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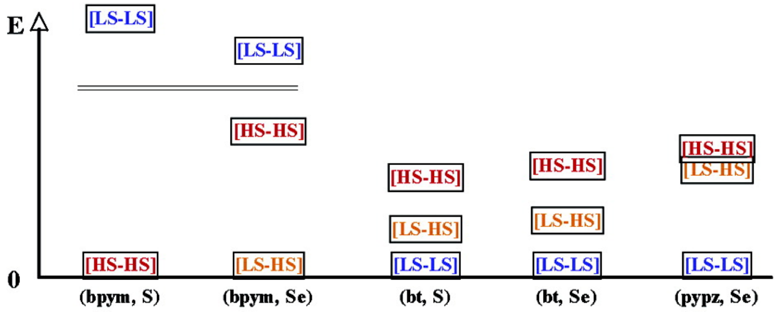

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Energetics of Binuclear Spin Transition Complexes

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Abstract: The electronic structures of five binuclear iron(II) complexes, four of which display spin transitions between the low-spin (LS) and high-spin (HS) electronic states, are studied by density functional theory (DFT) calculations. Three electronic states, corresponding to [LS−LS], [LS−HS], and [HS−HS] electronic configurations, are characterized. The nature of the ground state agrees with the experimentally observed magnetic state of complexes stabilized at low temperatures. The results of the calculations agree with the conclusion of the phenomenological model, that the enthalpy of the [LS−HS] state must be lower than the average enthalpy of the [LS−LS] and [HS−HS] states, to create conditions for a two-step spin transition. The exchange parameters between Fe(II) ions in the [HS−HS] states are evaluated. It is shown that all complexes are weakly antiferromagnetic and the synergy between two spin transition centers is mainly of elastic origin.

Introduction

Spin crossover and magnetic exchange are two basic phenomena in molecular magnetism.[1] The fundamental interest in these phenomena arises from their involvement in the creation of bistable molecular systems, that is, systems capable of being in two different states under the same conditions. This bistable behavior underlies the design of molecular systems for information processing. The spin crossover effect consists of reversible transformation between the low-spin (LS) and high-spin (HS) electronic states by variation of the temperature, or under external perturbation such as light irradiation, pressure, or magnetic field.[2] Although the spin transition can take place in an isolated molecule, the abruptness of the transition, necessary for its potential applications, can be achieved only in highly cooperative systems. The assemblage of spin transition molecules in a crystal gives rise to cooperative intermolecular interactions of a different nature. The information about the change of spin state in a molecule, accompanied by the "breathing" of the metal coordination sphere, is transmitted to other molecules through van der Waals interactions, hydrogen bonds, or π-stacking interactions. Attempts to increase the cooperativity of spin transition systems suggested the idea of linking isolated metal centers by covalent bridges. Synthetic work in this direction during the last 15 years resulted in numerous polynuclear and polymeric (one-, two-, and three-dimensional) spin transition species.[3,4]

Covalent bridges between spin transition centers can transmit not only elastic interactions but also electronic interactions. In particular, if two metallic ions possess at least at one spin state, a nonzero total spin, and the bridging ligand is not too extended, the magnetic centers can be linked by the exchange interaction. The interplay between spin crossover and magnetic ordering was recently studied within a phenomenological model.[5] For the most-studied spin transition ion Fe(II), the LS state is characterized by spin $S = 0$ and the HS state by $S = 2$. So the manifestations of magnetic exchange in Fe(II) polynuclear systems must be limited only by the HS state. However, this exchange is very difficult to observe directly, if its value is much smaller than kT_c, where T_c is the spin transition temperature. As a result, spin levels of the polynuclear aggregate are equally populated, and the magnetic exchange J value cannot be accessed by traditional magnetochemical methods.

Binuclear complexes occupy a special place among polynuclear spin transition systems. The number of such systems is very limited[6−8] and they present a challenge for studies of the possible synergy between spin transition and different forms of intra- and intermolecular interactions. The series of bpym

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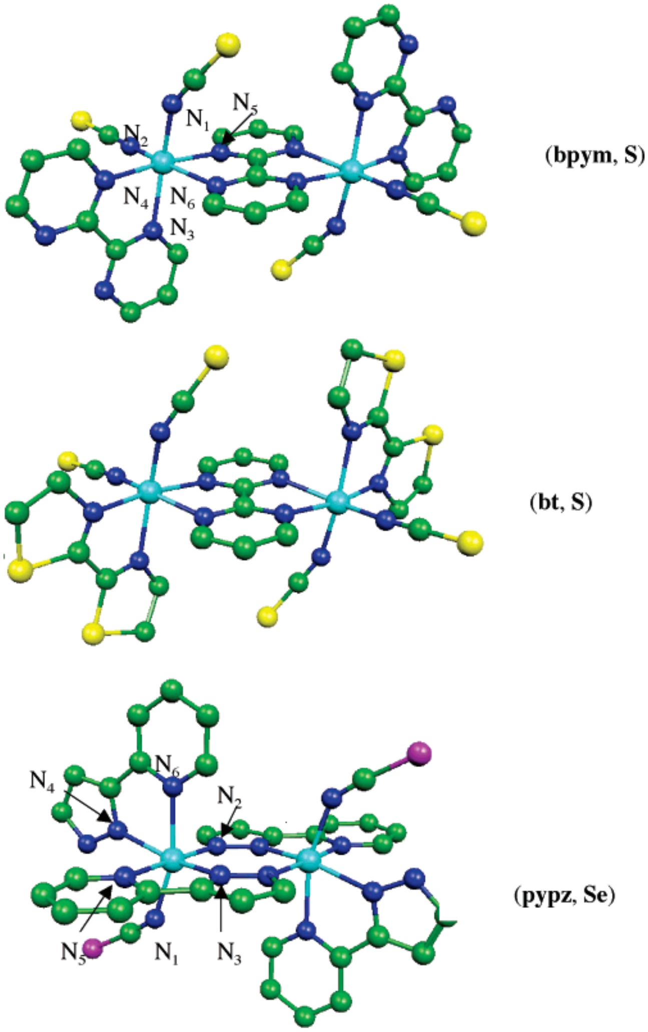

Figure 1. Ball-and-stick representations of structures for (**bpym**, **S**), (**bt**, **S**), and (**pypz**, **Se**) complexes in the [HS−HS] state.

(bpym = 2,2′-bipyrimidine) bridged binuclear complexes,[6] synthesized by the laboratory group of J. A. Real, is a well-studied family of binuclear spin transition complexes. The general formula of the complexes is $(Fe(L)(NCX)_2)_2(bpym)$ (Figure 1), where L = bpym or bt (bt = 2,2′-bithiazoline), and X = S or Se. As in previous publications, we will note these compounds as (**bt**, **S**), (**bt**, **Se**), (**bpym**, **S**), and (**bpym**, **Se**) (Figure 1).

The magnetic susceptibility data of (**bt**, **S**) and (**bt**, **Se**) display complete spin transitions. The remarkable feature of both transitions is their two-step character. The two steps for (**bt**, **S**) are centered at 197 and 163 K, and those for (**bt**, **Se**), at 265 and 223 K. In both cases, the plateaus correspond to approximately 50% spin conversion. It has been suggested that the plateau is constituted by dimers in which only one metal center has undergone spin transition, thus forming [LS−HS] pairs. This hypothesis was recently unambiguously confirmed by Mössbauer experiments in an external magnetic field for a similar binuclear spin crossover compound $[Fe(phdia)(NCS)_2]$-(phdia) (phdia = 4,7-phenanthroline-5,6-diamine).[9] The [LS−HS] and [HS−HS] states also can be obtained at low temperatures by photoexcitation through the LIESST (light-induced spin-state trapping) effect, as has been demonstrated for the (**bt**, **S**) complex.[10,11] The temperature dependence of $\chi_m T$ after light irradiation was explained by selective excitation of the ground singlet of the antiferromagnetically coupled pair [HS−HS]. The complex (**bpym**, **S**) remains in the HS state in the whole temperature range 0−300 K. The low-temperature stability of the [HS−HS] phase allowed determination of the parameter for antiferromagnetic exchange interaction between two HS Fe(II) ions through a bpym bridge. The exchange constant was found to equal -4.1 cm^{-1}. Finally, the (**bpym**, **Se**) compound shows an abrupt spin transition in the 125−115 K region, with $\chi_m T$ decreasing from 6 to only 3.5 cm^3·K·mol^{-1}, and then this value remains quasiconstant until near 0 K. One can suppose that the low-temperature phase is composed mainly from [LS−HS] pairs. The stabilization of mixed species down to very low temperatures was evidenced by the Mössbauer experiments in an external magnetic field.[12] Unfortunately, the X-ray crystallograhic data are available only for the **(bt, S)** compound above and below T_c[13] and for the nontransitioning (**bpym**, **S**) complex.[6a] For the other members of the series, the average Fe−N distances were found from extended X-ray absorption fine structure (EXAFS) experiments.[6c]

In this paper we present results of quantum-chemical studies by the DFT (density functional theory) technique of four binuclear compounds of the $(Fe(L)(NCX)_2)_2(bpym)$ series. We will try to characterize three different spin states of binuclear complexes, namely, [HS−HS], [LS−HS], and [LS−LS], and on this basis to understand their different behavior relative to the spin transition. For comparison, we also studied the recently synthesized binuclear complex (pypzH)(NCSe)Fe(μ-pypz)$_2$−Fe-(NCSe)(pypzH)[8] (pypzH = 2-pyrazolylpyridine) (Figure 1). The (**pypz**, **Se**) complex displays a single-step sharp spin crossover transition between [HS−HS] and [LS−LS] states with T_c = 225 K. DFT calculations were also used to determine the strength of exchange interactions effective in the [HS−HS] state of binuclear complexes.

Computational Details

As the experimental X-ray structures in different spin states were obtained only for (**bt**, **S**) and (**pypz**, **Se**) complexes, for all studied binuclear complexes the energies of [HS−HS], [LS−HS], [LS−LS] spin states were calculated for fully optimized molecular geometries. The geometry optimizations have been performed with the GAUSSIAN 98 (A7 version) package.[14] The LANL2DZ basis set, including the double-ζ basis with the Los Alamos effective core potential for Fe, S, and Se and the Dunning−Huzinaga all-electron double-ζ basis set with polarization functions for the H, C, and N atoms,[15,16] has been used. The choice of the exchange-correlation functional for spin transition systems presents a very delicate problem. We used hybrid B3LYP* potential, proposed recently especially for this class of systems.[17] We have previously demonstrated[18] that this potential ensures a correct order

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of different spin states for experimental structures of mononuclear spin transition complexes at low and high temperatures. In order for the optimization procedure to converge to a particular spin distribution in a binuclear complex, it is very important to properly define the departure geometry. For the complexes with experimentally known structure, we took the low-temperature structures to obtain the [LS−LS] state and the high-temperature structures for the [HS−HS] state. For all other complexes, the [LS−LS] and [HS−HS] states were preliminarily optimized with the ADF 04 package.[19] In these calculations, the Rev-PBE functional[20] with the triple-ζ basis set and nonfrozen core for all atoms has been used. Then the obtained structures were reoptimized with GAUSSIAN 98. In all calculations we supposed that the [LS−LS] and [HS−HS] structures possess a center of symmetry. The optimization of the [LS−HS] states was performed in two stages. First, the [FeN_6] cores were frozen at geometries obtained for “pure” [LS−LS] and [HS−HS] states, and positions of all other atoms were optimized. At the second stage, a full optimization was performed. The spin density in this manner was found to be about 0 at one metal center and about 3.8 at the second, confirming that the total dimer spin $S = 2$ is formed by local spins 0 and 2.

The exchange parameter in the [HS−HS] state of binuclear complexes has been calculated on the base of the broken symmetry (BS) method.[21] The energy of binuclear complexes was calculated for the state with the maximal total spin $S = 4$ and for the fictitious broken symmetry state. The following formula, proposed by Yamaguchi et al.[22] take into account the spin contamination of the broken symmetry solution was used for calculations of the exchange coupling parameter:

$$J = (E^{BS} - E^{HS})/(\langle S^2\rangle^{BS} - \langle S^2\rangle^{HS})$$

where E^{BS} and E^{HS} are the to tal energies of the broken symmetry and $S = 4$ states, respectively, and $\langle S^2\rangle^{BS}$ and $\langle S^2\rangle^{HS}$ are the spin eigenvalues in two states. In our calculations, $\langle S^2\rangle^{BS}$ and $\langle S^2\rangle^{HS}$ values varied in the ranges 4.2−4.6 and 20.2−20.6, respectively.

Results and Discussion

At the first stage, for each of the five complexes we optimized the geometries and calculated energies of three electronic states: [LS−LS], [LS−HS], and [HS−HS]. For the first two spin state distributions, the choice of the total dimer spin is unambiguously imposed as 0 and 2. For the later state where the exchange coupling can generate a series of spin multiplets with the total spin varying from 0 to 4, we considered the state with the maximal total spin, supposing that the structure is not very sensitive to the total spin value, when local spins are fixed. Selected distances for optimized [LS−LS] and [HS−HS] structures are given in Table 1. The comparison of optimized bond lengths with reported X-ray data (where available) shows rather satisfactory agreement. As usual in DFT calculations of spin transition complexes, agreement is better for the LS state. The total energies and atomic Cartesian coordinates for all optimized structures, as well as selected bond lengths for mixed [LS−HS] complexes, are given in the Supporting Information.

Table 1. Selected Bond Lengths in Optimized and Experimental[6a,8,13] Structures[a]

	(**bpym**, **S**)	(**bpym**, **Se**)	(**bt**, **S**)	(**bt**, **Se**)	(**pypz**, **Se**)
		(a) [HS-HS] State			
Fe−N_1	2.13 (2.08)	2.04	2.11 (2.07)	2.11	2.13 (2.14)
Fe−N_2	2.00 (2.05)	2.03	2.00 (2.04)	2.00	2.12 (2.11)
Fe−N_3	2.23 (2.20)	2.22	2.27 (2.24)	2.27	2.14 (2.10)
Fe−N_4	2.19 (2.21)	2.20	2.20 (2.11)	2.19	2.26 (2.21)
Fe−N_5	2.17 (2.22)	2.14	2.16 (2.20)	2.17	2.25 (2.20)
Fe−N_6	2.30 (2.32)	2.24	2.29 (2.26)	2.28	2.24 (2.29)
N_1−C_1	1.20	1.20	1.20	1.20	1.20
C_1−X_1	1.68	1.80	1.68	1.82	1.82
N_2−C_2	1.21	1.20	1.21	1.21	
C_2−X_2	1.66	1.80	1.66	1.79	
Fe−Fe	5.93 (6.02)	5.86	5.91 (5.89)	5.92	4.14 (4.10)
		(b) [LS−LS] State			
Fe−N_1	1.90	1.90	1.97 (1.95)	1.96	1.98 (1.96)
Fe−N_2	1.89	1.89	1.94 (1.93)	1.93	1.99 (1.98)
Fe−N_3	1.98	1.97	1.97 (1.97)	1.97	1.97 (1.99)
Fe−N_4	1.97	1.98	1.96 (1.95)	1.95	1.96 (2.00)
Fe−N_5	1.99	2.00	1.98 (1.98)	2.00	2.03 (1.98)
Fe−N_6	2.00	2.00	1.99 (1.98)	1.99	1.99 (2.03)
N_1−C_1	1.20	1.20	1.20	1.20	1.20
C_1−X_1	1.68	1.81	1.69	1.82	1.83
N_2−C_2	1.20	1.20	1.20	1.20	
C_2−X_2	1.67	1.81	1.67	1.81	
Fe−Fe	5.51	5.43	5.38 (5.35)	5.39	4.03 (4.00)

[a] Bond lengths are given in angstroms. Experimental values are shown in parentheses.

The comparison of the three energies (Figure 2) for all complexes immediately leads to important qualitative results. For the complexes (**bt**, **S**), (**bt**, **Se**), and (**pypz**, **Se**), the [LS−LS] pairs have the lowest energies. In agreement with the experimental results, a complete spin transition [LS−LS] → [HS−HS] can be observed only for these compounds. For the (**bpym**, **S**) complex, the ground state is represented by the [HS−HS] pair, whereas for the (**bpym**, **Se**) complex, the mixed pair [LS−HS] has the lowest energy. These ground states completely correspond to experimentally observed low-temperature phases. The most important stabilization has been found for the [HS−HS] state of the (**bpym**, **S**) complex, for which we were unable to calculate a converged [LS−HS] state. Indeed, this complex remains in the HS state at all temperatures studied experimentally. The order of energy gaps between the LS and HS states for two similar complexes (**bt**, **S**) and (**bt**, **Se**) agrees with the order of the spin transition temperatures for these two compounds. The reason for large differences between the calculated spin states and resulting magnetic properties of **bt** and **bpym** species can be looked for in important differences in the effective ligand field. The energy gap between the metal-centered highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) in the [LS−LS] state is about 100 kJ/mol larger for the (**bt, X**) complexes. The singularity of the (**bpym, Se**) compound manifested in the stabilization of the [LS−HS] ground state may arise from the quasi-resonance between t_{2g} orbitals of the LS site and e_g orbitals of the HS site.

When the mixed [LS−HS] state falls in the energy gap between the ground [LS−LS] and excited [HS−HS] states, its position relative to an average energy plays an important role in the shaping of the spin transition. The phenomenological model developed in ref 6b predicted that the [LS−HS] state enthalpy must be lower than the halfway point between the enthalpies of [LS−LS] and [HS−HS] states to have a two-step spin transition. It means that the factor $\rho = W/\Delta H$, where ΔH is the enthalpies difference between the [LS−LS] and [HS−HS] states and W is the difference between the [LS−HS] and

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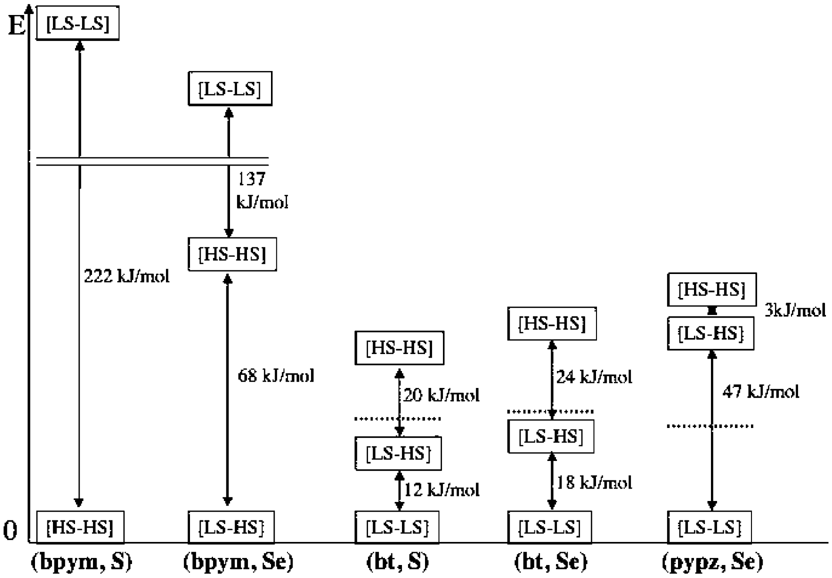

Figure 2. Relative energies of the [LS−LS], [LS−HS], and [HS−HS] states. Dashed lines indicate average energies between the [LS−LS] and [HS−HS] states.

average enthalpies, must be negative. This condition is necessary but not sufficient. The force of intermolecular cooperative interactions determines another condition. Less negative ρ values require stronger intermolecular interactions for a two-step spin transition to be possible. As can be seen from our results, among three complexes moving from the [LS−LS] to [HS−HS] state, the negative ρ values are obtained only for (**bt**, **X**) complexes, which display two-step spin transitions. Furthermore, the ρ factor obtained for the ((**bt**, **S**) compound from magnetic measurements and confirmed by the Mössbauer experiments is equal to −0.072, whereas from our calculations we obtain −0.059. Our quantum-chemical calculations clearly confirm the conclusions of the phenomenological model.[6b] The [LS−HS] state of the (**pypz**, **Se**) complex is strongly destabilized, and it lies just slightly lower than the [HS−HS] state. This picture agrees with a one-step character of the spin transition. One can look for the origin of such behavior in the geometry of the [LS−HS] state. If in the (**bt**, **X**) complexes the bridging ligand maintains a quasi-planar structure, in the (**pypz**, **Se**) dimer it is strongly distorted. A strong distortion of the bridging ligand breaks the electronic communication between metal centers and results in strong energetic destabilization.

Until now we have considered that the [HS−HS] state is presented by one energy level characterized by the maximal value 4 of the total spin $S = S_1 + S_2$. However, the exchange coupling of two local spins expressed by the Heisenberg−Dirac−Van Vleck Hamiltonian

$$H_{ex} = JS_1S_2$$

leads to appearance of five multiplets with total spin varying from 0 to 4 and energies

$$E = (J/2)S(S + 1)$$

The values of exchange parameters calculated by the BS method for the five studied complexes are given in Table 2. All complexes display antiferromagnetic exchange coupling, as expressed by the negative sign of exchange parameters. The experimental value is known only for the (**bpym**, **S**) complex, which remains in the [HS−HS] state down to very low temperatures. Our calculations result for this compound in $J = -2.1$ cm^{-1}, whereas the magnetic measurements give −4.1 cm^{-1}. For all other complexes, J values cannot be accessed by direct magnetochemical methods. If the exchange-coupled phase is realized at temperatures above 150−200 K and the exchange parameter does not exceed a couple of dozen wavenumbers, all spin multiplets are equally populated and the magnetic moment value is saturated. Theoretical methods allow one to override this difficulty and to calculate exchange parameters. We do not want to overinterpret a good agreement between the calculated and experimental J values obtained for the (**bpym**, **S**) complex. If one modifies parameters of the DFT BS approach, such as the exchange-correlation functional, the basis set, or the method of evaluation of spin contamination, the calculated exchange parameter will vary. Also, the BS method in application to multielectronic ions has some intrinsic problems.[23] However, we believe that calculations performed within the same approach for a series of similar compounds allow us to obtain some important qualitative results. In particular, we conclude that all compounds in the [HS−HS] state are more or less weakly antiferromagnetic. The antiferromagnetic coupling is more efficient for (**bt**, **X**) than for (**bpym**, **X**) compounds, and the (**pypz**, **Se**) complex is situated between these two families. The difference between the (**bt**, **S**) and (**bpym**, **S**) complexes requires further commentary. The apparent similarity of the temperature dependence of the (**bpym**, **S**) and photoexcited (**bt**, **S**) systems has been analyzed, suggesting a very close exchange interaction in both system. This approach

Table 2. Calculated Exchange Parameters in the [HS−HS] State

	J (cm^{-1})
(**bpym**, **S**)	−2.3
(**bpym**, **Se**)	−2.3
(**bt**, **S**)	−44.1
(**bt**, **Se**)	−25.2
(**pypz**, **Se**)	−8.9

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has been justified by the same chemical nature of the bridging network. Our calculations indicate that small structural differences in [FeN_6] coordination cores can induce rather important differences in J values. It can be noted in the experimental structures that the difference between Fe−N(bpym) distances for the (**bt**, **S**) and (**bpym**, **S**) is even larger than in the optimized calculated structures. The extrapolation of exchange parameter for the (**bpym**, **S**) to the (**bt**, **S**) complex must be done with care.

A question arises if the appearance of several spin multiplets resulting from the exchange interaction, instead of just one [HS−HS] state, cannot modify the condition for a two-step spin transition obtained within the phenomenological model.[6b] It seems to be a reasonable approximation for calculation of the effective ρ parameter to take as a position of the [HS−HS] state the energetic center of gravity for spin multiplets. It can be easily seen that, due to a small magnetic exchange value, this correction does not influence the sign of the ρ parameter and only slightly modifies its absolute value.

The earlier work on binuclear spin transition systems suggested that a synergy between electron-deformational and exchange interactions is responsible for the spin transition behavior of binuclear complexes. As it follows from our calculations, the first type of interaction mainly determines the characteristics of the thermal spin transition. The antiferromagnetic interaction is too weak to be determinant in the energy gaps between HS and LS states. However, the magnetic coupling must play an important role in photomagnetic properties at low temperatures.

Concluding Remarks

It is evident from the present study that quantum chemical calculations can provide a good deal of structural and magnetic information for binuclear spin transition systems. In particular, we were able to characterize the structure and energetic stability of intermediate [LS−HS] states, which are not accessible by experimental methods. Our calculations confirmed that the position of the intermediate [LS−HS] state is decisive for appearance of a two-step spin transition, as had been proposed by the phenomenological model.[6b] The obtained exchange parameters show that all studied complexes are weakly antiferromagnetic. The synergy between spin transitions on two dimer metal sites is determined mainly by vibronic correlations. A synthesis of new polynuclear spin transition systems with enhanced exchange interactions could modify this conclusion. This possibility represents an exciting opportunity, as it can lead to new spectacular effects in molecular magnetism.

Acknowledgment. We are grateful to J. A. Real for providing us with the structural data for the (**bt**, **S**) compound and to G. S. Matouzenko and V. Robert for fruitful discussions.

Supporting Information Available: Total energies and Cartesian coordinates for all optimized molecular structures, calculated bond length for the [LS−HS] states of binuclear complexes, and complete ref 14. This material is free of charge via the Internet at http://pubs.acs.org.

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