

**Theoretical investigations of a series of [hexakis(1-(tetrazol-1-yl)alkane-N4)iron(II)] bis(tetrafluoroborate) spin crossover complexes: Methyl- to pentyl substituted species in the approximation of free cations**

Markus Valtiner<sup>1,§,\*</sup>, Hauke Paulsen<sup>2</sup>, Peter Weinberger<sup>1</sup> and Wolfgang Linert<sup>1,\*</sup>

<sup>1</sup> Institute of Applied Synthetic Chemistry, Vienna University of Technology,

Getreidemarkt 9/163-AC, A-1060 Vienna, Austria.

§ Current address: Max-Planck-Institut für Eisenforschung, Max-Planck Str. 1, D-40239 Düsseldorf, Germany.

<sup>2</sup> Institute of Physics, University of Lübeck, Ratzeburger Allee 180, D-99889 Lübeck, Germany.

\* Corresponding authors: Wolfgang Linert and Markus Valtiner; Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163-AC, A-1060 Vienna, Austria. Tel.: +43/1/58801-15350 Fax.: +43/1/58801-15399; eMail: [w.linert@mail.zserv.tuwien.ac.at](mailto:w.linert@mail.zserv.tuwien.ac.at), [valtiner@mpie.de](mailto:valtiner@mpie.de).

(Received January 19, 2007)

## Abstract

Within this work the density functional theory approach was used to simulate the well-known series of [hexakis(1-(tetrazol-1-yl)alkane-N4)iron(II)] bis(tetrafluoroborate) spin crossover complexes ranging from methyl- to pentyl substituted species. The calculations were carried out in the approximation of free cations thus neglecting intermolecular interactions and solid-state effects. The resulting structural relaxation was compared with the experimentally obtained structure. Furthermore the vibrational frequencies were calculated and compared with experimentally obtained spectra to check the accuracy of the used simplifications. Finally, the spin transition temperatures were calculated using a simple thermodynamic model according to the law of mass action for a system of non-interacting molecules. An interesting behaviour of the calculated spin-transition temperature depending on the number of carbon atoms within the ligand was found. Complexes based on ligands with even and odd number of carbon atoms form two different series. This behaviour turned out to be related with the vibrational contribution to the entropy change of the spin-transition.

## 1. Introduction

It is well known that certain octahedral transition metal complexes with four to seven d-electrons can be present in different spin states: high-spin (HS) at elevated temperatures and low-spin (LS) at low temperatures. The phenomenon of the temperature dependent spin transition has been termed “spin crossover”. The outstanding behaviour of spin crossover compounds is one of the most striking and fascinating shown by relatively simple molecules and has been discussed intensively in the literature<sup>1</sup>. Past research was more focused on the synthesis and characterisation of new spin crossover compounds<sup>2-9</sup> than on the theoretical description of the spin transition<sup>10-14</sup>. Therefore, a still pending task for the future is better theoretical understanding of the factors governing the differences in the various spin transition behaviours on an ab initio level. Consequently, the application of modern ab initio quantum mechanical methods to describe spin crossover compounds will become an extremely important field of research. In the last years the fast development of modern microelectronics opened the doors to this very recent topic. First calculations, based on the density functional theory (DFT) approach, focused on the iron-ligand bond stretching vibrations. The good agreement of calculated and experimental normal modes justified the calculation of vibrational entropy and energy differences<sup>15-17</sup>. Up to now the most difficult issue was the calculation of the spin state splitting energies between high-spin and low-spin isomers, which Paulsen et al.<sup>18-20</sup> and Brehm et al.<sup>16, 21</sup> recently showed.

The idea behind this work is to identify the main factors governing different spin transition behaviour by investigating a series of complexes, where slight changes of the ligands cause a drastic change of the spin transition behaviour. Therefore this work is focussing on the simulation of the well-known series of [*hexakis*(1-(tetrazol-1-yl)alkane-*N*4)iron(II)] *bis*(tetrafluoroborate) spin crossover complexes ranging from methyl- to pentyl substituted species on an ab initio level. This series features very different spin-transition behaviour (i.e. incomplete, abrupt, gradual) simply due to the elongation of the alkyl-chain. Therefore, this series is considered to be an ideal model for theoretical investigations.

In this first approach, the complexes were modelled in the approximation of free cations thus neglecting any possible intermolecular interactions with anions and/or solvents or other cations. The spin-state splitting energies and vibrational frequencies of these tetrazole-based

spin transition compounds were calculated using the Gaussian03 code<sup>22</sup>. A comparison of calculated and experimentally measured IR-frequencies demonstrated on the one hand the accuracy of this approach to calculate IR-frequencies. On the other hand it justified the use of the obtained data to model finite temperature by employing simple statistical thermodynamic relations and thereby estimating the spin transition temperature in the ideal approximation of non-interacting complex cations.

## 2. Methods

### 2.1 *Quantum mechanical calculations.*

The quantum mechanical calculations were performed with the software package Gaussian03<sup>22</sup> implemented on a SGI Silicon Graphics power challenge with 64 parallel processors. In this paper the Gaussian03 nomenclature for DFT functionals and basis sets is used. All calculations were performed using a three parameter hybrid functional, as proposed by Becke, including Becke's exchange functional<sup>23, 24</sup> and the correlation functional of Lee, Yang and Parr<sup>25</sup> (shortcut: B3LYP) together with the 6-311G basis for first-row atoms and the Wachters-Hay<sup>26</sup> all electron basis set for the iron atom (shortcut: 6-311G).

It is well-known<sup>17, 19, 27</sup> that the choice of the density functional sensitively influences the calculated spin state splitting energies. The hybrid functional B3LYP has been found to give the most reasonable values for the spin-state splitting energies<sup>20</sup>. Therefore, within this work only the B3LYP functional together with the 6-311G basis set was used. Starting with experimental geometry data, if available, a geometry optimization was performed for both spin states of each of the five compounds. The energy differences were calculated after full geometry optimization for the respective spin states. A subsequent normal coordinate analysis allowed the estimation of thermodynamic properties. This calculation computes force constants and the resulting vibrational frequencies as well as IR intensities. For DFT methods the force constants are determined analytically in Gaussian03. Vibrational frequencies are computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates.

2.2 *Calculation of the thermodynamic properties.* In the approximation of non-interacting complexes the thermal behaviour of a spin crossover system can be described within the law

of mass action<sup>28</sup> for an ideal crystal with statistically independent (non interacting) complexes. According to this model the spin transition can be described by a simple monomolecular equilibrium



The temperature dependency of such a system can than be expressed as a Van't Hoff Plot within a simple linear approximation via  $\ln K$ , the energy- and entropy difference of reaction

$$\ln K(T) = \ln\left(\frac{\chi_{HS}}{1 - \chi_{HS}}\right) = -\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} \quad (\text{eq. 2})$$

where  $\Delta S$  and  $\Delta E_{el}$  are the quantum mechanically calculated entropy and electronic energy difference, respectively, and  $\chi_{HS}$  is the molecular HS fraction. Therefore, retrieving the energy and entropy difference from theory is necessary to estimate the transition temperature  $T_{1/2}$ . Within this work the energy differences were calculated as the electronic energy difference between LS and HS isomers. The entropy difference of spin crossover can be calculated as a sum of an electronic contribution and contributions originating from vibrational and, in the gas phase, from rotational degrees of freedom:

$$\Delta S = \Delta S_{el} + \Delta S_{vib} + \Delta S_{rot} \quad (\text{eq. 3})$$

Within this model the translational degrees of freedom are the same for both spin states and are therefore not taken into account. The electronic contribution is given by

$$\Delta S_{el} = R \ln\left(\frac{g_{HS}}{g_{LS}}\right) \quad (\text{eq. 4})$$

with the degeneracy  $g_{LS}$  of LS being one and the degeneracy  $g_{HS}$  of the HS being five for all iron(II) spin crossover compounds we get  $\Delta S_{el} = R \ln(5) = 13.38 \text{ J/(mol K)}$  for iron(II)-complexes. The rotational contribution to the entropy of spin crossover is neglected, because the entropy difference should be estimated for solid state, where free rotation is in any case

prohibited. Normal modes were calculated in order to retrieve the vibrational contribution according to the following partition function<sup>28</sup>

$$\Delta S_{vib} = N_A k_B \sum_i \ln \frac{\sinh \frac{hc \tilde{\nu}_i(HS)}{2k_B T}}{\sinh \frac{hc \tilde{\nu}_i(LS)}{2k_B T}} \quad [J \cdot mol^{-1} K^{-1}] \quad (\text{eq. 5})$$

where  $\tilde{\nu}_i$  is the calculated wavenumber of the corresponding  $i^{\text{th}}$  normal mode in  $[m^{-1}]$ .

**2.3 Calculation of the spin transition temperature.** The estimates of the spin transition temperature  $T_{1/2}$ , where half of the complexes are in LS-state and half of the complexes are in the HS-state (giving  $\chi_{HS=1/2}$ ), were consequently obtained via solving equation 6.

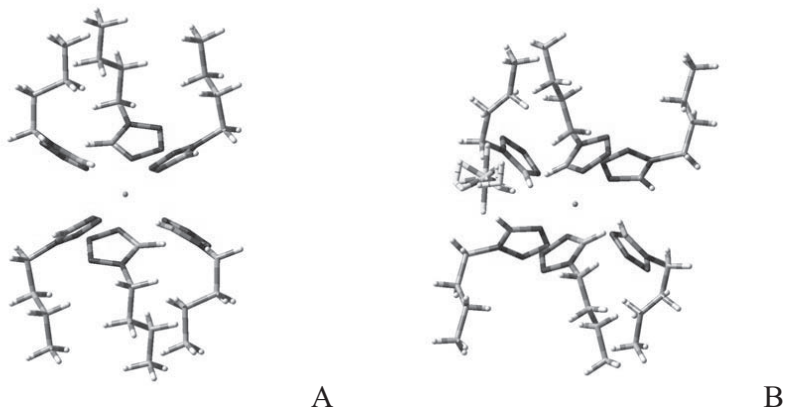
$$\ln K(T_{1/2}) = \ln\left(\frac{\chi_{HS}}{1 - \chi_{HS}}\right) = -\frac{\Delta E_{el}}{RT_{1/2}} + \frac{(\Delta S_{vib} + \Delta S_{el})}{R} = -\frac{\Delta E_{el}}{RT_{1/2}} + \frac{\Delta S}{R} = 0 \quad (\text{eq. 6})$$

### 3. Results and Discussion

#### 3.1 Structural relaxation.

The real systems were modelled as single cationic molecules thus neglecting any solid-state interactions (e.g. packing in the unit cell, interactions with anions). Starting from experimental data (XRD) a full DFT geometry optimization was performed for the respective spin states of the five  $[\text{Fe}(\text{ntz})_6]^{2+}$  compounds with  $n=1-5$ . The calculations were performed with Becke's three parameter hybrid functional (B3LYP) and the 6-311G basis set (see methods for details).

Despite of the omission of the anions and neglecting solid-state effects a good agreement of the calculated structure with experimental data was found. Exemplarily, the measured structure (XRD<sup>29</sup>, CCDC# 612.757) of the *HS*-isomer of the novel compound  $[\text{Fe}(4\text{tz})_6](\text{BF}_4)_2$  and the modelled  $[\text{Fe}(4\text{tz})_6]^{2+}$ -cation are shown in Figure 1. The iron-to-ligand bond lengths and  $\text{N}(1)\text{—Fe—N}(1')$  angles are compared in Table 1. One can see the very good agreement of the experimental and theoretical values for the first coordination sphere suggesting a nearly perfect octahedron.



**Figure 1.** Comparison of the theoretically (B3LYP/ 6-311G) obtained structure of  $[\text{Fe}(4\text{tz})_6]^{2+}$  (left) with the experimental  $[\text{Fe}(4\text{tz})_6](\text{BF}_4)_2$  structure (right).

**Table 1.** Comparison of selected bond length and angles of  $[\text{Fe}(4\text{tz})_6](\text{BF}_4)_2$  and the theoretically obtained parameters.

bond length/angle	B3LYP/6-311G	XRD
Fe—N [Å]	2.19(7)	2.193(2)
N(1)—Fe—N(1') [°]	180.00	180.00
N(1)—Fe—N(1') [°]	89.26(1)	89.14(8)
N(1)—Fe—N(1') [°]	90.73(9)	90.86(8)

The major difference between calculated and measured structures is naturally the omission of the anions and neglecting any solid-state effects in the calculations.

Due to this the tetrazolic CH-bonding can, of course, not interact with the anions within the calculated structure. As consequence, we found that the whole ligand tips over and forms a stabilizing H-bonding between the tetrazolic CH and the N3 of a neighbouring ligand ( $\text{CH}_{\text{tz}} \cdots \text{N3}$ ) upon structure relaxation (see Table 2/ Figure 1).

**Table 2.** Overview of  $\text{CH} \cdots \text{N3}$  distances (in Å) of calculated LS/HS structures of  $[\text{Fe}(\text{ntz})_6]^{2+}$  for  $n = 1-5$ .

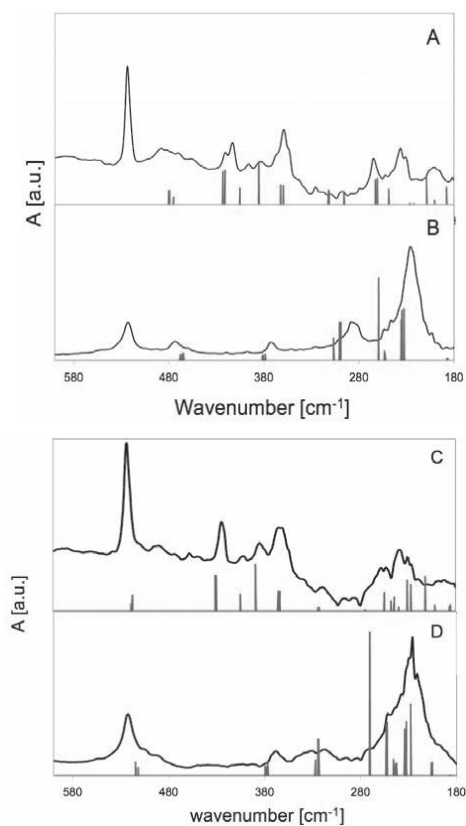
Compound	LS-species	HS-species
$\text{Fe}[(1\text{tz})_6]^{2+}$	2.316	2.560
$\text{Fe}[(2\text{tz})_6]^{2+}$	2.315	2.565
$\text{Fe}[(3\text{tz})_6]^{2+}$	2.319	2.569
$\text{Fe}[(4\text{tz})_6]^{2+}$	2.320	2.571
$\text{Fe}[(5\text{tz})_6]^{2+}$	2.322	2.573

**Table 3.** Calculated Fe—N bond lengths and differences  $\Delta$  of  $[\text{Fe}(\text{ntz})_6]^{2+}$  for  $n = 1-5$ .

Compound	HS	LS	$\Delta$
$\text{Fe}[(1\text{tz})_6]^{2+}$	2.199	2.009	0.190
$\text{Fe}[(2\text{tz})_6]^{2+}$	2.198	2.009	0.189
$\text{Fe}[(3\text{tz})_6]^{2+}$	2.197	2.009	0.189
$\text{Fe}[(4\text{tz})_6]^{2+}$	2.197	2.008	0.189
$\text{Fe}[(5\text{tz})_6]^{2+}$	2.196	2.008	0.188

In strong contrast to that the  $\text{CH}_{\text{tz}}$  shows an interaction with the anion in the real crystal (see structural data<sup>29-32</sup>). Anyway, despite of these differences between calculated and measured structures, the DFT calculations correctly predicted the structural changes due to the spin-transition; the change in the Fe—N bond length (approx. 10%), due to the population of anti-bonding  $e_g$ -orbitals within the HS species, was predicted quite well for all investigated compounds (see Table 3).

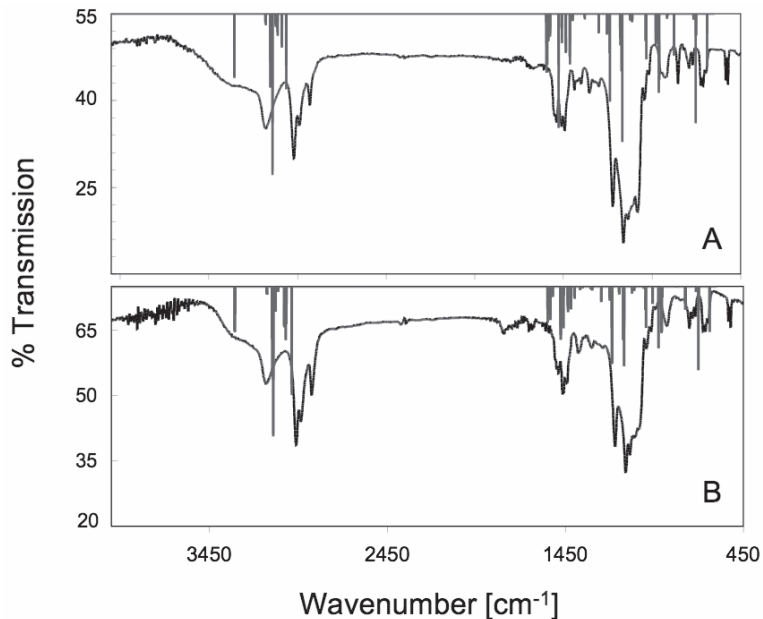
### 3.2 Normal coordinate analysis



**Figure 2.** Comparison of the calculated (bars) and experimentally (continuous spectra) obtained FIR spectra. (A) LS- species of 3tz, (B) HS.species of 3tz, (C) LS-species of 4tz, (D) HS.species of 4tz. LS spectra were recorded at 100K and HS spectra were obtained at 298K.

After the structure relaxation a subsequent normal coordinate analysis was performed for each compound proving that the geometry optimizations yield minimum structures on the potential energy surface, which was confirmed for all compounds and spin-states. As exemplarily depicted for the 3tz and the 4tz complexes in Figures 2-3, the calculated spectra are in good agreement with the experimental spectra. The calculated spectra are qualitatively comparable with the experimental far and mid IR spectra. The experimental spectra were obtained from M. Grunert<sup>33</sup>. The FIR spectra of the  $[\text{Fe}(\text{ntz})_6](\text{BF}_4)_2$  with  $n = 3-4$  were recorded at 100 K as well as 298 K reflecting the LS and the HS species of these complexes, respectively (Figure 2). The presented MIR spectra were measured at 298 K thus characterizing the HS species of the complexes (Figure 3).

The spectra for the LS isomer showed in all cases several modes in the range from  $350\text{cm}^{-1}$  to  $420\text{cm}^{-1}$  (see Figure 2), which are in the range where iron-to-ligand modes are expected. According to the literature<sup>34</sup> the modes at about  $523\text{cm}^{-1}$  were identified as anion modes. The other modes correspond perfectly with the calculated ones, whereas the normal coordinate pictures revealed in all cases that these modes include a significant iron-to-ligand motion. When going from the LS to the HS isomer all these modes vanished whereas the normal coordinate analysis perfectly reproduced these experimental findings as one can see in Figures 2C/2D. In all cases in this range two other modes that do not include any significant iron-to-ligand motion appeared and the iron-to-ligand vibrations shifted about  $100\text{cm}^{-1}$  to lower energies, which was perfectly reproduced by the normal coordinate analysis as well. The comparison of the MIR spectra yielded a good agreement for the various modes in the range between  $600\text{cm}^{-1}$  and  $1500\text{cm}^{-1}$ . Generally, the calculated  $\text{CH}_{\text{tz}}$ -stretching and  $\text{CH}_{\text{alkyl}}$ -bending modes were shifted about  $170\text{cm}^{-1}$  to higher energies, which can be seen in context with the model approach using single cations in vacuum, thus neglecting any solid state effects (e.g. interactions with anions).



**Figure 3.** Comparison of the calculated (bars) and experimentally (continuous spectra) obtained MIR spectra. (A) HS- species of 3tz, (B) HS.species of 4tz. All the spectra were recorded at 298K.



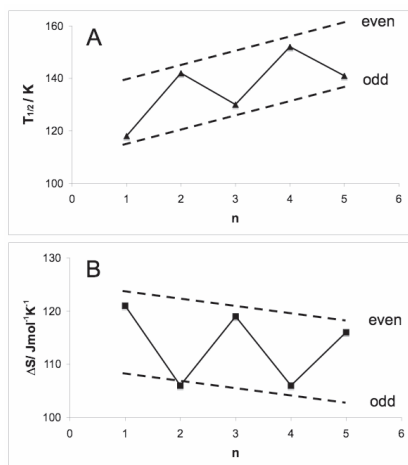
### 3.3 Simulation of thermodynamic properties

The hybrid functional B3LYP gave very reasonable values for the spin-state splitting energy of 12-14 kJ/mol. The important point is that the spin-state-splitting energies did not deviate within the calculated series of the differently substituted complex cations. The deviations that are shown within Table 4 are too low and within the error margin of the used methods<sup>19</sup>. Therefore, the substitution effects did not cause observable differences in the spin state splitting energies. To point this out clearly, this means the calculated spin splitting energies were not influenced intra-molecularly by different substitutions.

**Table 4.** Estimates of the thermodynamic properties of the series of  $[\text{Fe}(ntz)_6]^{2+}$  complexes.

	$\Delta E_{\text{el}}$ [J/mol]	$\Delta S_{\text{vib}}$ [J/mol K]	$\Delta S$ [J/mol K]	Theor. $T_{1/2}$ [K]	Exp. <sup>33</sup> $T_{1/2}$ [K]
$\text{Fe}[(1tz)_6]^{2+}$	12668	107.4	120.8	118	75
$\text{Fe}[(2tz)_6]^{2+}$	13126	92.3	105.7	142	100
$\text{Fe}[(3tz)_6]^{2+}$	13708	105.5	118.9	130	128
$\text{Fe}[(4tz)_6]^{2+}$	14115	92.8	106.2	152	140
$\text{Fe}[(5tz)_6]^{2+}$	14512	102.6	116.0	141	158

The vibrational entropy difference was calculated according to Eq. 5 using the computationally obtained normal modes of the respective complexes. The spin transition temperature was calculated by solving Eq. 6. All the calculated thermodynamic parameters are displayed in Table 4. Furthermore, the calculated spin-transition temperature (in the approximation of free cations) and the corresponding tendency of the total entropy difference are shown in Figure 4. The spin transition temperature shows an increasing tendency for the calculated series (Figure 4A). Obviously, the alkyl chains with even and odd numbers of carbon atoms form two different series. The  $T_{1/2}$  values have been found to be higher for the complexes having even-numbered



**Figure 4.**  $T_{1/2}$  (A) and  $\Delta S$  (B) as a function of the number of carbon atoms in the alkyl chain. The dashed lines are drawn to clearly show the separation of the data points into two series (even/odd) but have no further significance.

*ntz* ligands than for the odd-numbered ligands. The reason for this behaviour is clearly related to the oscillating behavior, as depicted in Figure 4B, of the calculated entropy difference, which is caused by the contribution of the vibrational entropy term (see Table 4). This is, in fact, a very interesting behaviour, which has recently been found experimentally for the series of the bridging bis(tetrazole-1-yl)alkane complexes<sup>2</sup>. Also in that case the  $T_{1/2}$  values have been found to be higher for the complexes having even-numbered *nditz* ligands than for the odd-numbered ligands. However, the calculated behavior does not perfectly reflect the experimental tendency of the spin-transition behavior. The experimental  $T_{1/2}$  values have been found to steadily increase for the investigated series. Experimentally no difference between ligands with even or odd number of carbons was found so far. Concluding, the different spin-transition behavior within the approximation of free cations is an entropy effect and is definitively not caused by a difference in the spin-state-splitting energy. The deviations from the experimental tendency can clearly be seen in context with the model approach, omitting solid-state effects.

#### 4. Conclusions

Quantum mechanical structure relaxations showed that the omission of anions forced the system to find another kind of stabilization via H-bonding structures of the  $\text{CH}_{\text{tz}}$ . This points out clearly that the used anions influence the resulting cationic structure and therefore probably the spin transition behavior as well. This finding suggests the role of different anions as a kind of fine-tuning system for the spin transition behavior. One can suppose that the exact position of the plane of the tetrazolic ring systems is an important factor for the resulting electronic energy difference in these systems, because twisting of the plane may lead to different overlapping of the d-orbitals of the iron(II) and the  $\pi$ -orbitals of the coordinating nitrogen atoms. Moreover, anions might be a governing factor for the formation of specific crystal structures, which has a great impact (solid state effects) on the spin transition behavior as well<sup>35</sup>.

Despite of these structural differences between XRD and theoretical investigations the normal coordinate analysis yielded a remarkably good agreement with the experimental observations in far and mid IR spectroscopy – even within the model approach omitting the non-coordinating anions and only simulating an isolated single cationic molecule in vacuum.

Especially, the really good agreement within the FIR region justified the calculation of the vibrational contribution to the entropy change due to the spin transition, because these modes contribute to a large extent to the entropy change.

Statistical thermodynamics on the basis of the law of mass action led to the assumption, that the entropy is not only one of the contributing but one of the influential factors that yield different spin transition temperatures within the approximation of free cations. In this approximation ligands with even and odd number of carbon atoms formed two different series. This behaviour is a consequence of the calculated vibrational entropy change of the spin-transition. This, in fact, interesting result suggests that molecular vibrations play a major role in thermally induced spin transitions, which is, indeed for some cases already well known in the literature<sup>36, 37</sup>. However, the tendency of the experimental  $T_{1/2}$  values cannot be explained entirely on the basis of this approach, which can be clearly seen as consequence of neglecting solid-state effects so far. The first three complexes in this series show incomplete ( $1tz$  and  $2tz$ ) and abrupt ( $3tz$ ) spin transition the other two show a gradual spin transition.

Nevertheless, this does not diminish the value of the presented study. Even though this approach does naturally not allow simulating solid-state effects and thereby non-ideal spin crossover behaviour, this work nicely revealed that solid-state effects (anions, crystal structure) have a great influence on the resulting cationic structure and thereby most probably on the resulting spin transition behaviour as well. However, in order to take solid-state effects into account explicitly, calculations with periodic boundary conditions must be employed. In comparison with the presented calculations solid-state calculation will allow to separate inter- and intra-molecular on the spin-state splitting energies and entropies.

## 5. Acknowledgements

Thanks for financial support are due to the "Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich" (Project 19335-N17). Furthermore we want to thank the Vienna University of Technology for granting a stay of M. Valtiner in the lab of Prof. A.X. Trautwein and Dr. habil. H. Paulsen in Lübeck (Germany).

## 6. References

1. P. Gütllich and H. A. Goodwin, *Spin-Crossover in Transition Metal Compounds I-III*, 2004.
2. A. Absmeier, M. Bartel, C. Carbonera, G. N. L. Jameson, P. Weinberger, A. Caneschi, K. Mereiter, J. F. Letard and W. Linert, *Chemistry-A European Journal*, 2006, **12**, 2235-2243.
3. P. Gütllich, P. J. van Koningsbruggen and F. Renz, in *Optical Spectra and Chemical Bonding in Transition Metal Complexes*, 2004, vol. 107, pp. 27-75.
4. M. Muttenthaler, M. Bartel, P. Weinberger, G. Hilscher and W. Linert, *Journal of Molecular Structure*, 2005, **741**, 159-169.
5. R. Boca, F. Renz, M. Boca, H. Fuess, W. Haase, G. Kickelbick, W. Linert and M. Vrbova-Schikora, *Inorganic Chemistry Communications*, 2005, **8**, 227-230.
6. C. M. Grunert, P. Weinberger, J. Schweifer, C. Hampel, A. F. Stassen, K. Mereiter and W. Linert, *Journal of Molecular Structure*, 2005, **733**, 41-52.
7. C. M. Grunert, J. Schweifer, P. Weinberger, W. Linert, K. Mereiter, G. Hilscher, M. Muller, G. Wiesinger and P. J. van Koningsbruggen, *Inorganic Chemistry*, 2004, **43**, 155-165.
8. R. Boca, M. Boca, H. Ehrenberg, H. Fuess, W. Linert, F. Renz and I. Svoboda, *Chemical Physics*, 2003, **293**, 375-395.
9. J. Schweifer, P. Weinberger, K. Mereiter, M. Boca, C. Reichl, G. Wiesinger, G. Hilscher, P. J. van Koningsbruggen, H. Kooijinan, M. Grunert and W. Linert, *Inorganica Chimica Acta*, 2002, **339**, 297-306.
10. P. Gütllich, H. Koppen, R. Link and H. G. Steinhauser, *Journal of Chemical Physics*, 1979, **70**, 3977-3983.
11. A. B. Koudriavtsev, A. F. Stassen, J. G. Haasnoot, M. Grunert, P. Weinberger and W. Linert, *Physical Chemistry Chemical Physics*, 2003, **5**, 3666-3675.
12. A. B. Koudriavtsev, A. F. Stassen, J. G. Haasnoot, M. Grunert, P. Weinberger and W. Linert, *Physical Chemistry Chemical Physics*, 2003, **5**, 3676-3683.
13. R. Boca and W. Linert, *Monatshefte für Chemie*, 2003, **134**, 199-216.
14. W. Linert, M. C. Grunert and A. B. Koudriavtsev, in *Spin Crossover in Transition Metal Compounds III*, 2004, vol. 235, pp. 105-136.
15. G. Baranovic and D. Babic, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 2004, **60**, 1013-1025.
16. G. Brehm, M. Reiher and S. Schneider, *Journal of Physical Chemistry A*, 2002, **106**, 12024-12034.
17. H. Paulsen, L. Duelund, H. Winkler, H. Toftlund and A. X. Trautwein, *Inorganic Chemistry*, 2001, **40**, 2201-2203.
18. H. Paulsen and A. X. Trautwein, in *Spin Crossover in Transition Metal Compounds III*, 2004, vol. 235, pp. 197-219.
19. H. Paulsen and A. X. Trautwein, *Journal of Physics and Chemistry of Solids*, 2004, **65**, 793-798.
20. H. Paulsen, J. A. Wolny and A. X. Trautwein, *Monatshefte für Chemie*, 2005, **136**, 1107-1118.
21. G. Brehm, M. Reiher, B. Le Guennic, M. Leibold, S. Schindler, F. W. Heinemann and S. Schneider, *Journal of Raman Spectroscopy*, 2006, **37**, 108-122.
22. M. Frisch and et.al., *Gaussian 03, Revision C.02*, 2004.
23. A. D. Becke, *Physical Review A*, 1988, **38**, 3098-3100.

24. A. D. Becke, *Journal of Chemical Physics*, 1993, **98**, 5648-5652.
25. C. T. Lee, W. T. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785-789.
26. A. J. Wachters, *Journal of Chemical Physics*, 1970, **52**, 1033-&.
27. H. Paulsen, L. Duelund, A. Zimmermann, F. Averseng, M. Gerdan, H. Winkler, H. Toftlund and A. X. Trautwein, *Monatshefte für Chemie*, 2003, **134**, 295-306.
28. A. B. Koudriavtsev, W. Linert and R. F. Jameson, *The Law of Mass Action*, 2001.
29. K. Mereiter, *to be published*.
30. J. Kusz, H. Spiering and P. Gülich, *Journal of Applied Crystallography*, 2001, **34**, 229-238.
31. R. Hinek, H. Spiering, P. Gülich and A. Hauser, *Chemistry-A European Journal*, 1996, **2**, 1435-1439.
32. P. L. Franke, J. G. Haasnoot and A. P. Zuur, *Inorganica Chimica Acta-Articles*, 1982, **59**, 5-9.
33. C. M. Grunert, *PhD Thesis - TU Vienna*, 2003.
34. A. S. Quist, J. B. Bates and G. E. Boyd, *Journal of Chemical Physics*, 1971, **54**, 4896-&.
35. M. Yamada, M. Ooidemizu, Y. Ikuta, S. Osa, N. Matsumoto, S. Iijima, M. Kojima, F. Dahan and J. P. Tuchagues, *Inorganic Chemistry*, 2003, **42**, 8406-8416.
36. A. Bousseksou, J. J. McGarvey, F. Varret, J. A. Real, J. P. Tuchagues, A. C. Dennis and M. L. Boillot, *Chemical Physics Letters*, 2000, **318**, 409-416.
37. A. Bousseksou, L. Salmon, F. Varret and J. P. Tuchagues, *Chemical Physics Letters*, 1998, **282**, 209-214.