

# Notes

## Free Energy of Spin-Crossover Complexes Calculated with Density Functional Methods

Hauke Paulsen,<sup>†</sup> Lars Duelund,<sup>†</sup> Heiner Winkler,<sup>†</sup>  
Hans Toftlund,<sup>‡</sup> and Alfred X. Trautwein\*<sup>†</sup>

Institut für Physik, Medizinische Universität Lübeck,  
D-23538 Lübeck, Germany, and Department of Chemistry,  
University of Southern Denmark, Main Campus: Odense  
University, DK-5230 Odense M, Denmark

Received August 21, 2000

### Introduction

The phenomenon of temperature-dependent spin crossover in transition metal complexes, which has been known for more than 60 years, has been studied with increased intensity in recent years after it was discovered that the spin state can be switched by pressure and light irradiation.<sup>1</sup> This makes spin-crossover complexes very promising materials for display and memory devices. The majority of the spin-crossover complexes that have been investigated so far are iron(II) complexes which exhibit a transition from the singlet low-spin state (LS) to the quintet high-spin state (HS) with increasing temperature. Gradual spin transition, where the fraction  $n_{\text{HS}}$  of complexes in the HS state changes smoothly over a large temperature interval, are observed in solids and in solutions and can in principle be explained on a molecular basis. Intermolecular interactions have to be taken into account in addition in order to understand abrupt spin transitions, where  $n_{\text{HS}}$  drops from 1 to 0 after decreasing the temperature by only a few degrees.

In a simple model restricted to isolated complexes,<sup>2</sup>  $n_{\text{HS}}(T)$  can be written as a function of the Gibbs free energy  $G$  and temperature  $T$ :

$$n_{\text{HS}}(T) = [1 + \exp(\Delta G/k_{\text{B}}T)]^{-1} \quad (1)$$

where  $\Delta G = G^{\text{HS}} - G^{\text{LS}}$  is the difference of the free energy between the HS and the LS state. In this model, the free energy  $G(T) = E_{\text{el}}(0) + E_{\text{vib}}(T) - TS(T)$  depends on the total electronic energy at zero temperature,  $E_{\text{el}}(0)$ , which includes the Coulomb repulsion between nuclei, the vibrational energy at temperature  $T$ ,  $E_{\text{vib}}(T)$ , and the product of temperature  $T$  and the entropy  $S(T)$  with respect to the vibrational states and to the substates of the spin multiplet. The temperature dependence of the total electronic energy due to the thermal occupation of excited electronic states is neglected here. The transition temperature  $T_{1/2}$ , defined by  $n_{\text{HS}}(T_{1/2}) = 1/2$  where  $\Delta G(T_{1/2})$  should vanish, is then given by the implicit equation

$$T_{1/2} = [\Delta E_{\text{el}}(0) + \Delta E_{\text{vib}}(T_{1/2})]/\Delta S(T_{1/2}) \quad (2)$$

To predict  $n_{\text{HS}}(T)$  from theory,  $E_{\text{el}}(0)$ ,  $E_{\text{vib}}(T)$ , and  $S(T)$  must be retrieved from electronic structure calculations. The Hartree–Fock method without configuration interaction turns out to be inadequate for iron(II) spin-crossover complexes, and a treatment of electron correlation by multiconfigurational procedures is computationally prohibitive. Instead, methods based on density functional theory (DFT) have been proven to give accurate results for many properties of transition-metal compounds with moderate computational expenses. For instance, the B3LYP method<sup>3</sup> has been used to calculate the equilibrium geometry and the normal modes of molecular vibration for the HS and LS isomers of  $[\text{Fe}(\text{tpa})(\text{NCS})_2]$  (tpa = tris(2-pyridylmethyl)amine).<sup>4</sup> While the zero-point vibrational energy and the entropy of spin-crossover complexes are thus accessible to calculation, the total energy difference  $\Delta E_{\text{el}}$ , which is more than 5 orders of magnitude smaller than the absolute energy values, remains a challenge to quantum chemistry. Only very recently, Chen et al.<sup>5</sup> published total energy differences for  $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot 2/3 \text{H}_2\text{O}$  (tpen = tetrakis(2-pyridylmethyl)ethylenediamine) that have been obtained with the B3LYP method and the 3-21G basis set. The results of Chen et al.<sup>5</sup> suggest that the spin-transition is induced by a gradual, temperature-dependent change of the molecular geometry, which makes the HS state more favorable at high temperature. However, we doubt that calculations with the B3LYP method can reproduce the total energy difference  $\Delta E_{\text{el}}(0)$  with the required accuracy. To corroborate this assumption, we have calculated the energy of the HS and the LS state of the  $[\text{Fe}(\text{tpen})]^{2+}$  complex in vacuo (complex **1**) using the X-ray structure<sup>6</sup> at  $T = 298 \text{ K}$ . In addition, a full geometry optimization has been performed for the LS and the HS state. To check whether the retrieved results are peculiar to  $[\text{Fe}(\text{tpen})]^{2+}$ , the same procedure has been applied to several other iron(II) spin-crossover complexes:  $[\text{Fe}(\text{tpa})(\text{NCS})_2]$  (**2**),<sup>7</sup>  $[\text{Fe}(\text{bptn})(\text{NCS})_2]$  (bptn = N,N'-bis(2-pyridylmethyl)-1,3-propanediamine) (**3**),<sup>8</sup>  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (phen = 1,10-phenanthroline) (**4**),<sup>9</sup>  $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$  (**5**),  $[\text{Fe}(\text{tpm})_2]^{2+}$  (tpm = tris(1-pyrazolyl)methane) (**6**),<sup>10</sup>  $[\text{Fe}(\text{bpp})_2]^{2+}$  (bpp = 2,6-bis(pyrazol-3-yl)pyridine) (**7**),<sup>11</sup>  $[\text{Fe}(\text{isoxazole})_6]^{2+}$  (**8**), and  $[\text{Fe}(\text{tmpm})_2]^{2+}$  (tmpm = tris(5-methyl-1-pyrazolyl)methane) (**9**).<sup>12</sup>

- (3) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (4) Paulsen, H.; Winkler, H.; Trautwein, A. X.; Grünsteudel, H.; Rusanov, V.; Toftlund, H. *Phys. Rev. B* **1999**, *59*, 975–984.
- (5) Chen, G.; Espinosa-Perez, G.; Zentella-Dehesa, A.; Silaghi-Dumitrescu, I.; Lara-Ochoa, F. *Inorg. Chem.* **2000**, *39*, 3440–3448.
- (6) Chang, H.-R.; McCusker, J. K.; Toftlund, H.; Wilson, S. R.; Trautwein, A. X.; Winkler, H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 6814–6827.
- (7) Højland, F.; Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand. A* **1983**, *37*, 251–257.
- (8) Winkler, H.; Sawaryn, A.; Trautwein, A. X.; Yousif, A. S.; Hermes, C.; Toftlund, H.; Herber, R. H. *Hyperfine Interact.* **1988**, *42*, 921–924.
- (9) Gallois, B.; Real, J.-A.; Hauw, C.; Zarembowitch, J. *Inorg. Chem.* **1990**, *29*, 1152–1158.
- (10) Winkler, H.; Trautwein, A. X.; Toftlund, H. *Hyperfine Interact.* **1992**, *70*, 1083–1086.
- (11) Goodwin, H. A.; Sugiyarto, K. H. *Chem. Phys. Lett.* **1987**, *139*, 470–474.
- (12) Toftlund, H.; Zimmermann, A. et al. To be published.

<sup>†</sup> Medizinische Universität.

<sup>‡</sup> University of Southern Denmark, Odense Campus.

(1) Gülich, P.; Hauser, H.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024.

(2) Gülich, P.; Köppen, H.; Link, R.; Steinhäuser, H. G. *J. Chem. Phys.* **1979**, *70*, 3977–3983.

## Methods

DFT calculations were performed using the B3LYP method<sup>3</sup> implemented in the Gaussian 98 program system.<sup>13</sup> For complexes **6** and **9** additional calculations have been done (i) using Becke's exchange functional<sup>14</sup> together with the correlation functional of Lee, Yang, and Parr<sup>15</sup> (known as BLYP method) and (ii) using Perdew and Wang's exchange functional and their gradient corrected correlation functional<sup>16</sup> (PW91 method). Three different basis sets were used: (I) the 3-21G basis, (II) the 6-311G basis for H, C, and N and the Wachters-Hay double- $\zeta$  basis for Fe,<sup>17</sup> and (III) the Dunning-Huzinaga all electron double- $\zeta$  basis for H, C, and N and the Los Alamos effective core potential plus double- $\zeta$  basis set on Fe.<sup>18</sup> The total energy  $E_{\text{el}}(0)$  for HS and LS states was calculated after full geometry optimization for the respective spin states. For part of the complexes the vibrational frequencies were calculated in order to determine  $E_{\text{vib}}(T)$  and  $S(T)$ . Additionally, for complex **1** an X-ray structure was used to calculate  $E_{\text{el}}(0)$  for the HS and the LS state.

## Results

The total energies  $E_{\text{el}}(0)$  for the HS and the LS state of **1**,  $-6790.01292$  and  $-6790.04752$  MJ/mol, respectively, which were calculated with the B3LYP method and the 3-21G basis set using the X-ray structure (site A) at 298 K given in ref 6, are essentially in agreement with the calculations of Chen et al.<sup>4</sup> ( $-6789.98530$  and  $-6790.07065$  MJ/mol) for  $T = 293$  K. However, the difference between the HS and the LS state,  $\Delta E_{\text{el}} = E_{\text{el}}^{\text{HS}} - E_{\text{el}}^{\text{LS}}$ , derived from our calculations (34.6 kJ/mol) is more than two times smaller than their result (85.4 kJ/mol). Since the applied methods are identical, these differences are probably due to very small differences in the X-ray structures given in refs 5 and 6. For the  $\langle S^2 \rangle$  expectation value of the HS state we got 6.1176 before annihilation of spin contaminants and 6.0003 afterward, which is almost identically equal to the results in ref 5. For the LS state, the calculated  $\langle S^2 \rangle$  is exactly 0 since we used a spin-restricted single determinantal wave function. Furthermore, we performed a full geometry optimization with B3LYP/3-21G for both isomers of complex **1**. The energy of the optimized HS isomer ( $-6790.16805$  MJ/mol) turned out to be lower than the energy of the geometry-optimized LS isomer ( $-6790.15848$  MJ/mol) leading to a negative energy difference  $\Delta E_{\text{el}}(0)$  of  $-9.6$  kJ/mol. Also, for most of the other complexes the HS isomers turned out to be lower in energy than the corresponding LS isomers if the B3LYP method is used (Table 1). For complexes **2** and **6**, a considerable influence of the basis set on  $\Delta E_{\text{el}}(0)$  was observed, whereas

**Table 1.** Experimental  $T_{1/2}$  (K), Calculated  $\Delta E_{\text{el}}(0)$ ,  $\Delta E_{\text{vib}}(T_{1/2})$ , and  $\Delta G(T_{1/2})$  (kJ mol<sup>-1</sup>), and Calculated  $\Delta S(T_{1/2})$  in (kJ mol<sup>-1</sup> K<sup>-1</sup>), Using Methods and Basis Sets As Described in Text

compd	$T_{1/2}^a$	method	basis	$\Delta E_{\text{el}}(0)$	$\Delta E_{\text{vib}}(T_{1/2})$	$\Delta S(T_{1/2})$	$\Delta G(T_{1/2})$
<b>1</b>	365	B3LYP	I	-9.6			
<b>2</b>	105	B3LYP	I	-16.7	-8.1	0.0371	-28.7
		B3LYP	II	-27.8	-8.8	0.0343	-40.2
<b>3</b>	170	B3LYP	I	-34.4	-11.6	0.0606	-56.3
<b>4</b>	176	B3LYP	I	-35.5	-10.5	0.0455	-54.0
<b>5</b>	231	B3LYP	I	-31.1	-6.9	0.0472	-48.9
		B3LYP	II	-12.9			
<b>6</b>	355	B3LYP	III	0.6	-4.0	0.0592	-24.4
		BLYP	III	85.0	-3.6	0.0835	51.8
		PW91	III	103.6	-3.2	0.0699	75.6
<b>7</b>	178	B3LYP	II	-7.3			
		B3LYP	III	9.6	-9.4	0.0466	-8.1
<b>8</b>	95	B3LYP	III	7.9	-13.3	0.0642	-11.5
<b>9</b>	200	B3LYP	III	-23.8	-6.0	0.0555	-40.9
		BLYP	III	43.3	-5.7	0.0687	23.9
		PW91	III	60.4			

<sup>a</sup> Experimental transition temperatures (taken from references given in the text) may vary considerably for different counterions and crystal phases.

$\Delta E_{\text{vib}}(T)$  and  $\Delta S(T)$  seemed to be less dependent on the basis set. The calculated  $\Delta S(T_{1/2})$  for complexes **4** and **5**, 45.5 and 47.2 kJ/mol, were in agreement with experimental values for the complexes in solution, 48.8 and 51.2 kJ/mol, respectively,<sup>19</sup> and comparison of calculated and measured frequencies suggests that the calculated  $\Delta E_{\text{vib}}(T)$  should be qualitatively correct.<sup>4,20</sup> For all complexes investigated with the B3LYP method the calculated total electronic energy difference  $\Delta E_{\text{el}}(0)$  was negative, which means that these complexes should be in the HS state even at zero temperature, contrary to experimental evidence for solid samples. Since several of the complexes under study exhibit spin transitions in solutions and in solids at similar temperatures there are no indications that the disagreement between experiment and theory is due to the neglect of solid-state effects. Assuming  $\Delta E_{\text{vib}}(T)$  and  $\Delta S(T)$  to be roughly correct, the deviations of the calculated values for  $\Delta G(T_{1/2})$  from zero (Table 1) serve as an estimate for the error of the calculated total electronic energy difference  $\Delta E_{\text{el}}(0)$ .

## Discussions

The calculated total energy differences for complexes **1** to **9**, using optimized geometries, have errors of some 10 kJ/mol that are of the same order of magnitude as  $\Delta E_{\text{el}}(0)$  itself. Also, if X-ray structures would be available for both spin states the calculated total energy differences remain questionable due to the extreme sensitivity of  $\Delta E_{\text{el}}(0)$  toward small changes in the X-ray structure, as has been demonstrated here for complex **1**. The question remains whether other DFT methods might lead to better results. A possible approach might be to use nonhybrid density functional methods, since there are indications that they give better relative energies of states that differ in spin multiplicity.<sup>21</sup> Calculating  $\Delta E_{\text{el}}(0)$  for complexes **6** and **9** applying the BLYP method with basis set III yielded  $+85.6$  and  $+43.3$  kJ/mol, respectively. Even larger positive energy differences were obtained with the PW91 method. Different from the hybrid method B3LYP (see Table 1 for comparison) the nonhybrid methods BLYP and PW91 correctly predict a LS ground state at zero temperature for these two complexes.

- (13) Gaussian 98, Revision A.7: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.
- (14) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (15) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.
- (16) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533–16539.
- (17) (a) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. (b) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377–4384.
- (18) (a) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.

(19) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555–570.

(20) Paulsen, H.; Winkler, H.; Trautwein, A. X. et al. To be published.

(21) Harris, D.; Loew, G. H.; Kormornicki, A. *J. Phys. Chem. A* **1997**, *101*, 3959–3965.

Total energy differences as defined in ref 5, using the same geometry for the HS and the LS state, cannot be used to explain the nature of the spin transition in complex **1**. This complex exhibits a rapid interconversion of spin states with a rate larger than  $10^7$ – $10^8$  Hz.<sup>6</sup> With X-ray diffraction only the weighted average of the HS and the LS geometries can be measured. To understand the mechanism of the spin transition the energy for the HS state has to be calculated with the HS geometry and the energy of the LS state with the LS geometry. Contrary to the assumptions made by Chen et al., the geometries of the LS and HS isomers of complex **1** are practically temperature indepen-

dent (except from small anharmonicity effects), and the observed changes in the X-ray structure are not the cause of the spin transition but a consequence of the fact that the HS fraction  $n_{\text{HS}}(T)$  increases with temperature. The actual cause of the spin transition in solid samples as well as in solutions is obviously the difference of entropy between the HS and the LS state.

**Acknowledgment** is made to the European Union for financial support of this research via the TMR-TOSS-network (ERB-FMRX-CT-0199).

IC000954Q