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Topology of Spin-Crossover Polymers and Mutual Influence of Ligands

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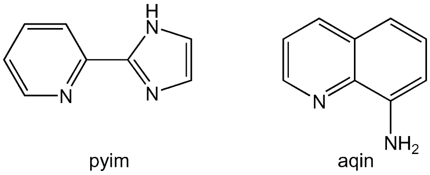
Density functional quantum-chemical calculations for mononuclear fragments, $[Fe^{II}(pyim)_2(bpy)]^{2+}$ [pyim = 2-(2-pyridyl)imidazole] and $[Fe^{II}(aqin)_2(bpy)]^{2+}$ (aqin = 8-aminoquinoline), of two recently synthesized spin-crossover compounds forming zigzag and linear coordination polymers, respectively, have been performed. The calculations suggest that the overall structure of the polymers is defined by the preference of the bidentate ligands for the *cis* or *trans* coordination mode, which in turn is determined by the character and efficiency of metal–ligand π-interactions. This hypothesis is used to predict the structures of two other spin-transition compounds, which have not been studied by X-ray crystallography.

Introduction

Extended spin-crossover systems occupy a special place in molecular magnetism.[1–4] It has been supposed for a long time that the covalent linking of transition metal centres in 1D, 2D, and 3D species enhances the cooperativity in these systems, which would lead to a more abrupt spin transition – probably with hysteresis.[5–7] Although the generality of this statement has been questioned in several studies,[8–12] extended spin-crossover systems remain an attractive area of research because of their interesting electronic and structural features.

Recently, a self-assembly strategy based on the use of mixed organic ligands acting as spacers and coligands has been proposed for the synthesis of spin-crossover polymers.[8,10–12] The ability to surround the metal centres with different ligands provides more possibilities of fine-tuning the spin-transition characteristics than when the metal coordination sphere is formed by identical bridging ligands, such as in the widely studied coordination polymers with triazol and tetrazol, or their derivatives.[13,14]

The utility of this approach was illustrated by the synthesis of several spin-crossover polymers with pyim [pyim = 2-(2-pyridyl)imidazole] or aqin (aqin = 8-aminoquinoline) coligands (Scheme 1).



Scheme 1.

Three different bipyridyl-like bridging ligands [4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane, and 1,2-bis(4-pyridyl)ethene] have been used for the synthesis of the polymers with the pyim ligand,[8,10] whereas the aqin-containing polymers included 4,4′-bipyridine (bpy)[11] or dicyanamide[12] bridges. The three pyim-containing polymers display rather gradual spin transitions at 205, 198, and 176 K, respectively. The spin transitions for the aqin complexes are also gradual, with one step at 220 K for the bpy-bridged polymer and two steps at 215 and 186 K for the polymer with the dicyanamide bridge. The synthesized polymers display a remarkable structural feature: the pyim polymers form zigzag chains, whereas the aqin polymers are organized in linear chains with both 4,4′-dipyridyl and dicyanamide bridges (Figure 1).

The polymer structure plays an important role in the spin-transition behaviour. It determines a possible spreading pattern of interchain links such as hydrogen bonding and π-stacking, as well as the positions of eventual solvent and counter ion species, which can also participate in interchain interactions. Recent studies suggest that these noncovalent interactions, rather than interactions through the bridging ligands, may be the largest contributing factor to the cooperativity in these systems.[8–12]

It seems reasonable to suppose that the overall structure of the polymers described above is defined by the coordination mode of the coligand. In the present paper, we study by DFT quantum-chemical calculations the relative stability of two model mononuclear isomers containing aqin and pyim bidentate ligands (Scheme 2). As for both co-ligands the polymers with the bpy bridging ligands are known, two pyridine rings completed the coordination sphere of metal centers. According to the positions of the pyridine groups, two isomers will be referred to below as *trans* and *cis*. Keeping

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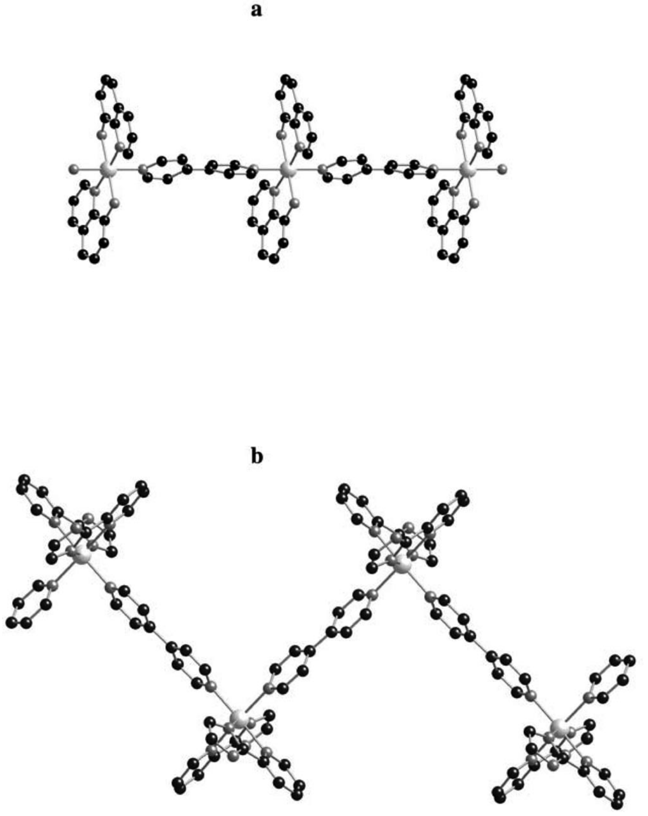
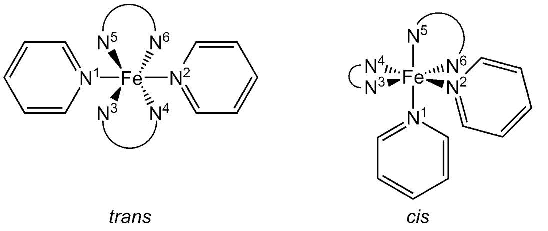


Figure 1. Molecular structure of the bpy-bridged spin-crossover polymers: (a) linear polymer with the aqin ligand; (b) zigzag polymer with the pyim ligand.

in mind the spin crossover observed in the coordination polymers, formed by mononuclear fragments, two spin states of Fe^{II} ions will be considered: low-spin (LS, $S = 0$) and high-spin (HS, $S = 2$).



Scheme 2.

Results and Discussion

The structures of both isomers with pyim and aqin ligands were initially optimized for the LS and HS states. The calculations were performed with two exchange-correlation functionals (see Computational Details). The coordination geometry of the FeN_6 cores in the experimentally studied polymers is satisfactorily reproduced by the calculations for the *trans*-aqin and *cis*-pyim complexes for both spin states. However, the agreement is slightly better for the structures obtained using the BP86 functional (Table 1). The description of the spin state energetics by DFT methods is very sensitive to the choice of the exchange-correlation functional.[15–18] In our case, the calculations with the B3LYP functional fail to correctly reproduce the multiplicity of the ground state of mononuclear complexes. Since spin crossover is an entropy-driven phenomenon, these transition complexes should possess LS ground states. Only the energies obtained through BP86 calculations satisfy this condition. Therefore, if not specified, we only refer to these calculations in the following. However, as it will be shown below, the calculations with both functionals give quite similar energy gaps between *cis* and *trans* isomers.

Table 1. Calculated bond lengths [Å] in the mononuclear complexes and the corresponding experimental distances in the coordination polymers.

	BP86		B3LYP		Exp.
	$S = 0$	$S = 2$	$S = 0$	$S = 2$	$S = 2$
pyim (*cis*)					
Fe–N^1	2.01	2.22	2.07	2.24	2.20
Fe–N^2	2.01	2.22	2.07	2.24	2.20
Fe–N^3	1.98	2.18	2.04	2.19	2.18
Fe–N^4	2.02	2.27	2.08	2.32	2.22
Fe–N^5	2.02	2.27	2.08	2.32	2.22
Fe–N^6	1.98	2.18	2.04	2.19	2.18
aqin (*trans*)					
Fe–N^1	2.04	2.27	2.11	2.29	2.22
Fe–N^2	2.02	2.26	2.09	2.28	2.20
Fe–N^3	1.97	2.20	2.03	2.22	2.17
Fe–N^4	2.04	2.25	2.07	2.27	2.16
Fe–N^5	2.04	2.26	2.07	2.27	2.16
Fe–N^6	1.97	2.20	2.03	2.22	2.17

Let us consider now the relative stability of the different isomers (see Table 2). For the pyim complexes we obtain a pronounced preference for the *cis* isomer. This behaviour is found with both exchange-correlation functionals. The stabilization energy of the *cis* isomer for the LS state is equal to 27.3 and 20.1 kJ/mol in the BP86 and B3LYP calculations, respectively. For the HS state, these values are reduced to 21.1 and 15.3 kJ/mol, respectively. We can note that the *cis* coordination mode of iron(II) has been found not only in spin-transition polymers, but also in the methanol-bridged iron(II) pseudodimer,[19] which does not display spin crossover. However, in the latter case the coordination sphere is completed by two NCS ligands.

For the aqin complexes we also find the energy of the *cis* isomer to be lower than that of the *trans* isomer; however, this effect is much less appreciable. The gain in energy found in the BP86 calculations is equal to 4.1 and 4.2 kJ/mol for the LS and HS states, respectively. The corresponding energy differences found with B3LYP calculations (4.2 and 3.7 kJ/mol, respectively) are very similar.

The preference for the *cis* isomers found for the pyim complexes agrees with their tendency to form zigzag polymers. The more stable *cis* form of the aqin complexes, however, does not correspond to the linear structure of the synthesized polymers. However, the stabilization energy of the *cis* versus *trans* form for the aqin complex is much less than

Table 2. Relative energies [kJ/mol] of the *cis* and *trans* isomers for the $Fe(L)_2(py)_2$ mononuclear complexes in different spin states. All energies are given relative to the most stable state.

	BP86				B3LYP			
	cis		*trans*		*cis*		*trans*	
	$S = 0$	$S = 2$	$S = 0$	$S = 2$	$S = 0$	$S = 2$	$S = 0$	$S = 2$
aqin								
ΔE[a]	0.0	59.0	0.0	59.1	31.8	0.0	32.3	0.0
$\Delta E_{S=0}$[b]	0.0		4.1		0.0		4.2	
$\Delta E_{S=2}$[c]		0.0		4.2		0.0		3.7
pyim								
ΔE[a]	0.0	53.3	0.0	47.1	43.0	0.0	47.9	0.0
$\Delta E_{S=0}$[b]	0.0		27.3		0.0		20.1	
$\Delta E_{S=2}$[c]		0.0		21.1		0.0		15.3
2-(aminomethyl)pyridine								
ΔE[a]	0.0	53.0	0.0	51.0	37.8	0.0	38.3	0.0
$\Delta E_{S=0}$[b]	0.0		5.8		0.0		3.4	
$\Delta E_{S=2}$[c]		0.0		3.8		0.0		2.9
2-(2-pyridyl)imidazoline								
ΔE[a]	0.0	46.9	0.0	44.5	51.1	0.0	48.6	0.0
$\Delta E_{S=0}$[b]	0.0		19.2		0.0		14.7	
$\Delta E_{S=2}$[c]		0.0		16.7		0.0		17.2

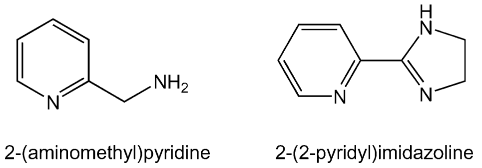
[a] ΔE is the energy difference between two spin states for each isomer. [b] $\Delta E_{S=0}$ is the energy difference between two isomers for the LS state. [c] $\Delta E_{S=2}$ is the energy difference between two isomers for the HS state.

that for the pyim complex and is practically within the error limits of DFT methods. This difference can be easily compensated for by collective effects in the polymer or by packing effects in the solid state.

The observed tendencies in the energies of the *cis* and *trans* isomers can be rationalized by considering the relative role of metal–ligand π-interactions. If we consider for simplicity only the LS state, six electrons populate three orbitals of the "t_{2g}" block, which participate in π-interactions. In the *trans* isomer, two bidentate ligands should share the same orbital of the central atom. As it has been rationalized through a simple perturbation approach in the early paper by Burdett and Albright,[20] such sharing is not favoured if the metal–ligand bonding orbital is occupied. In the case of a *trans* isomer, the orbitals of the nitrogen atoms belonging to the two pyim ligands share the same d_{xy} metal orbital. Although it is difficult to attribute a particular character to the metal–ligand π-bond in the studied complexes, it is generally supposed that the pyridine ligand in Fe^{II} complexes acts as a weak π-acceptor.[21,22] We can consider that the occupied "t_{2g}" orbitals are stabilized through π-interactions. In this case, the *trans* isomer is predicted to be energetically unfavourable, and this effect is reproduced in our DFT calculations. In the HS state, the number of electrons occupying the orbitals involved in π-interactions decreases, as two valence electrons are transferred to "e_g" orbitals. As a result, we find a smaller gain in energy for the *cis* isomer in the HS state.

In the case of the aqin ligand, the role of π-interactions is much less important. This results from the different electronic nature of the nitrogen donor atoms. In particular, the participation of the aliphatic nitrogen atom of the aqin ligand in π-interactions can be considered to be negligible. The reduction of π-interactions in the aqin complexes can be easily seen from the spreading of orbital energies of the "t_{2g}" block. In the LS state of the pyim complexes, this spreading is equal to 0.325 and 0.228 eV for the *trans* and *cis* isomers, respectively, whereas the corresponding values for the aqin complexes are equal to 0.091 and 0.096 eV, respectively. As a result of the weakening of the π-interactions, the energy gain for the *cis* isomer in the LS state becomes just about 4 kJ/mol. This value, being already rather small, is not modified significantly upon transition to the HS state.

In order to corroborate the hypothesis about the role of π-interactions in the stabilization of different isomers and predict the structure of other polymers, we performed the calculations for two isomers (Scheme 3) with two other bidentate ligands: 2-(2-pyridyl)imidazoline and 2-(aminomethyl)pyridine.



Scheme 3.

The complexes with both ligands and bpy have been synthesized and have manifested spin transitions.[23] Although the X-ray studies have not been performed, the polymeric structure can be supposed for both complexes. For the complex with the 2-(2-pyridyl)imidazoline ligand we found a gain in energy of 19.2 and 16.7 kJ/mol for the *cis* isomer in the LS and HS states, respectively. This result is consistent with the presence of two aromatic nitrogen donor atoms involved in π-interactions and agrees with our previous conclusions. We can predict a zigzag structure for the corresponding coordination polymer. The π-interactions can be expected to be less pronounced for the 2-(aminomethyl)pyridine ligand because of the presence of the aliphatic nitrogen atom. In agreement with this fact, we found a rather small stabilization of the *cis* isomer of 5.8 and 3.8 kJ/mol for the LS and HS states, respectively. One can suggest that the polymer should be on the border between zigzag and linear structures.

Conclusions

Our goal in the present study was to clarify the electronic features underlying the self-assembly of spin-crossover coordination polymers. The polymer structures are defined by the coordination modes of the coligands, which in turn are dictated by the electronic properties of their nitrogen donor atoms – especially their involvement in π-interactions. The calculations show that the electronic properties of the pyim ligand dictate a *cis* coordination mode around the iron(II) centre, which results in a zigzag topology of the polymer species. Because of the different electronic nature of the nitrogen atoms in the aqin ligand, the tendency of the complex to form *cis* isomers is much less pronounced. The experimentally studied linear aqin polymers are formed by *trans* isomers, and one can suggest that this structure is imposed by collective intrachain interactions and packing effects. On the whole, the aqin mononuclear complexes can be classified as being on the border between *cis* and *trans* structures. Thus, future syntheses of zigzag polymers from such building blocks cannot be excluded. In particular, kinetic factors might play a determining role in the formation of one isomer or the other. Our theoretical analysis was also applied to two other spin-transition complexes, whose structures have not yet been determined. It appears that electronic effects are one of the key factors in the formation of extended structures, and these must be taken into account in the rational design of new spin-crossover materials.

Computational Details

DFT calculations on both isomers with different ligands in the LS and HS states were carried out with the Gaussian 03 (Revision D.01) package.[24] Since the choice of the exchange-correlation functional for the calculation of the energy gap between LS and HS states is widely debated in the literature,[15–18] we used both the pure GGA (generalized gradient approximation) BP86 functional[25,26] as well as the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP).[27,28] The 6-31g(d,p) basis sets were used for C, H, and N atoms. Fe atoms were described with the "Stuttgart/Dresden" SDD basis sets and effective core potentials.

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