (Hr), the R2 subunit of ribonucleotide reductase (RNR-R2), and the hydroxylase component of soluble methane monooxygenase (sMMO) are featuring examples of carboxylate-bridged diiron active sites of non-heme proteins which are known to interact with dioxygen. The variety of coordination modes makes carboxylates key building blocks in the synthesis of polynuclear complexes, ranging from discrete dinuclear complexes[13] to supramolecular networks.[14−16] In particular, the dynamics of carboxylate ligands (the so-called "carboxylate shift"[17−19]) has been under intense NMR investigations[20] motivated by intriguing systems such as metalloproteins as well as polynuclear metal catalysts. Interestingly, the influence of the carboxylate bridging mode on the magnetic properties has also been addressed.[21] It has been shown that the exchange constants are very sensitive to the bridging mode. Let us stress that the understanding of a hybrid material's structure has also taken advantage of IR spectroscopy by inspecting the particular Δ parameter.[22]

Considering this importance of carboxylate anions in organometallic and biological systems, we felt that a theoretical investigation of the correlation between the coordination mode and the Δ parameter would be desirable. Thus, the aim of this paper is to trace the changes in $\Delta = \nu_{as} - \nu_s$ in a series of Fe(II) analogues, namely, **1**, **2** and **3**. We performed density functional theory (DFT) calculations in order to (i) support the use of IR measurements to investigate carboxylate coordination symmetry (compounds **2a**, **2b**, and **3**), and (ii) clarify the coordination mode symmetry of complexes for which crystal

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data are not available (compound **1**). Evidently, this combination of experimental and theoretical analysis would be particularly useful in the elucidation of active sites of metalloproteins. To assess the reliability of our strategy, we also introduced and determined by means of DFT calculations the deviation of the Δ parameter with respect to local geometry distortion. Let us mention that all our calculations were performed in the gas phase and did not incorporate the environmental effects (so-called "site symmetry approximation"). We rather focused on the comparison between the Δ values in the complexes and within the noncoordinated carboxylates.

2. Theoretical Approach and Technical Details

Since we were primarily interested in looking at the changes in the difference between the symmetrical and asymmetrical stretching mode frequencies (i.e., the Δ value), we first performed full optimizations of the geometries without any geometrical constraints. From magnetic measurements, all the complexes under investigation are high-spin (i.e., $S = 2$), exhibiting four unpaired electrons. Thus, the calculations were performed in an unrestricted density functional theory (UDFT) scheme for which spin contamination can be a major issue. Indeed, the mono-determinant structure of the wave function does not allow one to build exact $\hat{S}^2$ eigen-function as soon as the spatial parts of the α and β spin orbitals differ. However, Noodleman et al. showed that a state of mixed-spin symmetry can be obtained by means of a spin-polarized self-consistent procedure allowing the singly occupied molecular orbitals (i.e., magnetic orbitals) to interact.[23,24] This method is referred to as the "broken symmetry" calculations. It has been the mother land of numerous exchange constant calculations.[25-28] A clear probe of the spin mixing amplitude is the $\hat{S}^2$ expectation value. In an unrestricted formalism, the deviation from the $S(S + 1)$ value is a measure of the so-called spin contamination. For all of our calculations, we checked that the $\hat{S}^2$ value was close enough to the expected $S(S + 1) = 6$ value so that spin contamination was negligibly small. In this case, the converged state is almost a pure sextet spin state. This numerical result perfectly agrees with the experimental magnetic moment measurements reflecting the presence of four unpaired electrons. If the number of magnetic electrons were larger, then the unrestricted sextet solution would probably be spin-contaminated. Then, using the optimized geometries, the corresponding IR spectra were calculated. Special attention was dedicated to the symmetric and asymmetric stretching modes of coordinating carboxylates. The effect of the environment was not taken into account in this work. As a matter of fact, our goal was primarily to look into the electronic and coordination mode factors. One may assume that the solvent effects should not greatly modify the frequency differences we looked for since they would affect both ν_s and ν_{as}. All of our calculations were performed using the Gaussian98[29] package. Double-ζ GTO basis sets were used for H, C, N, and O atoms. As far as the Fe atom is concerned,

the effects of the core electrons were accounted for with the Los Alamos pseudo-potential.[30] We used the standard generalized gradient-corrected hybrid functional B3-LYP, consisting of the exchange Becke three parameter functional and the Lee–Yang–Parr correlation functional. Such combination of correlation functional and hybrid exchange functional is known to produce very good geometries.[31] One should mention that hybrid density functional theory has been used to study mechanisms for redox-active enzymes containing complexes with a variety of different transition metals.[32] Since some crystallographic data were available, we were able to evaluate the accuracy of the geometry optimization procedure. In particular, we checked that the inclusion of polarization functions[33] on all the atoms of **2b** leads to negligible changes in the geometry and the IR spectrum. The use of the well-accepted exchange-correlation functional BP86 leads to very similar conclusions upon the featuring aspects of **2b**. Let us mention that geometry optimizations are out of reach of correlated ab initio techniques, which are currently used in spectroscopic studies. As soon as agreement between the simulated and experimental $\Delta = \nu_{as} - \nu_s$ values is reached, we will show that the coordination mode symmetry for unresolved structures can be determined from the calculated geometries.

At this point, the question of the reliability of the optimized geometry might be raised. Considering the number of degrees of freedom, one may wonder whether the actual absolute minimum has been reached. It can be expected that the frequencies we are interested in should be sensitive to the local symmetry, that is, the Fe–O distances d_1 and d_2 (see Figure 2). Evidently, the larger the frequency changes upon distortion, the more reliable the correlations between the IR Δ values and the symmetry of the coordination mode. The original strategy we developed is the following. We first favorably confronted the optimized structure of **2b** to the available crystal data. Starting from this calculated optimal structure, one particular geometry deformation was considered, setting the Fe–O distances d_1 and d_2 to $d_1 - \delta d$ and $d_2 + \delta d$, respectively. Such deformation accounts for the deviation of the coordination mode from a strictly C_{2v} symmetry. Then, geometry optimization was performed using these modified and frozen Fe–O distances. By recalculating the IR spectrum, we finally defined the deviation of Δ with respect to d_1 and d_2 changes as

$$\Delta = \Delta_0 + \frac{\partial \Delta}{\partial d}\delta d = \Delta_0 + \sigma \delta d$$

where Δ_0 stands for the frequency differences $\nu_{as} - \nu_s$ at optimal geometry; σ is a measure of the uncertainty in the attribution of a given coordination mode symmetry using a calculated Δ value. Evidently, a similar estimation could be carried out using **3**. However, we concentrated on **2b** by setting δd to values in the range of 0.05–0.15 Å to extract a linear fit of Δ, which fully defines σ.

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Table 2. Calculated Fe−O and Fe−N Bond Distances (Å)

	d_1	d_2	Fe–N_1	Fe–N_2	Fe–N_3	Fe–N_4
1	1.99	3.28	2.15	2.18	2.15	2.16
2a	1.98	3.10	2.15	2.19	2.15	2.15
2b	2.18	2.30	2.16	2.16	2.16	2.16
3	2.20	2.30	2.15	2.15	2.16	2.16

Table 3. Calculated Δ Values (cm^{-1}) and Relative Differences ($\rho = |\Delta - \Delta_{\text{ionic}}|/\Delta_{\text{ionic}}$; σ (cm^{-1}/Å) is a calculated measure of the deviation of Δ with respect to the deformation $d_1 \rightarrow d_1 - \delta d/d_2 \rightarrow d_2 + \delta d$)

	Δ	Δ_{ionic}	$10^2 \rho$	$|\sigma|$
1	320	340	5.8	
2a	250	300	17	
2b	115	300	62	200
3	75	300	75	

Due to the frequent overestimation of bond distances in DFT calculations, we believe that this particular inspection of the potential energy surface would be very insightful in any calculations of IR spectra.

3. Results and Discussion

The most relevant optimized bond distances in complexes **1**, **2**, and **3** are summarized in Table 2. **2a** and **2b** structures were obtained by using different sets of Fe−O distances in the starting points for geometry optimization. The calculated energy difference is less than 60 meV, which supports the simultaneous presence of both complexes **2a** and **2b** at room temperature (~25 meV). First, the Fe−N distances are almost all equal and independent of the carboxylates. The agreement with the reported crystal structure of **2** and **3** is very satisfactory since these bond distances deviate by less than 3% as compared to the experimental ones.[10] However, the calculated Fe−O distances in **2a** significantly differ and suggest a quasi-monodentate mode for the acetate group. We believe that the inclusion of intermolecular interactions may change this state of affairs. Let us mention that geometry optimization does not strongly depend on the functional. Using a different method (i.e., BP86), complex **2b** displays Fe−O distances $d_1 = 2.19$ Å and $d_2 = 2.29$ Å, as compared to 2.18 and 2.30 Å values reported in Table 2.

From our calculations, the formiate is preferentially monodentate in **1**. This particular coordination mode has been speculated but not fully established in the crystal structure. Thus, the simultaneous presence of symmetrical and asymmetrical structures in rapid equilibrium is an important issue. Such mechanism would involve decoordination/coordination steps. We thus investigated the stability of an intermediate geometry of **1**, performing geometry relaxation with frozen Fe−O distances equal to the average value of 2.635 Å. A barrier value of ~400 meV was found, suggesting a static situation with rather different Fe−O distances in **1**. Conversely, the difference between d_1 and d_2 is reduced in **2b** and **3**, in agreement with the available crystallographic data.[10] Finally, despite the overestimation of one Fe−O distance, our results suggest a more asymmetric coordination mode in **2a**, in agreement with the experimental data.

We then turned to the simulations of the IR spectra of the different complexes and the corresponding isolated carboxylates. The Δ and Δ_{ionic} values are summarized in Table 3. Let us first mention that Δ_{ionic} is sensitive to the presence of an alkyl group

but not to its nature. Since the C−O distances are almost all identical (~1.29 Å), one may argue that the bond strengths are not significantly affected. However, due to the presence of the alkyl group (either methyl or tolyl), the changes in ν_s and ν_{as} should differ as a result of the steric effects. The asymmetric mode can be depicted as a simultaneous shortening and lengthening of C−O bonds and should not be significantly modified. Conversely, the symmetric mode is expected to be hardened given that both C−O bonds are shortened or lengthened. Therefore, Δ_{ionic} decreases from formiate to phenylacetate (see Table 3). Even though our major concern is not the absolute values of ν_s and ν_{as}, we will stress that a similar interpretation holds for the coordinated carboxylates. Considering our theoretical calculations, the coordination modes of acetate in **2a**, **2b**, and phenylacetate in **3** may be tentatively assessed by comparison with the Δ_{ionic} value. From Table 2, the coordination modes in **2b** and **3** are almost identical, but strongly differ from that of **2a**. Clearly, DFT calculations cannot differentiate between the coordination modes of **2b** and **3**. However, our theoretical results agree with experimental observations that (i) for Δ values smaller than the references Δ_{ionic}, the coordination mode approaches C_{2v} symmetry, and (ii) the larger the relative difference $\rho = |\Delta - \Delta_{\text{ionic}}|/\Delta_{\text{ionic}}$, the more symmetrical the coordination mode (see Table 3). Thus, ρ can be directly correlated with the coordination symmetry, regardless the carboxylate nature. Inspection of the individual frequencies which clearly indicate the presence of carboxylate groups shows that the reduction of Δ results from a simultaneous "blue shift" of ν_s (~1250 cm^{-1}) and "red shift" of ν_{as} (~1550 cm^{-1}). Comparing complexes **1** to **3**, the general trend in d_1 is toward increasing (see Table 2), which may account for a softening of both vibrations. Nevertheless, ν_s in **2b** and **3** increases as a consequence of the bidentate character of carboxylates, which deeply affects the simultaneous shortening and lengthening of C−O bonds in this mode. Let us mention that the inclusion of solvent effects (hydrogen bonds) would probably have a greater influence on the Δ_{ionic} values than on the Δ ones since the ability of oxygen atoms to form hydrogen bonds is reduced in bound carboxylates.

At this point, the reliability of the geometry optimizations is questionable. Indeed, one may ask how much Δ is sensitive to the bond distances of interest, d_1 and d_2. Such information is contained in $|\sigma|$, which is a direct measurement of the Δ variations with respect to the disymmetrizing distortion $d_1 \rightarrow d_1 - \delta d$ and $d_2 \rightarrow d_2 + \delta d$. Evidently, other deformations might be considered. However, this particular one is likely to affect the symmetry-dependent Δ value. The larger $|\sigma|$, the more relevant the correlations between Δ and the symmetry of the carboxylate coordination mode. The $|\sigma|$ value (~200 cm^{-1}/Å) calculated for **2b** (see Table 3) validates the use of IR in the determination of coordination characteristics. Typically, a simultaneous shortening and lengthening of the Fe−O distances of 0.1 Å leads to a change in Δ of ~20 cm^{-1}, a value which is larger than the commonly accepted numerical uncertainty.

Since the correlation between the symmetry of the coordination mode and the Δ value is supported by our theoretical calculations, we used this strategy to elucidate the coordination structure of formiate in **1** (see Figure 4). As seen in Table 3, a large Δ value is calculated and almost identical to Δ_{ionic}, in agreement with experimental observations. Considering the σ
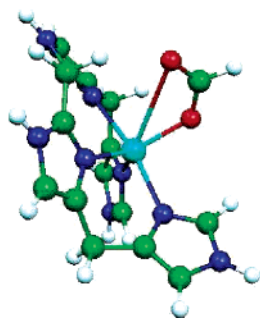
Figure 4. Optimized structure of **1** exhibiting significantly different Fe−O distances.

estimation, the DFT optimized and experimental structures must be very similar. One can conclude that formate is monodentate, a coordination mode which had been speculated though not evidenced due to the lack of crystallographic structure.

On the basis of magnetic moment measurements, all of our calculations have been performed assuming high-spin state complexes. Following the idea that IR data can be used to investigate the coordination mode of carboxylates, we wondered whether magnetic information over the spin state could be extracted. Thus, full geometry optimization of **1** was carried out assuming a low-spin electronic (i.e., $S = 0$) configuration. The optimized geometry displays very similar Fe−O distances ($d_1 = 2.10$ Å and $d_2 = 2.16$ Å, i.e., rather symmetrical coordination mode), while a Δ value of 200 cm^{-1} was estimated. However, the important difference (140 cm^{-1}) between this calculated value and the reference Δ_{ionic} (340 cm^{-1}) as compared to the experimental difference (~15 cm^{-1}; see Table 1) rules out this particular unrealistic geometry. Therefore, the low-spin electronic configuration must be discarded in a favor of a high-spin one on the basis of an IR spectrum analysis. Even though all of our calculations have been performed in the absence of solvation effects, the differences between the Δ and Δ_{ionic} values have been favorably compared to the reported experimental ones. One may argue that the solvent would certainly modify these absolute values but not significantly the relative differences we have focused on.

4. Conclusion

In the present work, we have shown that a combination of experimental and theoretical IR data can be used to investigate the coordination mode symmetry of various carboxylates. The reliability of the suggested approach was first evaluated by favorably comparing reported and calculated parameters, namely, (i) the complexes structures and (ii) the changes in the symmetric and asymmetric stretching frequencies of carboxylates accompanying coordination (i.e., $\Delta_{ionic} \rightarrow \Delta$). The sensitivity of Δ to the coordination mode symmetry was estimated to show that IR measurements can be used to efficiently probe the structure and the magnetic properties of iron−carboxylato complexes. Characteristic stretching mode frequencies of ligands (e.g., cyano) and molecules (e.g., carbon monoxide) are currently recorded to investigate the electronic structures of metallic centers and active surfaces. For a given carboxylate ligand, we have shown that the $\Delta = \nu_{as} - \nu_s$ value determines the coordination mode symmetry, making IR measurements an interesting structural probe. Besides, the comparison between the calculated and measured Δ values allowed us to clearly confirm the spin state of complex **1**. With this respect, DFT calculations have turned out to be very insightful in structure determination. The comparison between experimental and simulated Δ values was shown to be suitable for crystal determination by inspecting the carboxylate IR data−complex structure correlations. Clearly, the methodology strengthens the use of spectroscopies other than X-ray and opens up a wide perspective for the elucidation of intriguing and sophisticated systems, such as active sites of metalloproteins.

Supporting Information Available: Complete ref 29. This material is available free of charge via the Internet at http://pubs.acs.org.

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