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Theoretical Insights into the Visible Near-Infrared Absorption Spectra of Bis(hexafluoroacetylacetonate) copper(II) in Pyridine

K. J. de Almeida,^{*,[a]} T. C. Ramalho,^[a] M. C. Alves,^[a] and O. Vahtras^[b]

The density functional theory calculations were performed to investigate the specific solvent effects on the optical absorption spectrum of copper(II) hexafluoroacetylacetonate complex in pyridine. The effects of single and double coordination of pyridine molecules at axial position of bis(hexafluoroacetylacetonate) copper(II) indicate that both positions and intensities of 3d–3d electronic transitions are strongly dependent on the coordination

environment around the copper(II) complex. The results indicate that the nature of the electron-acceptor atoms in the equatorial ligands plays an important role in the number of solvent molecules in the first solvation shell of copper(II) acac systems.
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Introduction

The behavior of copper(II) compounds in solution has been of great interest due to biological importance of these systems. Cu(II) complexes are frequently used as prototypes of the larger copper systems encountered in biomolecules, such as in the electron transfer blue copper and prion proteins.^[1] Investigations of the visible near-infrared absorption spectra of the copper(II) complexes can provide important information of these systems since the 3d–3d electronic transitions are highly sensitive indicators of the d⁹ electronic configuration, coordination environment around metal center, and ligand-field strength of the copper(II) systems.^[2–4]

Bis(hexafluoroacetylacetonate)copper(II), henceforth Cu(hfacac)₂, (Fig. 1), is one of most important related copper(II) acac complexes. This is due to the fact that highly electronegative fluorine atoms, which are substituted on the 1 and 5 carbon of the ligand, give rise to significant change in the affinity of the copper atom for axial ligation. Extensive experimental and theoretical studies have been performed to analyze the optical and Electron Paramagnetic Resonance (EPR) spectra of the closely related Cu(II) acac complexes.^[5–9] In particular, Ortolano and Funck^[10] studied the experimental absorption spectra of Cu(hfacac)₂ in pyridine solution. The behavior of absorption bands on alteration of quantity of solvent was investigated in an attempt to apply group theoretical and qualitative crystal field prediction in assignment the 3d–3d bands of Cu(hfacac)₂ and of its analogous Cu(acac)₂ complex. In our previous studies, we have investigated the optical and magnetic properties of Cu(acac)₂, in the gas-phase and solution model, indicating the preferential coordination of this complex in pyridine solution.^[11–13] Ames and Larsen have also reported EPR parameters of Cu(acac)₂ within the tetrahydrofuran and pyridine solvent models.^[14]

In this work, we report an investigation of the solvent effects on the visible absorption spectrum of Cu(hfacac)₂ in pyridine. In this investigation, we use only a microsolvation model, where the specific and direct interactions with Cu(II) center were taken into

account. Density functional response theory has been applied to compute the 3d → 3d electronic transitions in the gas-phase and supra-molecular solvated models of Cu(hfacac)₂ pyridine systems. The focus of this study is to assess information about the effects of the closest solution environment of Cu(hfacac)₂ as well as the presence of fluorine atoms in the acac ligands on the absorption spectrum of this complex. The present results are so compared to the previous results of Cu(acac)₂ system to provide some insights into the analysis of absorption spectra of copper(II) systems, including those found in the active sites of proteins and enzymes containing copper dication in the similar chemical environment.

Computational Details

All calculations were performed at the density functional theory (DFT) level by using hybrid Becke3–Lee–Yang–Parr (B3LYP) exchange-correlation functional.^[15,16] We used the standard Gaussian basis sets: 6-31G(d)^[17] for copper and 6-311G**^[18] for carbon, oxygen, fluorine, and hydrogen atoms. The geometry optimizations of solvated complexes were performed by explicitly attaching one and two molecules of pyridine at the axial position of the chelate complex. The cis and trans conformations of the solvent molecules in the axial position of the Cu(hfacac)₂ complex (see Fig. 2) were considered in the calculations of the optical spectra. The description of the first solvation shell by using the supermolecule model has been proved to be quite reliable for describing the solvent effects on the copper(II) molecular systems.^[13,14]

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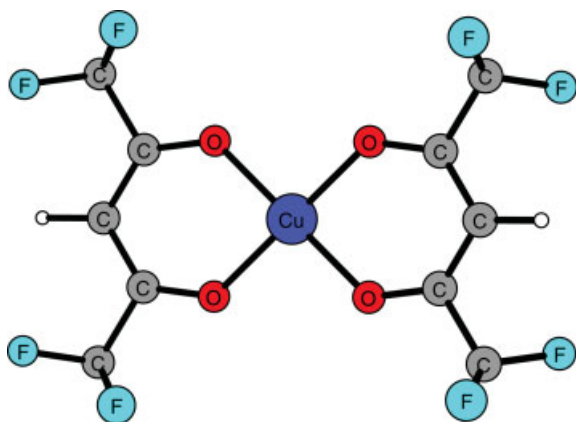


Figure 1. Molecular structure of bis(hexafluoroacetylacetonato)copper(II) and $\text{Cu}(\text{acac})_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

All geometrical calculations were performed with no symmetry constraint using the grid-based DFT implementation in the GAMESS-US.^[19] The electronic absorption transitions were computed by means of the spin-restricted open-shell density functional linear response (DFT-LR) formalism^[20] in DALTON 2.0 quantum chemistry package.^[21] Polarized continuum model

(PCM) calculations were performed to compute the electronic transitions of the gas-phase $\text{Cu}(\text{hfacac})_2$ complex as well as the thermodynamic stability of the $\text{Cu}(\text{hfacac})_2^-$ and $\text{Cu}(\text{acac})_2^-$ pyridine systems.^[22] The present methodology has been successfully used in our previous calculations of the $\text{Cu}(\text{II})$ complexes in the gas-phase and solvent models.^[11,13,23]

Results and Discussion

Complex geometries

The optimized molecular structures of the $\text{Cu}(\text{hfacac})_2$ and its pyridine-coordinated complexes are shown in Figures 1 and 2, respectively. The B3LYP-optimized bond lengths and bond angles of these complexes are collected in Table 1, together with the experimental bond parameters of the gas-phase $\text{Cu}(\text{hfacac})_2$ structure. The present calculations indicate a D_{2h} symmetry model for the $\text{Cu}(\text{hfacac})_2$ complex. The computed bond lengths and bond angles of this complex are accurately described as compared to the experimental electron diffraction data. A comparison of $\text{Cu}(\text{hfacac})_2$ data with the results of the pyridine-coordinated $\text{Cu}(\text{hfacac})_2$ complexes gives us some information about the solvent effects on the

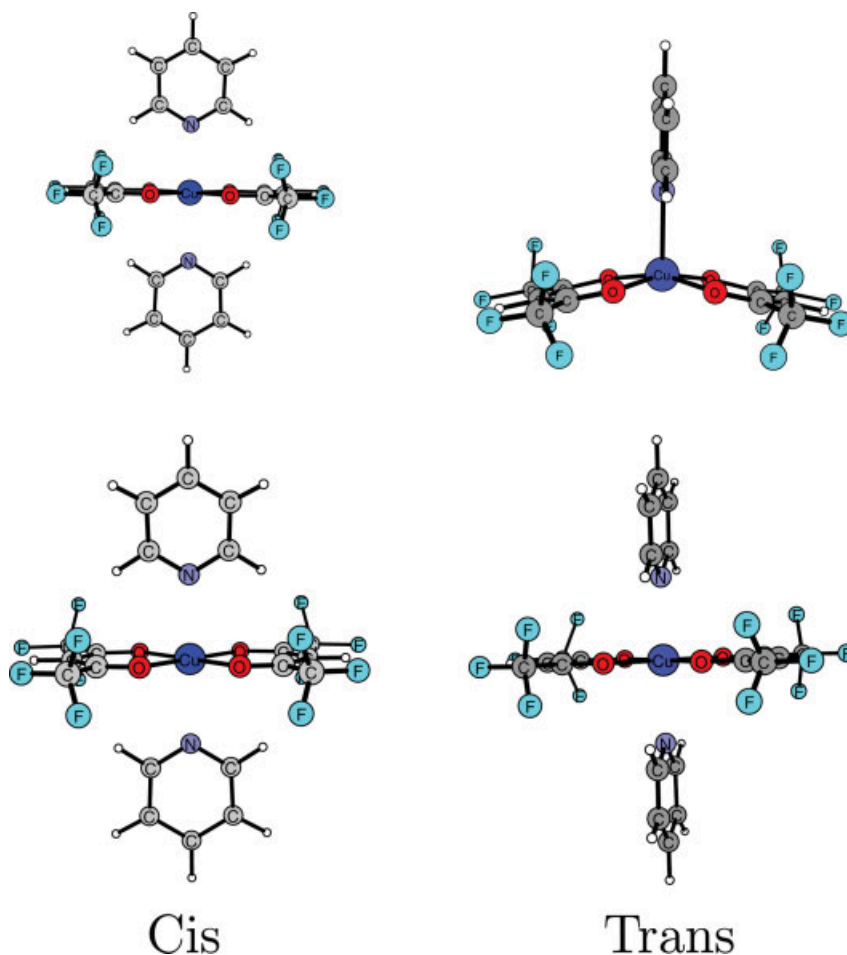


Figure 2. Optimized molecular structures of the $\text{Cu}(\text{hfacac})_2$ -pyridine complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. The bond lengths (Å) and bond angles (in degree), of Cu(hfacac)₂ complexes.

Parameters	Cu(hfacac) ₂		Cu(hfacac) ₂ · (py)		Cu(hfacac) ₂ · (py) ₂	
	Gas Phase	Exp. ^[a]	cis	trans	cis	trans
Cu—O	1.923	1.919 ± 0.008	1.960	1.955	1.999	1.977
C—O	1.251	1.276 ± 0.009	1.253	1.247	1.243	1.245
C—CH	1.392	1.392 ± 0.015	1.394	1.393	1.396	1.394
C—CF ₃	1.535	1.558 ± 0.009	1.533	1.535	1.536	1.535
C—F	1.334	1.339 ± 0.003	1.338	1.335	1.337	1.336
C—H	1.070	—	1.073	1.071	1.071	1.071
Cu—N	—	—	2.210	2.240	2.441	2.435
∠Cu—O—C	127.52	127.7 ± 1.3	127.2	127.3	127.9	126.5
∠O—C—CH ₃	113.24	112.8 ± 1.2	113.4	113.2	113.3	113.5
∠O—C—CH	127.46	127.4 ± 1.4	127.6	127.8	127.7	127.8
∠O—Cu—O	90.28	90.6 ± 1.2	89.5	89.5	88.2	89.6

[a] Experimental results of electron diffraction in gas phase from Ref. [24].

geometrical structure of this complex. Only significant changes are observed in the Cu—O bond lengths and O—Cu—O bond angles, whereas the geometrical structure of the hfacac ligand remains nearly unchanged. A progressive average increase of 0.04 and 0.07 Å is observed in the Cu—O bond lengths of Cu(hfacac)₂ · (py) and Cu(hfacac)₂ · (py)₂ complexes, respectively. On the other hand, a gradual decrease of about 1 and 2 degree is observed in the O—Cu—O bond angles of these complexes. The Cu atom in *cis*- and *trans*-Cu(hfacac)₂ · (py) complexes are displaced 0.182 and 0.153 Å, respectively, out of the plane containing the four O atoms toward the coordinated pyridine molecule. These results follow similar trends observed in the previous calculations as well as in the experimental crystal structure analyses of the copper(II) compounds.^[13,14,23,24] The change of substituted group, that is, the hydrogen atoms of the methyl groups of Cu(acac)₂ by fluorine atoms in Cu(hfacac)₂, leads only to a very small variation in the Cu—O bond lengths, which become in average 0.01 and 0.02 longer in Cu(hfacac)₂ · (py) and Cu(hfacac)₂ · (py)₂ complexes, respectively. A considerable decrease is observed in the Cu—N(py) distances of the pyridine Cu(hfacac)₂ complexes as compared to those in the pyridine Cu(acac)₂ systems. The average values of 2.3 and 2.5 Å were computed in the Cu(acac)₂ · (py) and Cu(acac)₂ · (py)₂ complexes, respectively, whereas the values of 2.2 and 2.4 Å are found in the analogous Cu(hfacac)₂ structures. These results can be taken as indicative of more effective interactions of the pyridine solvent molecules at axial position of the Cu(hfacac)₂ complex, which should be favored by the presence of fluorine atoms in the equatorial ligands.

Electronic transitions

The computed and experimental excitation energies of the Cu(hfacac)₂ complex are listed in Table 2. Four nondegenerate electronic transitions were computed in both gas-phase and PCM calculations. The pattern of four electronic transitions in which 3d orbitals lie relatively close together in a range from about 13,500 to 18,000 cm^{−1} is correctly reproduced in our calculations. Overall, an averaged error around 600 cm^{−1} is observed between the gas-phase and experimental excitation energies, with the largest deviations of 624 and 776 cm^{−1}

Table 2. The 3d → 3d excitation energies (in cm^{−1}) of the gas-phase Cu(hfacac)₂ complex.

Transition	Gas phase	PCM ^[a]	Exp. ^[b]
I	14,124	14,018	13,500
II	14,530	14,485	14,000
III	16,341	16,182	15,800
IV	18,776	18,565	18,000

[a] PCM calculations in carbon tetrachloride. [b] Experimental data of Cu(hfacac)₂ in dry carbon tetrachloride solution from Ref. [10].

obtained for the transitions I and IV, respectively. The PCM calculations slightly improve the theoretical prediction of the 3d→3d electronic transitions, which are computed in lower energies with an average value of 130 cm^{−1}.

The computed and experimental excitation energies and oscillator strengths of the Cu(hfacac)₂ pyridine complexes are listed in Table 3. Four nondegenerate electronic transitions were computed for both Cu(hfacac)₂ · (py) and Cu(hfacac)₂ · (py)₂ systems. The oscillator strengths computed without vibronic coupling effects show values equal to zero for the electronic transitions of the Cu(hfacac)₂ · (py)₂ complexes (D_{2h} symmetry), whereas the oscillator strengths of transitions II and IV in Cu(hfacac)₂ · (py)

Table 3. The 3d → 3d excitation energies and oscillator strengths for Cu(hfacac)₂-pyridine complexes.

Transition	cis		trans		Exp.	
	E (cm ^{−1})	f ^[a]	E (cm ^{−1})	f ^[a]	Sol. ^[b]	f ^[a,b]
Cu(hfacac) ₂ · (py)						
I	9247	0.0	9598	0.0	10,200	3.8
II	12,662	4.0	12,377	6.0	11,300	9.5
III	13,965	0.0	13,624	0.0	13,000	2.9
IV	15,876	13.8	15,077	6.8	14,900	9.2
Cu(hfacac) ₂ · (py) ₂						
I	6461	0.0	7265	0.0	8100	2.1
II	12,504	0.0	12,135	0.0	12,000	1.4
III	14,652	0.0	14,457	0.0	13,900	2.7
IV	15,550	0.0	15,330	0.0	15,300	2.6

[a] Oscillator strength × 10^{−4}. [b] Experimental data obtained from Gaussian analyses for the Cu(hfacac)₂-py systems from Ref. [10].

complexes are calculated between 4.0×10^{-4} and 13.8×10^{-4} . These results arise from the fact that these two transitions gain electronic allowedness in the mono-pyridine complex (C_{2v} symmetry), whereas the other transitions remain electronically forbidden by Laport selection rule. Overall, the B3LYP calculations overestimate the electronic transitions of pyridine-coordinated systems in an average value of 433 cm^{-1} with the largest deviation of about 1300 cm^{-1} observed for transition II of mono-*cis*-pyridine system. On the other hand, the electronic transition I is underestimated in more than 500 cm^{-1} for both models of solvated complexes. A better agreement with experimental data available is found for both trans structures of the $\text{Cu}(\text{hfacac})_2$ pyridine systems. The most remarkable aspect of solvent effect on the absorption spectrum is that all excitation energies are red shifted with the presence of one or two molecules of pyridine at axial position of $\text{Cu}(\text{hfacac})_2$. Comparing $\text{Cu}(\text{hfacac})_2$ pyridine systems, there is a close similarity among the DFT results obtained for the three highest electronic transitions localized in the visible region, whereas the position of transition I, which is localized in near-infrared region, is strongly modified depending on the coordination model used to describe the first solvation shell of $\text{Cu}(\text{hfacac})_2$ complex. A difference of about 2000 cm^{-1} is verified in the transition I when onefold and twofold coordinated pyridine systems are compared. This result indicates, therefore, that the near-infrared transition plays the most pronounced feature of the solvent effects on the absorption spectrum of $\text{Cu}(\text{hfacac})_2$. In Figure 3, we determine the degree of correlation between the experimental and theoretical excitation energy results. As it can be seen, there is a very good correlation ($R^2 = 0.987$) between these data, thus indicating that the present methodology reproduces well the visible near-infrared absorption energies of the copper(II) systems.

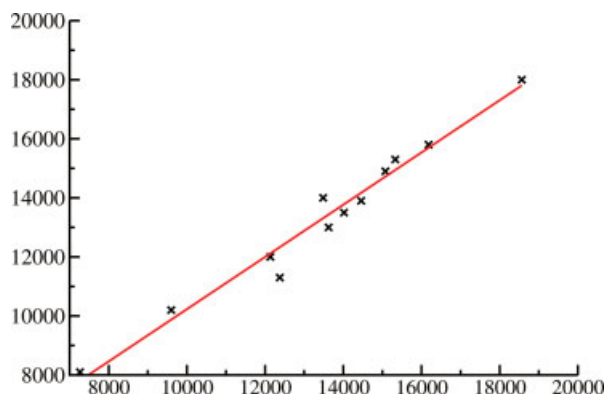


Figure 3. Correlation between experimental and theoretical excitation energies. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

Assignment and interpretation of spectra

The visible near-infrared excitation energies in the investigated complexes are assigned to $3d \rightarrow 3d$ transitions mainly localized on the copper(II) ion as shown in Figure 4. The ground-state d_{xy} , which is well established experimentally for $\text{Cu}(\text{acac})_2$ and the related acac complex,^[25] was correctly accounted for by

B3LYP calculations of all $\text{Cu}(\text{hfacac})_2$ complexes. Comparing to the analogous acac complex, the same ordering of 3d orbitals is found in the gas-phase $\text{Cu}(\text{hfacac})_2$ complex, that is, $d_{xy} > d_{xz} > d_{x^2-y^2} > d_{yz} > d_{z^2}$. This fact indicates that the electronic structure of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfacac})_2$ complexes are indeed quite similar to each other. On the other hand, distinct features appear to modify the positions of 3d–3d electronic transitions of these systems in pyridine. The ordering of 3d orbitals in the $\text{Cu}(\text{acac})_2$ -pyridine systems is given as being $d_{xy} > d_{z^2} > d_{yz} > d_{x^2-y^2} > d_{xz}$, whereas the present calculations indicate the following order $d_{xy} > d_{z^2} > d_{xz} > d_{yz} > d_{x^2-y^2}$ for the 3d orbitals in the $\text{Cu}(\text{hfacac})_2$ -pyridine systems. The difference in the ordering of 3d orbitals indicates a larger splitting between d_{xz} and d_{yz} orbitals in the $\text{Cu}(\text{acac})_2$ -pyridine compounds relative to that computed in the $\text{Cu}(\text{hfacac})_2$ -pyridine complexes. This is likely caused by a smaller difference between the two O–O distances in the $\text{Cu}(\text{hfacac})_2$ -pyridine systems. The values of 0.02 and 0.03 Å are computed in $\text{Cu}(\text{acac})_2 \cdot (\text{py})$ and $\text{Cu}(\text{acac})_2 \cdot (\text{py})_2$, respectively, whereas the values in the analogous $\text{Cu}(\text{hfacac})_2$ systems are 0.01 and 0.02 Å. The present results are in complete agreement with the data reported by Ortolano and Funck.^[10] In Figure 5, we plotted the computed and experimental (dashed line) excitation energies of the gas-phase $\text{Cu}(\text{hfacac})_2$ and $\text{Cu}(\text{hfacac})_2$ -pyridine complexes to better visualize the solvatochromic shifts on absorption transitions of $\text{Cu}(\text{hfacac})_2$. The main features observed in this figure can be summarized as follows:

- All electronic transitions in pyridine-coordinated systems are red shifted relative to their respective positions in the gas-phase complex.
- The electronic transitions of $\text{Cu}(\text{hfacac})_2 \cdot (\text{py})$ are computed to be in lower energies compared to those computed in the octahedral model. This trend may be related to the shorter bond Cu–N distances observed in the mono-pyridine adducts as compared to those found in $\text{Cu}(\text{hfacac})_2 \cdot (\text{py})_2$.
- The position of the $d_{x^2-y^2} \rightarrow d_{xy}$ transition remains nearly unchanged after the coordination of second molecule of pyridine at axial position of $\text{Cu}(\text{hfacac})_2$. The results of oscillator strengths indicate that the intensity of this electronic transition should not be modified by the presence of solvent molecules. The computed $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$ transitions show a small variation of their positions around 1200 cm^{-1} , whereas the major change is observed in their intensities, which are significantly modified with the coordination of one or two molecules of solvents.

iv. The most notable feature in Figure 5 is the large red shift ($11,300 \text{ cm}^{-1}$) observed in the $d_{xy} \rightarrow d_{z^2}$ transition, which goes from the visible region in the gas-phase $\text{Cu}(\text{hfacac})_2$ spectrum to the near-infrared region in the $\text{Cu}(\text{hfacac})_2$ -pyridine spectra. The B3LYP calculations overestimate the experimental red-shift value in about 1000 cm^{-1} . It is interesting to note that common shifts in organic compounds due to solvent effect is around $1000\text{--}3000 \text{ cm}^{-1}$. This large solvatochromic shift is a result of the strong and specific interactions between the coordination compounds and basic solvent molecules. The experimental results of $\text{Cu}(\text{hfacac})_2$ and other correlated acac complexes in chloroform and crystal phase agree very well with respect to the assignment

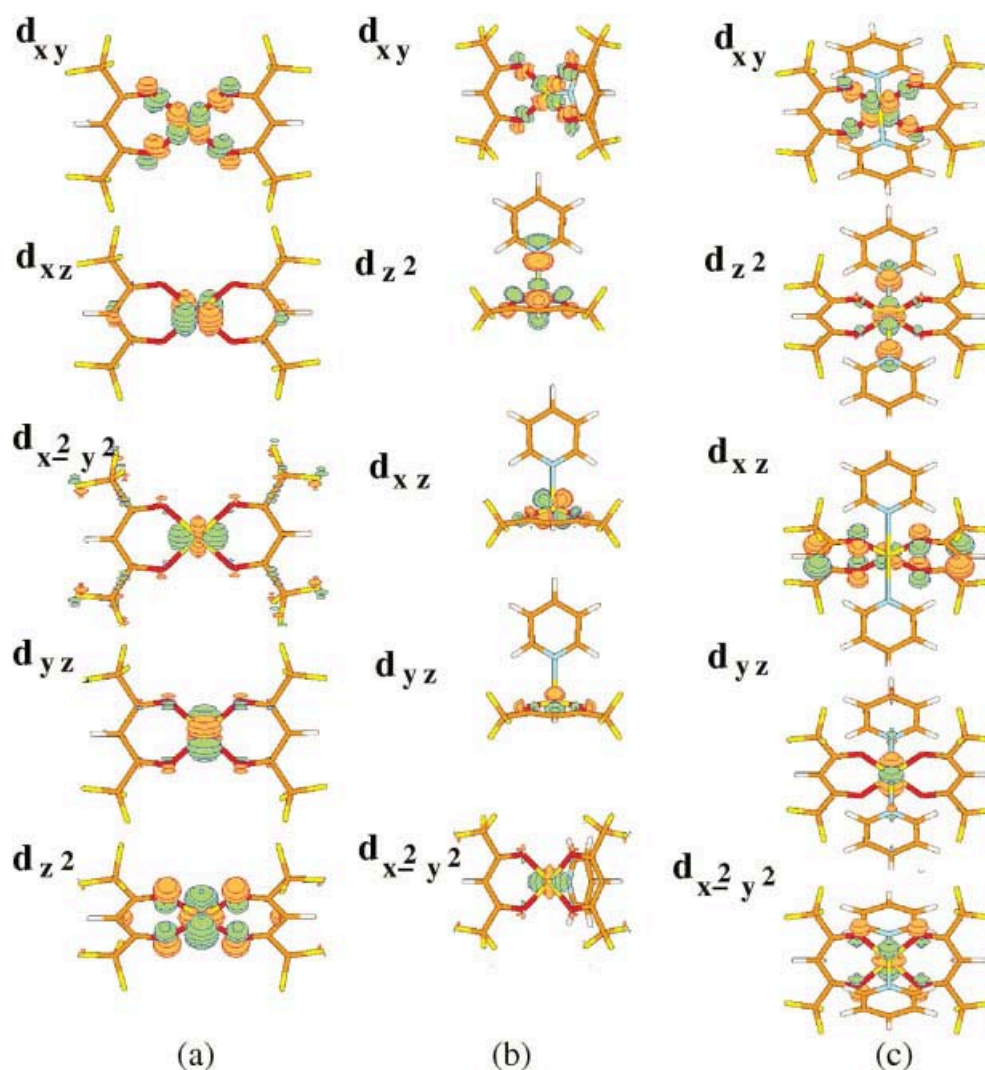


Figure 4. The optimized B3LYP molecular orbitals involved in the 3d–3d electronic transitions of Cu(hfacac)₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

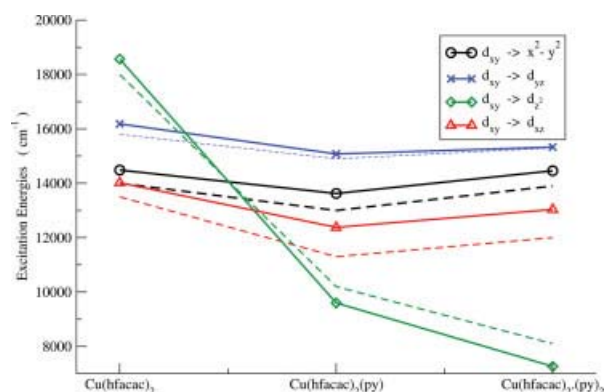


Figure 5. The solvatochromic shifts of the 3d–3d electronic transitions of Cu(hfacac)₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the highest excitation energy (around 18,000 cm^{−1}) as being due to $d_{xy} \rightarrow d_{z^2}$ transition.^[5,10,26] On the other hand, the experimental results of Ortolano and Funck^[10] show a large

band and a shoulder, which is assigned as $d_{xy} \rightarrow d_{z^2}$ transition and is localized at near-infrared region of spectrum (around 8000 cm^{−1}). The results of oscillator strengths for this transition are equal to zero independent on the solvent model considered, indicating a low intensity for this absorption transition in all spectra of Cu(hfacac)₂.

The effects of the single and double additions of pyridine on the absorption spectrum of Cu(hfacac)₂ have been investigated by Funck and Ortolano in an attempt to assign the 3d–3d bands in acac complexes. The B3LYP results for the Cu(hfacac)₂–pyridine complexes reproduce correctly the experimental findings, which show that each model of the solvated complex gives rise to a particular pattern of the absorption spectrum, where both positions and intensities of the visible near-infrared electronic transitions can be used to characterize the coordination environment around the Cu(hfacac)₂ in pyridine solution. An important aspect to be noted is that the pyridine adducts of Cu(hfacac)₂ afford an important insight about the solvent effects on the copper(II) compounds, especially about

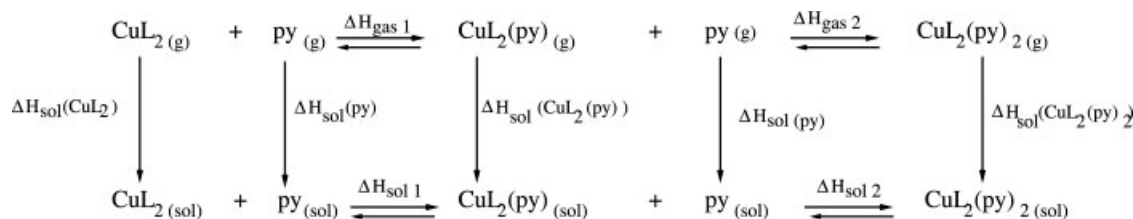


Figure 6. Thermodynamic cycle.

the nature of equatorial ligands in copper(II) complexes. The presence of highly electronegative fluorines in equatorial ligands of $\text{Cu}(\text{hfacac})_2$ seems to decrease the electronic density on d orbital of the Cu(II) atom so that the solvent molecules can force the way to form two reasonably strong chemical interactions, thus favoring the coordination of the second molecule of solvent at the axial position of $\text{Cu}(\text{hfacac})_2$. In contrast, when weak electron-acceptor atoms (like hydrogen, in $\text{Cu}(\text{acac})_2$) are substituted on 1 and/or 5 carbon of acac ligand, the affinity of the copper for axial ligation is decreased to the extent that only one molecule of basic solvent may be added.^[27] To prospect a little further in this direction, we calculate the relative enthalpies for the coordination of one and two pyridine molecules at axial position of $\text{Cu}(\text{hfacac})_2$ and $\text{Cu}(\text{acac})_2$ complexes. These calculations were performed by using the thermodynamic cycle (Fig. 6) and following equations:

$$\Delta H_{\text{sol } 1} = \Delta H_{\text{gas } 1} + \Delta H_{\text{sol}}(\text{CuL}_2(\text{py})) - [\Delta H_{\text{vap}}(\text{py}) + \Delta H_{\text{sol}}(\text{CuL}_2)] \quad (1)$$

$$\Delta H_{\text{sol } 2} = \Delta H_{\text{gas } 2} + \Delta H_{\text{sol}}(\text{CuL}_2(\text{py})_2) - [\Delta H_{\text{vap}}(\text{py}) + \Delta H_{\text{sol}}(\text{CuL}_2(\text{py}))] \quad (2)$$

where $L = \text{acac}$ and hfacac . $\Delta H_{\text{sol } 1}$ and $\Delta H_{\text{sol } 2}$ are defined as the enthalpy of complexation of one and two pyridine molecules in solution, respectively. It is important to notice that the entropic contributions were computed to be small and were, therefore, neglected in our calculations. The computed results are shown in Table 4 and as can be seen, the highest $\Delta H_{\text{sol } 1}$ value was obtained for $\text{Cu}(\text{hfacac})_2$. This indicates that the interactions of pyridine solvent molecules at axial position of the $\text{Cu}(\text{hfacac})_2$ are more efficient than those with the $\text{Cu}(\text{acac})_2$ system. Turning now to $\Delta H_{\text{sol } 2}$ values, we can also observe the same trend. For instance, on going from $\text{Cu}(\text{acac})_2$ to $\text{Cu}(\text{hfacac})_2$ (Table 4) the concomitant $\Delta H_{\text{sol } 2}$ values are -101.29 and $-162.10 \text{ kJ mol}^{-1}$, respectively. This means that the coordination of one and two pyridine molecules is more stable for the $\text{Cu}(\text{hfacac})_2$ than $\text{Cu}(\text{acac})_2$ about 36.54 and

$60.81 \text{ kJ mol}^{-1}$, respectively. These results suggest, therefore, that the electronegative fluorine atoms in equatorial ligand might favor the coordination of two axial solvent molecules in copper(II) acac systems. Finally, from a thermodynamics point of view, our data point out that electronegative atoms in the acac systems might significantly modify the electronic density on the metallic center favoring strongly the coordination of solvent molecules of the medium. This conclusion is in good agreement with our previous spectroscopic findings.

Summary

DFT calculations have been performed to evaluate the solvent effects on the visible absorption of the $\text{Cu}(\text{hfacac})_2$ complex. The super-molecule solvent model was used for describing the solvent interaction with the $\text{Cu}(\text{hfacac})_2$ complex. The present results indicate four nondegenerate $3d \rightarrow 3d$ electronic transitions independent on the complex model considered.

Distinct solvent shifts are found for four $3d - 3d$ transitions. Although neither the position nor the intensity of $d_{xy} \rightarrow d_{x^2-y^2}$ transition is greatly affected by axial interaction with solvent molecules, the intensities of $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$ transitions vary pronouncedly when $\text{Cu}(\text{hfacac})_2$, $\text{Cu}(\text{hfacac})_2 \cdot (\text{py})$, and $\text{Cu}(\text{hfacac})_2 \cdot (\text{py})_2$ models are considered. The largest solvatochromic effect is observed in $d_{xy} \rightarrow d_{z^2}$ transition which shows a red shift of $11,300 \text{ cm}^{-1}$ with the increasing number of axial ligation. This transition appears in near-infrared region of spectrum with a difference of 2000 cm^{-1} being observed between the computed values in onefold and twofold pyridine-coordinated $\text{Cu}(\text{hfacac})_2$ models.

A comparison with the previous results of $\text{Cu}(\text{acac})_2$ and our thermodynamic results indicate that the coordination of the second molecule of solvent at axial position of Cu(II) acac systems is favored only when the strongly electron-acceptor atoms are present in the equatorial ligands. The electron-acceptor effect of highly electronegative atoms decreases the electronic density on the Cu(II) ion so that the affinity of the copper atom for axial ligation is increased by extension that two molecules of the basis can be added.

Keywords: DFT • optical transitions • copper(II) • spectroscopy

Table 4. Enthalpy values (kJ mol^{-1}) for the coordination of one and two pyridine molecules at axial position of $\text{Cu}(\text{hfacac})_2$ and $\text{Cu}(\text{acac})_2$ complexes.

	$\text{Cu}(\text{hfacac})_2$	$\text{Cu}(\text{acac})_2$
$\Delta H_{\text{sol } 1}$	-142.92	-106.38
$\Delta H_{\text{sol } 2}$	-162.10	-101.29

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