



Quantum-mechanical study on three complex compounds of Fe(II) containing related (N, N) ligands which are basically formed by two heterocyclic rings

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Abstract:

The paper reports the results of a quantum-mechanical study performed for three organic ligands, namely 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole and two of its derivatives) and three of their complex compounds with Fe(II), containing two 2,2'-dipyridyl molecules beside the above-mentioned ligands.

For all of them, the results of the elemental analysis, as well as the ones of a physical-chemical study (involving molar conductivity measurements, together with mass and electronic spectroscopy) have been presented in a previous paper.

The quantum-mechanical study – consisting in applying the HOMO-LUMO method to perform EHT calculations (based on specialized chemistry software), shows that the complex compounds of Fe(II) containing one of these ligands (denoted L, L' or L'') are octahedral, the three bidentate ligands being coordinated by means of nitrogen atoms to the central metal ion, this result supporting the deduction that all the studied complex compounds with three (N, N) bidentate ligands exhibit an octahedral geometry.

Keywords: complex compounds, heterocyclic (N, N) ligands, quantum-mechanical theory, HOMO-LUMO method, EHT calculations

1. INTRODUCTION

In a previous paper [1], a study has been reported, involving three (N, N) heterocyclic ligands (2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole and two of its derivatives) and the three Fe(II) complexes obtained with each of them and two 2,2'-dipyridyl molecules.

This study has suggested that the investigated complex compounds with these (N, N) bidentate ligands exhibit an octahedral geometry [2, 3].

The present work presents the results of a quantum-mechanical study about the previously investigated chemical compounds (ligands and their complexes with divalent iron, also containing two 2,2'-dipyridyl molecules).

One of the reasons for the synthesis and investigation of these iron complexes involves was introducing into the coordination sphere of a complex possessing a photosensitive moiety, $[\text{Fe}(\text{dpy})_2]^{2+}$ a bidentate ligand of (N, N) type that would modify the electronic structure of the complex and thus would make it possible to utilize the energy of the quantum absorbed along one of the predetermined deactivation channels (luminescence, charge transfer, *etc.*).

Inasmuch as the directional synthesis of complexes with desired properties is impossible without the understanding of the relation between the composition of the coordination sphere, electronic structure of the complex, and the observed characteristics of its excited states [2, 3], a significant attention is paid to quantum-mechanical studies of the electronic structure of polypyridine iron complexes and to the interpretation of electronic spectra based on the calculations of the excited electronic states [4].

Within this study, we have investigated the effect on the spectral characteristics of the complexes of two substituents added to the ligand ($-\text{COOH}$, $-\text{COO}-\text{CH}_2-\text{C}\equiv\text{CH}$) located in the peripheral part of a pyridine imine, 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole.

It was presumed that the introduction of these ligands into the composition of the studied polypyridine Fe(II) complexes might result in a shift of the absorption band in the visible region, that presumption being confirmed by the electronic spectral analysis that we have formerly reported [1].

2. MATERIALS AND METHODS

2.1. Materials

Preparation of the ligands, as well as the preparation of their complexes with Fe(II), were described in the anterior paper that we have mentioned above.

2.2. Methods

A specialised chemistry software, namely HyperChem 8.0.10 - trial version [5] was used for this quantum-mechanical study based on HOMO-LUMO – EHT (Extended Hückel Theory) calculations.

3. RESULTS AND DISCUSSION

3.1. Computational modeling of ligands structure

As far as the three organic compounds are concerned, we shall remind that they are the following ones:

- 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole, referred to as L;
- 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid, referred to as L' ;
- prop-2-yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate, referred to as L''.

The structures of these three organic compounds (obtained by using the specialised chemistry software HyperChem 8.0.10 – trial version [5]) are shown in Figures 1-3:

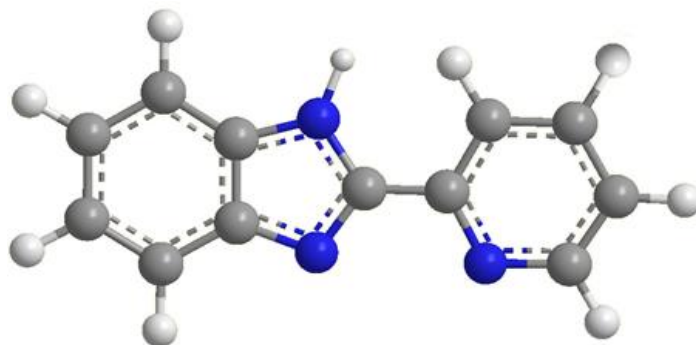


Figure 1. Computational modeling for the structure of the ligand L [5].

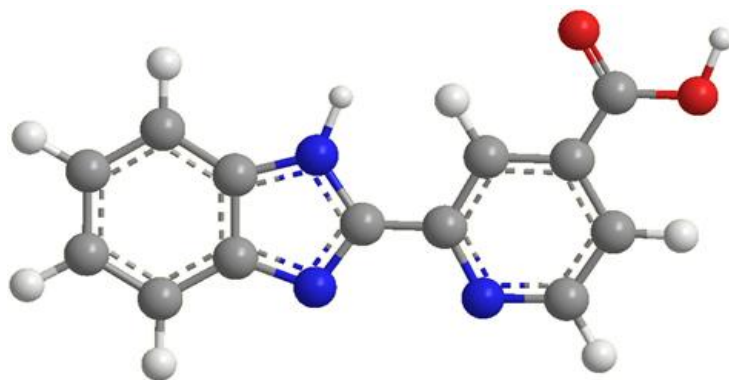


Figure 2. Computational modeling for the structure of the ligand L' [5].

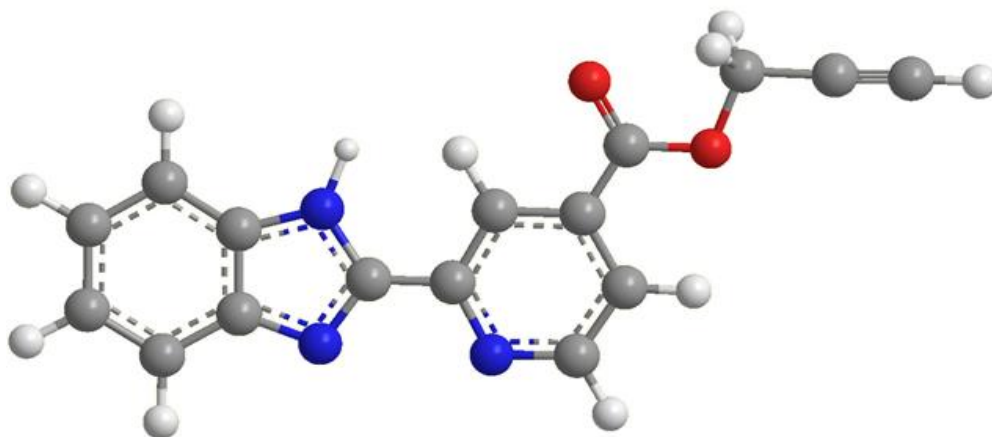


Figure 3. Computational modeling for the structure of the ligand L'' [5].

The molecular geometry was optimized using the Molecular Mechanics approach (MM⁺), the cartesian coordinates for all the atoms being obtained by using HyperChem 8.0.10 - trial version [5].

Previous data [1] suggest that all these organic compounds are able to act as bidentate ligands in complex compounds formed with Fe(II), involving two nitrogen atoms in the coordination, so as the chelate rings obtained contain five atoms each ($[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, $[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$ and $[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$).

In order to verify the accuracy of this statement, a quantum-mechanical study was performed on the ligands and their corresponding complex compounds.

The results of this study, along with their interpretation, will be presented in what follows.

3.2 HOMO-LUMO – EHT calculation

Energies and contributions of different molecular fragments on the higher occupied molecular orbitals (HOMOs) and lower unoccupied molecular orbitals (LUMOs) of complex compounds are presented in Table 1.

Table 1. Energies and contributions of different molecular fragments on the HOMOs and LUMOs of complex compounds (%)

MO	Complex compound																	
	[Fe(dpy) ₂ L ₂] ²⁺					[Fe(dpy) ₂ L'L' ₂] ²⁺						[Fe(dpy) ₂ L''L'' ₂] ²⁺						
	E ,	Fe(II)	dpy1	dpy2	L (*)	E ,	Fe(II)	dpy1	dpy2	L' (*)	L' (**)	E ,	Fe(II)	dpy1	dpy2	L'' (*)	L'' (**)	L'' (***)
-10	8.76	2.3	78.1	5.3	14.3	8.70	0.7	8.1	55.3	35.7	0.2	8.54	0	0.2	0.3	10.4	53.7	35.3
-9	8.67	0.6	7.8	51.5	40	8.61	0.3	44.5	50.8	4.4	0.2	8.53	0.3	1.1	2.4	91	4.7	0.4
-8	8.62	0.3	44.7	50.1	4.9	8.52	0.3	1.1	2.3	90.3	6.1	85	0	0	0	11.4	48.5	40.2
-7	8.40	0.4	1.2	1.6	96.8	8.16	0	0	0	15.9	84	7.96	0.1	0.1	0	1.6	5.7	92.5
-6	7.42	1.4	55.7	41.3	1.6	7.45	2.4	63.3	24.2	9.6	0.4	7.45	2.3	62.1	26.2	8.7	0.4	0.2
-5	7.38	0.5	41	57.7	0.8	7.40	0.8	22	74.4	2.8	0	7.40	0.8	23.7	72.3	3	0	0
-4	7.6	8.8	5.6	1.2	84.4	7.29	5.7	16.8	0.9	74.8	1.9	7.29	5.5	15.8	0.8	75.3	1.8	0.7
-3	6.88	2.5	0.8	0.6	96.2	7.19	1	0.5	0.8	93.7	4	7.20	1.3	0.7	0.9	92.5	4.1	0.5
-2	6.13	74	7.9	10.5	7.5	6.19	74.3	7.9	10.4	7.4	0	6.19	74.3	7.9	10.4	7.4	0	0
-1	6.5	72	9.4	6.4	11.8	6.11	72.4	9.4	6.5	11.7	0.1	6.12	72.4	9.4	6.5	11.7	0.1	0
0	5.89	72	6.3	7.6	14.2	5.96	73.1	6.6	7.6	11.7	0.2	5.97	73.9	6.6	7.6	11.7	0.2	0
+0	2.63	0.2	28.8	40.4	30.6	2.84	1.9	2.4	3	85.9	6.7	2.85	1.9	2.3	2.8	85.3	7.3	0.4
+1	2.52	5.9	54.9	2.1	37.1	2.61	3.2	44.2	47.9	4.3	0.5	2.62	3.1	42.9	49.4	4.1	0.5	0
+2	2.52	6.3	11.5	52.5	29.6	2.55	6.3	48.4	44	1.3	0	2.55	6.3	49.7	42.7	1.3	0	0
+3	1.82	1	34.1	43	21.9	1.93	1.1	12.2	15.4	58.9	12.4	1.95	1.2	9.8	12.2	60.3	15.5	0.9
+4	1.60	1.7	36.7	2.7	58.9	1.77	2.3	31.6	32	23.3	10.7	1.78	2.2	31.9	34.8	20.3	10.2	0.6
+5	1.54	2.2	45.3	48.5	4	1.60	1.3	34.3	4.4	53.8	6.2	1.61	1.3	33.6	2.4	57	5.4	0.4
+6	1.49	2.2	17	75.8	5	1.57	2.1	46.3	45	6.1	0.4	1.57	2.2	46.1	46.8	4.7	0.2	0
+7	1.45	1.4	61.7	24.5	12.3	1.50	1.8	11.2	78.3	7.8	0.9	1.50	1.9	12.3	77.7	7.3	0.7	0
+8	0.61	2	2.3	1.1	94.6	1.47	1.2	59.7	20.3	17.8	0.9	1.48	1.2	61.5	21.2	15.4	0.6	0
+9	0.26	0.7	28.8	43.8	26.7	0.78	1.3	2.3	0.9	95	0.4	0.78	1.3	2.3	0.9	94.9	0.4	0.1
+10	0.19	0.8	28	6.7	64.5	0.26	0.9	46.4	49.8	2.9	0	0.26	0.9	45.6	50.5	2.9	0	0
+11	0.14	0.9	45.1	49.1	5	0.16	0.8	51.4	46.6	1.2	0	0.16	0.8	52.2	45.8	1.2	0	0
+12	0.1	42	24	9.1	24.6	0.4	42.5	22	30.3	25.1	0	0.9	3.4	1.1	1.5	18.3	18.9	56.8
+13	0.8	42	17.6	31.5	8.7	0.2	42.1	19.5	30.4	8	0	0.4	41.2	22.3	9.5	23.9	0.7	2.4

* - the benzo[d]imidazole fragment

** - the carboxyl group

*** - the prop-2-yn-1-yl fragment

In order to establish the electronic structure of the free ligands L, L' and L'', a quantum-mechanical study was carried out in two modes: with the optimization of the geometric structures, and then using geometric parameters corresponding to the ligand state in the coordination sphere of the complex.

The ligands have planar structure. In their free state, the nitrogen atoms of the dipyrindyl ligands, as well as the nitrogen atoms in the ligands, are in the *trans* position with regard to the C–C bond between the cyclic aromatic fragments.

To facilitate the involvement in the coordination to the iron(II) ion, the three bidentate ligands should suffer a transition into a less energy state, this engaging a considerable rising of the energy of the molecular orbital (MO) ruling the donor properties of the ligand (~1.2 eV). The main contribution to this MO originates in the atomic orbitals of the nitrogen atoms located in the ligand plane. An orbital from the ligand dpy becomes the highest occupied molecular orbital (HOMO, simply denoted as “-0” in Table 1), whereas an orbital from the ligands L, L' or L'' becomes HOMO-1 (simply denoted as “-1” in Table 1).

The energies of the other occupied frontier MOs suffer smaller changes (up to 0.2 eV) and can either increase or decrease.

The energy of the lowest unoccupied molecular orbital (LUMO, simply denoted as “+0” in Table 1) will be interesting in explaining the spectral characteristics of the studied complex compounds, remaining practically unchanged while the ligand conformation changes.

In the electronic state right before coordination, the LUMOs of ligand dpy and L, L' or L'' (called “+0”, “+1”, “+2” *etc.*) have the same energy (within an accuracy of 0.5 eV). The presence of a substituent introduced at the benzo[d]imidazole fragment of the first ligand (–COOH or –COO–CH₂–C≡CH) leads to a decrease in energy of MOs formed by the AOs of the acceptor nitrogen atom. In particular, LUMO of the ligands L' and L'' are lower by about 0.5 eV than LUMO of L.

In Table 1 energies and contributions of different molecular fragments on the higher occupied and lower unoccupied molecular orbitals of complexes (%) are presented of highest occupied and lowest unoccupied molecular orbitals of the three complex compounds, [Fe(dpy)₂L₂]²⁺, [Fe(dpy)₂L'₂]²⁺ and [Fe(dpy)₂L''₂]²⁺.

The accounting for the solvation shell is found for the most part of the orbitals with an important contribution of substituent atoms.

Consequently, taking into account the large negative charge on the oxygen atoms of the substituent, the symmetry of the solvate shell of the complex seem to be distorted, so the energy of the corresponding MOs decrease compared to the energy of MOs localized on the dpy ligands of the studied complexes.

Amongst the frontier orbitals of all three complex compounds, the following orbitals can be stressed out as having a major contribution from the *d*-orbitals of the central Fe(II) ion: (HOMO-2 ("-2"), HOMO-1 ("-1"), HOMO ("-0"), LUMO+12 ("+12"), LUMO+13 ("+13"), the rest of MOs being localized on the ligands.

The introduction of the acceptor substituent (-COO-CH₂-C≡CH or -COOH) into the benzo[*d*]imidazole fragment of the ligand L affects the MO energy as follows [11]:

- additional MOs come out among the frontier MOs: for [Fe(dpy)₂L'₂]²⁺: HOMO-7 ("-7"), LUMO+4 ("+4"); for [Fe(dpy)₂L''₂]²⁺: HOMO-8 ("-8"), HOMO-7 ("-7"), LUMO+4 ("+4"), HOMO+12 ("+4"); therefore, the occupied orbitals (HOMOs) are practically localized on the atoms of the substituent, whereas the occupied orbitals (LUMOs) are delocalized over all ligand surrounding;

- the energy decreases for the MOs whose formation occur with the involvement of AOs of the substituent atoms with about 0.15 eV for HOMO-4 ("-4") and 0.24 eV for HOMO-3 ("-3"), (these being localized on the benzo[*d*]imidazole fragment with the contribution from the AOs of the substituent ~2% and ~4% respectively); a proportionality can be observed between the energy decrease of the MOs and the contribution of the acceptor fragment to the MOs (as presented in Table 1);

- the gap that appears between the HOMO and LUMO in complexes [Fe(dpy)₂L'₂]²⁺ and [Fe(dpy)₂L''₂]²⁺ decreases by about 0.2 eV compared with the one in complex [Fe(dpy)₂L₂]²⁺.

The effective charges distribution on atoms (calculated by using the EHT method) in the three complexes – [Fe(dpy)₂L₂]²⁺, [Fe(dpy)₂L'₂]²⁺ and [Fe(dpy)₂L''₂]²⁺ – are quite identical except for the benzene ring in the ligands L, L' or L'' – where the charge distribution depends on the presence of the substituent.

By introducing the carboxylic substituent, the negative charge on the carbon atom increases, so the atoms next to it become less negative.

Moreover, introducing the prop-2-yn-1-yl fragment leads to a stronger polarization of the benzene ring.

The same charge on the central atom in all the three complexes indicates the equal degree of the overall transfer of the electron density during the formation of the coordinative bond metal-ligand in these compounds, disregarding the presence of a substituent at the benzene ring.

As previously stated, all these observations may be made by carefully analyzing the computational results gathered in Table 1.

3.3 Comparison between the experimental and theoretical spectra

Within this study, the experimental and theoretical spectra were compared. Therefore, this calculation method allowed a detailed analysis about the effect of the substituents on the absorption electronical spectrum of the three Fe(II) complex compounds (all the three spectra were presented in the previous paper [1]).

As far as the electronic spectrum is concerned, it was presumed that the introduction of these ligands into the composition of the complex compounds $[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, $[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$ and $[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$ might lead to a shift of the absorption band in the visible region [11].

Indeed, due to the potential opportunity of the application of the Fe(II) dipyriddy complexes for sunlight conversion, the visible part of the electronic spectra of these compounds is the most interesting.

Experimental absorption spectra of the complex compounds performed in the visible range (in 10^{-4} M ethanolic solutions) was given in the former paper¹. All the three electronic spectra are characterized by a wide band having a maximum at about 460 nm (the extinction coefficient was $3000 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-1}$, indicating that the presence of a substituent introduced at the benzo[*d*]imidazole fragment of the first ligand (either $-\text{COOH}$ or $-\text{COO}-\text{CH}_2-\text{C}\equiv\text{CH}$) does not significantly influence the absorption spectrum in the visible range [1].

None of the energies over 4.5 eV occurring in the experimental spectrum in the region 200-250 nm was taken into account.

Although the energy of the transitions was overestimated in some way (by 0.2-0.3 eV), the results of this calculation were consistent with the experimental findings.

To be more specific, the performed HOMO-LUMO EHT calculations showed that the absorption spectrum of all the three complex compounds taken into study shall be divided in three regions:

- The first region (2.5-3.5 eV) corresponds only to charge-transfer (CT) transitions from the 4*d* orbitals of Fe(II) to antibonding orbitals of the ligand surrounding, n*(L, L' or L''); the close energy values of the low unoccupied MOs of ligands dpy and L, L' or L'' provides an availability of their mixing within the complex leading to a delocalization of the electron density obtained by photo-excitation over the three ligands (dpy1, dpy 2 and L, L' or L'')

- The second region (3.5-4.2 eV) involves mixed transitions where MOs of different kinds are involved: from *d*(Fe) to either n (L, L' or L'') or n*(L, L' or L'').

- The third region (the one over 4.2 eV) generally contains the ligand-ligand MO transitions.

Table 2 presents the theoretical and experimental values of energy, the oscillator force and the extinction coefficient for different HOMO-LUMO transitions in the first complex compound.

Table 2. Information about different HOMO-LUMO transitions in the complex compound [Fe(dpy)₂L₂]²⁺.

		Theoretical spectrum		Experimental spectrum	
E , eV	Oscillator force, N	Assignment		E , eV	Extinction coefficient, L·mol ⁻¹ ·cm ⁻¹
2.64	0.140	<i>d</i> (Fe)	→ dpy1, dpy2, L	2.56	2810
		<i>d</i> (Fe)	→ π(Fe-dpy1), δ(Fe-L)		
		<i>d</i> (Fe)	→ δ(Fe-dpy2), δ(Fe-L)		
2.78	0.124	<i>d</i> (Fe)	→ dpy1, dpy2, L	2.69	2010
		<i>d</i> (Fe)	→ π(Fe-dpy1), δ(Fe-L)		
		<i>d</i> (Fe)	→ δ(Fe-dpy2), δ(Fe-L)		
2.82	0.133	<i>d</i> (Fe)	→ π(Fe-dpy1), δ(Fe-L)	3.54	3300
		<i>d</i> (Fe)	→ δ(Fe-dpy2), δ(Fe-L)		
3.61	0.237	<i>d</i> (Fe)	→ dpy2, dpy1	3.94	1782
3.65	0.375	<i>d</i> (Fe)	→ dpy1, dpy2		
3.70	0.241	<i>d</i> (Fe)	→ L, dpy1	3.94	1782
		<i>d</i> (Fe)	→ σ(Fe-dpy2), σ(Fe-dpy1), σ(Fe-L)		
3.73	0.328	<i>d</i> (Fe)	→ L, dpy1	3.94	1782
		L	→ dpy1, dpy2, L		
		<i>d</i> (Fe)	→ σ(Fe-dpy2), σ(Fe-dpy1), σ(Fe-L)		
3.75	0.428	L	→ dpy1, dpy2, L		

Theoretical spectrum				Experimental spectrum	
$\ E\ , \text{eV}$	Oscillator force, N	Assignment		$\ E\ , \text{eV}$	Extinction coefficient, $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$
		L	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
3.78	0.855	$d(\text{Fe})$	$\rightarrow \text{L}, \text{dpy1}$		
		L	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
3.76	0.935	$d(\text{Fe})$	$\rightarrow \text{dpy2}, \text{dpy1}$		
		$d(\text{Fe})$	$\rightarrow \text{L}, \text{dpy1}$		
		$d(\text{Fe})$	$\rightarrow \text{dpy1}, \text{dpy2}$		
3.82	0.465	$d(\text{Fe})$	$\rightarrow \text{dpy2}, \text{dpy1}$		
		L	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
		$d(\text{Fe})$	$\rightarrow \text{dpy1}, \text{dpy2}$		
3.87	0.434	$d(\text{Fe})$	$\rightarrow \text{dpy1}, \text{dpy2}$		
3.88	0.431	L	$\rightarrow \delta(\text{Fe-dpy2}), \delta(\text{Fe-L})$		
		$d(\text{Fe})$	$\rightarrow \text{dpy1}$		
		$d(\text{Fe})$	$\rightarrow \text{dpy2}$		
3.89	0.352	$d(\text{Fe})$	$\rightarrow \text{dpy1}, \text{dpy2}$		
		$d(\text{Fe})$	$\rightarrow \sigma(\text{Fe-dpy2}), \sigma(\text{Fe-dpy1}), \sigma(\text{Fe-L})$		
3.91	0.635	$d(\text{Fe})$	$\rightarrow \sigma(\text{Fe-dpy2}), \sigma(\text{Fe-dpy1}), \sigma(\text{Fe-L})$		
		$d(\text{Fe})$	$\rightarrow \text{dpy1}, \text{dpy2}$		
3.94	0.232	L	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
		L	$\rightarrow \delta(\text{Fe-dpy2}), \delta(\text{Fe-L})$		
		$\pi(\text{Fe-pb})$	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
40	0.144	$\pi(\text{Fe-pb})$	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
41	0.146	$d(\text{Fe})$	$\rightarrow \text{dpy1}, \text{dpy2}$	4.32	2310
		$d^*(\text{Fe})$	$\rightarrow \text{dpy2}, \text{dpy1}$		
4.25	0.193	$\text{dpy2}, \text{dpy1}$	$\rightarrow \text{dpy1}, \text{dpy2}, \text{L}$		
4.29	0.215	$\text{dpy1}, \text{dpy2}$	$\rightarrow \text{dpy1}, \text{dpy2}, \text{L}$		
		$\text{dpy2}, \text{dpy1}$	$\rightarrow \delta(\text{Fe-dpy2}), \delta(\text{Fe-L})$		
4.42	0.258	$\text{dpy1}, \text{dpy2}$	$\rightarrow \delta(\text{Fe-dpy2}), \delta(\text{Fe-L})$		
		$\text{dpy1}, \text{dpy2}$	$\rightarrow \pi(\text{Fe-dpy1}), \delta(\text{Fe-L})$		
4.44	0.142	$\text{dpy2}, \text{dpy1}$	$\rightarrow \delta(\text{Fe-dpy2}), \delta(\text{Fe-L})$		
		$\text{dpy1}, \text{dpy2}$	$\rightarrow \text{dpy1}, \text{dpy2}, \text{L}$		
4.48	0.515	$d(\text{Fe})$	$\rightarrow \sigma(\text{Fe-dpy2}), \sigma(\text{Fe-dpy1}), \sigma(\text{Fe-L})$		
4.53	0.597	L	$\rightarrow \text{dpy1}, \text{dpy2}, \text{L}$		

There is no need to present the other two tables, all being similar.

Indeed, even though the presence of an acceptor substituent in ligands L' and L'' leads to a lower energy in the corresponding n* MO and therefore to the already mentioned reduced energy gap between the occupied and occupied molecular orbitals (HOMOs and LUMOs) of complexes [Fe(dpy)₂L'₂]²⁺ and [Fe(dpy)₂L''₂]²⁺, these facts do not create a considerable modification of the waves in the first region, whereas the lowest energy transitions (HOMO-LUMO transitions) in the complexes [Fe(dpy)₂]²⁺, [Fe(dpy)₂L'₂]²⁺ and [Fe(dpy)₂L''₂]²⁺ are similar for the three complex compounds.

The MOs with a large contribution (over 70%) of AOs of the carboxylic substituent (–COOH or –COO–CH₂–C≡CH) only take part in the transitions of high energy (*i.e.*, over the energy of 4.2 eV).

4. CONCLUSION

The comparison between the experimental and theoretical spectra shows that complexes [Fe(dpy)₂L'₂]²⁺ and [Fe(dpy)₂L''₂]²⁺ exhibit absorption in the same spectral region of the spectrum as [Fe(dpy)₃]²⁺.

Moreover, the complex compound [Fe(dpy)₂L₂]²⁺ proved itself to exhibit the availability to act as an “antenna”, so that the ligands L' and L'', containing in their structure a second group able to be involved in the coordination to the Fe(II) ion, may be used as “bridging ligands” in the synthesis of polynuclear supramolecular structures of the “antenna-bridge” kind.

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