Nuclear Inelastic Scattering and Density Functional Theory Studies of a One-Dimensional Spin Crossover $[\text{Fe}(\text{1,2,4-triazole})_2(\text{1,2,4-triazolato})](\text{BF}_4)$ Molecular Chain.

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Nuclear Inelastic Scattering (NIS) experiments have been performed in order to study the vibrational dynamics of the low- and high-spin states of the polynuclear 1D spin crossover compound $[\text{Fe}(\text{1,2,4-triazole})_2(\text{1,2,4-triazolato})](\text{BF}_4)$ (**1**). Density functional theory (DFT) calculations using the functional B3LYP* and the basis set CEP-31G for heptameric and nonameric models of the compound yield the normal vibrations and electronic energies for high-spin and low-spin isomers of three models differing in the distribution of anionic trz[−] ligands and BF₄[−] anions. On the basis of the obtained energies a structural model with a centrosymmetric Fe(trzH)₄(trz)₂ coordination core of the mononuclear unit of the chain is proposed. The obtained distribution of the BF₄[−] counteranions in the proposed structure is similar to that obtained on the basis of X-ray powder diffraction studies by Grossjean *et al.* (*Eur. J. Inorg. Chem.*, 2013, 796). The NIS data of the system diluted to 10 % Fe(II) content in a 90 % Zn(II) matrix (compound (**2**)) show a characteristic change of the spectral pattern of the low-spin centres, compared to the low-spin phase of the parent Fe(II) complex (**1**). DFT calculations reveal that this is caused by a change of the structure of the neighbours of the low-spin centres. The spectral pattern of the high-spin centres in (**2**) is within a good approximation identical to that of the high-spin Fe(II) isomer of (**1**). The inspection of the molecular orbitals of the monomeric model systems of $[\text{Fe}(\text{trzH})_4(\text{trz})_2]$ and $[\text{Fe}(\text{trzH})_6]$, together with calculations of spin transition energies, point towards the importance of an electrostatic effect caused by the negatively charged ligands. This results in the stabilisation of the low-spin state of the complex containing the anionic ligand and shortening of the Fe-N(trz[−]) compared to the Fe-N(trzH) bond in high-spin, but not in low-spin $[\text{Fe}(\text{trzH})_4(\text{trz})_2]$.

Introduction

Spin crossover (SCO) complexes¹ continue to be the subject of extensive studies because of both (i) a fascinating dependence of spin transitions on small changes in ligand and crystal packing¹ and (ii) possible technological applications² like molecular switches, memory elements³, temperature sensors⁴ and in photovoltaic elements⁵. On the other hand, the calculation of spin transition energies provides a challenge for modern quantum chemistry methods ranging from ligand field molecular mechanics (LFMM)⁶ through density functional theory (DFT) to *ab initio* calculations⁷.

Of particular interest are 1D polynuclear chain Fe(II) spin crossover materials based on 1,2,4-triazole ligands⁸ in which generally an abrupt transition occurs, apparently induced by an efficient propagation along the chains through direct covalent connections of the local modifications due to the SCO^{8b}. The classical example of these materials is the $[\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ complex⁹ (**1**). Its spin

transition type is dependent on the method of synthesis allowing a very sharp transition with a hysteresis of 40 K. Although obtained 20 years ago this system has been a subject of extensive investigations in recent years¹⁰. Single crystal X-ray data are not yet available, but powder X-ray studies^{10b,d} yielded values of Fe-N distances of 1.827(5) and 1.981(6) Å for the low-spin (LS) and 2.042(5) and 2.04(2) Å for the high-spin (HS) phase. The Fe-Fe distances are 3.671(1) and 3.891(1) Å for the LS and HS phases, respectively^{10d}. Refs. 10b and 10d give the difference of the above distances to be 0.22–0.23 Å. A recently published single crystal X-ray structure of $[\text{Fe}(\text{bntrz})_3][\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ^{10k} (bntrz = 4-benzyl 1,2,4-triazole) gives the values of Fe-N bonds to be 2.189(3) and 2.190(3) Å for the HS state and 1.991(4) and 1.998(4) Å for the LS one. The essential difference between the structural element $[\text{Fe}(\text{trzH})_2(\text{trz})]^+$ and its 1,2,4-aminotriazole (atrz) $[\text{Fe}(\text{atrz})_3]^{2+}$ or $[\text{Fe}(\text{Rtrz})_3]^{2+}$ analogues is the presence of one anionic ligand. The ligand deprotonation occurs spontaneously during the synthesis. It is ascribed to an additional stability of the linearly arranged chain of cations on introducing the negatively charged ligand^{8a}. Recently, it has been shown that DFT calculations for oligomeric models of 1D 1, 4-amino-1,2,4-triazole Fe(II) complexes provide insight into their structure¹¹ and, in combination with synchrotron-based Nuclear Inelastic Scattering (NIS)¹², can reveal subtle structural effects of the spin-state of the neighbours on the Fe(II) centre of a given spin¹³.

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This motivated us to perform the NIS study of $[\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ at temperatures corresponding to its LS and HS phase presented herein. Subsequently, DFT calculations of the heptameric and nonameric models of the title 1D system (**1**) have been performed in order to obtain the normal modes involving the movement of the iron atoms. Three different patterns of the distribution of the triazolato anion within the chain were modeled. The optimised structures yielded the Fe-N bond distances for the Fe-N(trzH) and Fe-N(trz⁻) pairs in both LS and HS states, revealing that there is a significant difference between them for a HS iron centre, the Fe-N(trz⁻) one being ca. 0.07 Å shorter than the Fe-N(trzH) one.

Additionally, the zinc diluted $^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ has been studied by NIS for a sample containing iron and zinc in a 1:9 ratio. Zn(II) serves as a Mössbauer silent structural analogue of the HS Fe(II)^{1b} that also downshifts the transition temperature. This allows to observe the vibrational signature of LS Fe(II) centres in a matrix corresponding to HS Fe(II) neighbours.¹³

Experimental and Calculation Section

The compound (**1**) was synthesized according to ref. 9 (modification 1a described there) using the 98 % enriched $^{57}\text{Fe}(\text{BF}_4)_2 \cdot (\text{H}_2\text{O})_6$. The Zn(II) – diluted sample (**2**) was obtained according to the same protocol using a 1:9 mixture of $^{57}\text{Fe}(\text{BF}_4)_2 \cdot (\text{H}_2\text{O})_6$ and Zn(II) tetrafluoroborate. $^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{CH}_3\text{SO}_3)]$ was prepared via the same method, using the 98 % $^{57}\text{Fe}(\text{CH}_3\text{SO}_3)_2 \cdot (\text{H}_2\text{O})_6$.

NIS and NFS spectra were recorded at the Dynamics Beamline P01 at Petra III, DESY in Hamburg, Germany¹⁴. This beamline has a two-step monochromatisation. The first monochromatisation step is performed with a Si(111) double-crystal monochromator which renders the incident beam to a bandwidth of approximately 2 eV. The following high resolution monochromator (HRM) decreases the bandwidth of the incident beam down to 1 meV. This beam is used to excite the 14.4125 keV level of the ^{57}Fe nuclei in the sample. The excited nuclear state with a lifetime of 141 ns decays in the ground state under emission of conversion electrons with a probability of 90 %. The subsequent 6.4 keV K-fluorescence radiation which is delayed compared to electronic scattering is measured with fast avalanche photodiodes (APD) with a time resolution of 1 ns. Measurements were taken at different temperatures of the sample. The temperatures from 400 K down to 80 K were accomplished with a cryostream from Oxford Cryosystems. For lower temperatures the sample was cooled with a helium closed-cycle-cryostat.

DFT calculations were performed with the Gaussian programme¹⁴ using the B3LYP* functional¹⁵ and CEP-31G basis set.¹⁶ Further details of the calculations are the same as described in ref. 11 and 13.

Results and Discussion

The partial density of states (pDOS) obtained from the NIS data of the LS form of the ^{57}Fe enriched complex (**1**) is shown in Figure 1a, together with the pDOS of its analogue with methanesulphonate as an anion (Fig. 1b). The pDOS of the LS 4-amino-1,2,4-triazole system¹³ is shown for comparison in Figure 1c. The pDOS of the title

triazole complex represents a typical vibrational pattern of a LS Fe(II) centre with a N₆-coordination core. Most of the vibrations involving the displacement of iron atoms are in the energy region of 400-500 cm⁻¹. Similarly to the previous findings for the aminotriazole analogues^{11b} the pDOS are practically independent on the type of anion, as seen from comparison of the data for tetrafluoroborate (Fig. 1a) and methanesulphonate (Fig. 1b) salts. The comparison of the triazole systems with that of the aminotriazole one shows that the characteristic bands in the pDOS of the latter are significantly shifted to lower frequencies (ca. 350-450 cm⁻¹). This implies that the higher elasticity of the Fe-N stretching mode for the amino-substituted ligand is caused by weaker Fe-N bonds.

Figure 1

The thermal behaviour of (**1**) as detected by nuclear forward scattering (NFS) spectra and the obtained pDOS for its HS isomer are discussed in Supplementary Materials (Fig S1 and Fig S2). Notably, also for the HS state of the complex under study the shift of the NIS bands towards higher frequencies is observed, compared to the aminotriazole (atrz) analogues¹¹: the latter showing two strong bands in the 200 - 250 cm⁻¹ area, while the triazole system reveals such a spectral feature in the area of 270 - 315 cm⁻¹. (see Suppl. Materials, Fig S2).

The pDOS of the $^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ diluted in $[\text{Zn}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ (**2**), obtained from the NIS data obtained at 300 and 20 K is shown in Figure 2a and 2b, respectively. This sample contained ca. 10 % of iron and revealed a very gradual transition with T_c of ca. 220 K, reaching the χ_{HS} = 1 state at room temperature and the χ_{LS} = 1 at ca. 100 K, as shown by Mössbauer spectra (see Suppl. Materials, Fig S4.).

Figure 2

The NIS data of the HS state displays low statistics. The calculation process of the pDOS is sensitive to spectral noise in the NIS data, especially for higher wavenumbers. Therefore, for the pDOS calculation presented in Fig. 2a a binning of 1 meV was used to minimize statistical fluctuations in the pDOS. The structure of the pDOS above 300 cm⁻¹ is due to statistical noise. For details of the data processing see the Suppl. Materials, Fig. S5.

DFT modeling

Applied models

Similarly to the previously described calculation on the Fe(II) polymers of 4-amino-1,2,4-triazole^{11,13} (atrz) the 1D-chains were modelled with oligomeric linear chains. We begin with the heptameric model $[\text{Fe}_7(\text{trzH})_{12}(\text{trz})_6(\text{H}_2\text{O})_6](\text{BF}_4)_8$, shown schematically in Figure 3.

For the DFT calculation the two terminal iron atoms, revealing the FeN₃O₃ coordination are always kept high-spin. For the inner five centres the considered distributions of HS and LS centres were calculated (see Ref. 13) using the approach of modelling the starting geometry of HS centres with the corresponding Zn(II) analogue, as described in Ref. 11a. In few cases, for the nonameric models for which the pDOS of LS centres in a HS matrix was of interest, the HS centres were modeled with Zn²⁺ centres.

Figure 3

For further discussion we will denote the spin isomers using the notation used previously.^{11,13} HLLLLLH denotes a heptamer with all inner Fe(II) centres being in the LS state. HHHHHHH denotes a heptamer with all Fe(II) centres being in the HS state, etc.

Contrary to previously calculated 4-amino-1,2,4-triazole systems, the complexes revealing an effective $[\text{Fe}(\text{trzH})_2(\text{trz})]^+$ coordination may show isomerism due to a different distribution of the triazolato anions within the chain but also due to different distributions of the anions around the chain. We have therefore used three molecular models, differing in the way the anionic triazolato ligands are distributed. The pdb files of the optimised HHHHHHH and HLLLLLH structures for all three models are given in the Suppl. Materials.

For a heptameric model molecule, such as that shown in Figure 3 there are six triads of triazole ligands, each one bridging two particular irons. If we assume a centrosymmetric character of the molecule the following distribution patterns of the triazolato anion are possible:

- (i) That with each triad containing one anionic ligand. We denote this as a 111111 isomer.
- (ii) That with two symmetrically located triads containing two, one and none anions. There are six possible isomers, of which we have tested the 012210, i.e. the one for which the iron in the centre of symmetry is coordinated with four anionic ligands.
- (iii) That with two symmetrically located triads containing three anionic ligands. Again, three isomers are possible, of which the 003300 one was used for calculation, i.e. with the iron in the centre of symmetry coordinated with six triazolato anions.

For the 111111 model the *trans* arrangement of each two anions coordinating to a given iron was assumed, therefore all of them lie in one plane (see pdb files in Suppl. Materials). The eight BF_4^- anions in the starting geometry of this isomer were distributed in such a way that they were placed most evenly along the chain. Additionally, the anion close to a given triad was placed in between two trzH ligands, in order to minimize the coulomb repulsion with the trz⁻ anion. For the two other isomers the tetrafluoroborates in the starting geometries were placed so as to keep them in the vicinity of triads containing no or only one triazolato anion ligand. Noteworthy, for both 012210 and 003300 models the optimisation leads to a significant shift of the distribution of the BF_4^- anions.

The so obtained optimised structures (see pdb files in Supplementary Materials) and calculated electronic energies of both LS (HLLLLLH) and HS (HHHHHHH) isomers show that the 111111 distribution is the best model of the 1D-polymer of $[\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$. It has the lowest energy in its LS state and the 012210 and 003300 isomers are higher in energy (87 and 207 kJ/mol, respectively (B3LYP*/CEP-31G - functional/basis set)).

The corresponding HS isomers are 208, 267 and 199 kJ/mol higher in energy, with respect to their LS isomers for the 111111, 012210 and 003300 distributions, respectively. This yields average spin transition energies of 42, 53 and 40 kJ/mol. The high destabilization of the 012210 and 003300 configurations implies a significant

importance of the electrostatic interactions within the 1D chain of the complexes. It should also be noted that the even distribution of the BF_4^- anions along the chain corresponds well to that observed in the powder X-ray structure (cf. Figure 4).

The calculated pDOS are quite similar for all three models (see Fig. S5 in Supplementary Materials). An explanation of this fact may be the collective character of the observed modes: if all iron centres, revealing different coordination (triazole/triazolato anion), contribute to a given mode, their different elastic properties are averaged, resulting in similar mode frequencies and iron amplitudes for different distributions of the anionic ligands.

Geometry of low-spin and high-spin isomers

In this part we discuss the geometrical parameters calculated for the LS and HS isomers of the title complex using the heptameric model with the 111111 distribution of triazolato ligands and its nonameric analogue. The so obtained bond-lengths are given in Table 1.

Figure 4**Figure 5****Table 1**

The analysis of the data from Table 1 allows the following conclusions:

The calculated Fe-N bonds are in the range of the values obtained from the powder X-ray structure^{10d} of the LS state (1.827(5) and 1.981(6) Å). The calculated values of the bond lengths for the HS state are significantly higher than 2.040-2.042 Å^{10d}. On the other hand the calculated averaged values of the Fe-Fe distance fit quite well to the experimentally obtained 3.671(1)^{10b} and 3.891(1) Å. The calculated difference thereof, being 0.221 and 0.243 Å, for the heptameric and nonameric model compares well the corresponding experimentally obtained difference of 0.22-0.23 Å given in Ref. 10b and 10d.

The calculated LS Fe-N_{trzH} bonds lie in the range of the previously calculated ones with B3LYP*/CEP-31G for the pentameric models of the aminotriazole analogue, for which values of 1.981-1.988 and 2.184-2.202 Å were obtained, for the LS and HS (HLLH and HHHH) isomers, respectively^{11a}. These are close to the values given in ref. 10k for the $[\text{Fe}(\text{bntrz})_3][\text{Pt}(\text{CN})_4]\cdot\text{H}_2\text{O}$ complex quoted above (1.991, 1.998 and 2.189, 2.190 Å, for the LS and the HS isomer, respectively).

Although the obtained values of the Fe-N_{trz} distances for the LS centres are comparable to those of Fe-N_{trzH}, the ones obtained for the HS centres are significantly shorter than the HS Fe-N_{trzH} ones. The differences are in the range of ca. 0.07-0.13 Å. Moreover, the Fe-N_{trzH} bond lengths differ up to 0.07 Å for a given HS centre, while the calculated values the N_{trz} ones are on average 2.13 Å, with the minimal and maximal ones of 2.124 and 2.137 Å, respectively. The average values and the corresponding standard deviations are 2.218(0.023) and 2.131(0.003) Å, for Fe-N_{trzH} and Fe-N_{trzH-*tr*}, respectively, pointing towards lower elasticity of the shorter triazolato anion – iron bond.

The last, somewhat unexpected effect can be explained as a combination of two factors. On the one hand, the negatively charged ligand is expected to form a stronger bond than its neutral analogue, particularly for the HS isomer, for which the electrostatic effects are more important than in the more covalent LS one. On the other hand, although the 1,2,4-triazole ligand is a σ -donor and π -acceptor, the corresponding anion displays π -donor properties (*vide infra*). This, in combination with lower elasticity of the stronger bonds compensates the electrostatic effects in the LS isomer. The present situation resembles the case of classical spin crossover complexes of π -donor thiocyanate ligands for which the HS Fe-N_{NCS} bond is shorter than the Fe-imine bonds, which is not the case for the LS isomer^{18, 19}.

Partial density of states and normal vibrations

The frequency calculations yielded 603 normal vibrations for the heptameric models and 777 normal vibrations for the nonameric ones. As for all four HS and LS models the C_i symmetry was used and retained in optimised structures, all vibrations have either A_u or A_g symmetry. The NIS selection rule requires the non-zero amplitude of the ^{57}Fe atom in order to observe a signal due to given mode, excluding therefore the NIS bands due to symmetric vibrations in mononuclear systems. However, as discussed previously^{11b} for the polynuclear iron systems there are the symmetric vibrations which involve non-zero iron movement and can be hence observed via NIS.

Low-spin [$^{57}\text{Fe}(\text{trzH})_2(\text{trz})$](BF₄)

The pDOS of the title complex and the results of the simulation using heptameric HLLLLLH and nonameric HLLLLLLLH models are shown in Figure 6. Both models reasonably reproduce the experimental spectrum. The nonameric model fits slightly better the band structure at 400 - 500 cm^{-1} , probably because it predicts more vibrational modes. In the following we give the assignments of the experimental pDOS bands to particular modes. The corresponding movies visualizing the calculated modes are given in Suppl. Materials.

In the experimental pDOS there is a broad structure ranging from 470 to 500 cm^{-1} with a maximum at 484 cm^{-1} . DFT calculations predict in this area a maximum at 470 cm^{-1} , that corresponds to the A_u vibration involving the Fe-N stretching of all five LS iron centres, resulting in an in-phase shift of all irons along the long axis of the chain (movie LS_470Au in Suppl. Materials). The nonameric model predicts two peaks due to two similar modes: An asymmetric one at 472 cm^{-1} and a symmetric one at 466 cm^{-1} . The former involves the symmetric in-phase movement of all but the terminal iron atoms along the chain axis (cf. the movies non_LS_472Au and non_LS_466Ag).

The most intensive bands in the pDOS occur in 400 - 465 cm^{-1} area, with two first maxima at 452 and 442 cm^{-1} . The DFT calculations for the heptameric model predict in this region three A_u NIS

Figure 6

active vibrations at 451, 442 and 441 cm^{-1} (cf. the movies LS_451Au, LS_441Au and LS_442Au) as well as the A_g one at 459 cm^{-1} and 440 cm^{-1} (movie LS_459Ag and LS_440Ag). The first two ones can be

described as a collective stretching of all LS iron atoms, leading to an in-phase shift perpendicular to the long axis of the oligomer, while the latter one involves the movement along the long axis of the molecule. For the mode calculated to occur at 441 cm^{-1} this shift leads to a collective movement of iron atoms in the plane defined by the trzH ligands while for that at 451 cm^{-1} this movement takes place in plane defined by the *trans* located trz⁻ ligands (see movies aLS_441/451Au). The symmetric vibration at 459 cm^{-1} is similar to those predicted in the 466 and 472 cm^{-1} , i.e. there is a displacement of iron atoms along the long axis of the chain. The mode representing an A_g vibration at 440 cm^{-1} is similar to the A_u one at 442 cm^{-1} . The nonameric model gives similar results (see the movies non_LS_457/452/439Au and non_LS_448/443/438Ag in Suppl. Materials).

The next maximum in the pDOS displayed in Fig. 6a occurs at ca. 420 cm^{-1} . DFT calculations for the heptameric model exhibit eight NIS active modes in the area of 405-431 cm^{-1} (see the movies LS_431/414/412/410Ag and LS_424/423/409/405Au). The corresponding modes are essentially similar to those discussed above, including a mode which involves movement of iron atoms along the long axis of the chain calculated to occur at 414 cm^{-1} . The bands at 424, 412 and 408 cm^{-1} involve the movement of iron atoms in the plane defined by two "edges" of pairwise *trans*-coordinating trzH ligands. Interestingly, these vibrations occur at frequencies ca. 20 cm^{-1} lower than those for the corresponding movement in the plane defined by the anionic trz⁻ ligands. The nonameric model (Fig. 6c) yields essentially the same results.

Furthermore, there are two bands at 327 and 317 cm^{-1} in the experimental pDOS. The heptameric model displays several vibrations in the 306 - 315 cm^{-1} area (see the movies LS_315/311/310.9/310.5/306Au and LS_312/311/308Ag). These bands are similar to those described above, occurring at higher frequencies, yet the movement of specific iron centres seems to be less correlated, i.e. there is no clearly defined plane of movement for all centres.

Finally, there is a weak, broad band at ca. 245 cm^{-1} . The DFT analysis gives stretching modes with significant admixture of bending (see the movies LS_243/239Ag and LS_225Au).

A qualitative comparison of the pDOS of the [$\text{Fe}(\text{trzH})_2(\text{trz})$](BF₄) complex and that of the 4-aminotriazole ones^{11b,13} shows that for the first one the most intensive bands of the LS isomer occur in the area 415-450 cm^{-1} , while the aminotriazole complexes reveal the most intensive signals in the 350-400 cm^{-1} range. In both cases these bands are due to Fe-N stretching modes resulting in the displacement of iron atoms along and perpendicular to the long axis of the chain, with no particular difference in the frequency of both types of modes. Thus, somewhat stronger Fe-N bonds are inferred for the triazole/triazolato complex, probably due to a better compensation of the positive charge within the iron chain.

Guillaume et al.^{10c} reported the LS Raman marker bands for the title compound **1** to occur at ca. 200, 213, 287 and 300 cm^{-1} . The DFT calculations for the heptameric model reveal the previously mentioned Raman-active A_g bands at 312, 311 and 308 cm^{-1} as well as the ones predicted at 304, 301, 299 and 297 cm^{-1} . They may be ascribed to the band observed at 300 cm^{-1} . The latter three involve

mainly the libration of the azole ligands (see movie LS_301Ag). The LS Raman marker band at 287 cm^{-1} may be assigned to the modes predicted at 292, 288, 287, 282, 276 and 275 cm^{-1} . Again, these modes involve the librations of the ligands. However, for the former bands the libration involves flipping along the line parallel to the long axis. The modes assigned to the band at 287 cm^{-1} involve rotation along an axis perpendicular to the ring planes (see movie LS_282Ag). Noteworthy, the intensive non-resonant Raman bands are predicted at 270 and 263 cm^{-1} , which correspond to a classical Fe-N_{core} breathing mode (see movie LS_270Ag). The bands at ca. 200 and 213 cm^{-1} may be assigned to yet another type of librational modes of the ligands, predicted at 217, 207, 206, 200, 196 and 191 cm^{-1} (see movies LS_207/196Ag).

Low-spin [$^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ diluted in a [$\text{Zn}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ matrix

The experimental pDOS of [$\text{Zn}_{0.9}^{57}\text{Fe}_{0.1}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ and the calculated pDOS of the central LS iron centre in the HHHLHHH heptameric model are shown in Figure 7. The experimental pDOS of [$^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ (**1**) in the LS state and the pDOS for LS [$^{57}\text{Fe}(\text{atrz})_3](\text{CH}_3\text{SO}_3)_2$ and [$\text{Zn}_{0.9}^{57}\text{Fe}_{0.1}(\text{atrz})_3(\text{CH}_3\text{SO}_3)_2$] (ref. 13) at 80 K are shown for comparison.

Figure 7

In contrast to the pDOS of the parent LS system (**1**), for which the three groups of bands are observed in the $400 - 500\text{ cm}^{-1}$ region, the spectrum of the zinc diluted sample shows a narrow double-peak structure with maxima at 404 and 419 cm^{-1} . The overall change of the spectral pattern of LS Fe(II) upon dilution in the zinc matrix resembles closely to that reported previously for the aminotriazole analogues (cf. Ref 13) i.e. wiping out of vibrations at lowest and highest frequencies within the band cluster due to stretching vibrations, and a concomitant narrowing of the observed stretching band which shifts towards lower frequencies for the diluted complex.

The DFT calculations for the heptameric HHHLHHH model reveal two vibrational modes in the pDOS, at 426 and at 409 cm^{-1} . The first one (see movie HHHLHHH_426Au) involves stretching of the central LS Fe(II), with a very small movement of the two nearest HS neighbours. This mode stretches mainly the two Fe-N_{trz} bonds, while the other four triazole ligands are involved in vibrations of more bending-type. The second one (see movie HHHLHHH_409Au) corresponds to a quite similar mode, yet with stretching which involves two *trans* coordinated triazole ligands. The observed shift may correspond to a somewhat stronger bonding of the anionic ligand. The vibration at 426 cm^{-1} for HHHLHHH is similar to that predicted at 451 cm^{-1} for HLLLLLH, regarding the movement of Fe(**1**). Yet, similarly to the findings for the aminotriazole complex (Ref. 13), there is nearly complete decoupling of the movement of the HS neighbours. Similarly, the vibration at 409 cm^{-1} predicted for the HHHLHHH system resembles that predicted at 423 cm^{-1} for HLLLLLH. As discussed previously for the aminotriazole complexes (Ref. 13) the downshift upon changing the LS neighbours to the HS (or zinc) ones is due to an elongation of the Fe-N bonds^{11a}. Indeed, there is an increase of the LS Fe-ligand bond distances for the HHHLHHH model, all of them being over $2.00\text{ \AA}$.

High-spin [$^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ diluted in [$\text{Zn}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ matrix

The essential results for the HS system are shown in Figure 8.

Figure 8

The results of the simulation for the heptameric models yield the following assignment of the modes present in the experimental pDOS.

The peaks observed in the $300\text{--}320\text{ cm}^{-1}$ area for both parent (**1**) and diluted (**2**) may be assigned to the modes predicted at 310 cm^{-1} and 302 cm^{-1} for the heptameric HHHHHHH model. The modes involve the movement similar to that observed at 451 cm^{-1} for the LS HLLLLLH, i.e. to a collective movement of iron atoms in the plane defined by the trz^- ligands (see movies aHS_310Au/302Ag).

The strong bands in the $260\text{--}280\text{ cm}^{-1}$ region correspond to similar vibrations involving in this case the movement in the plane defined by *trans* coordinated trzH ligands (see movie aHS_269Au, aHS_255Au), predicted in the $250\text{--}280\text{ cm}^{-1}$ region. Note that in this case the difference between stretching of the bonds of anionic ligands and those of the neutral ones is at least 30 cm^{-1} compared to 20 cm^{-1} predicted in the LS isomer, reflecting the shortening of the HS Fe-N bonds on going from trzH to trz^- anion.

There are at least four significant bands in the region of $160\text{--}240\text{ cm}^{-1}$. The heptameric model yields four NIS peaks at 240, 209, 169 and 159 cm^{-1} (see movies HS_240/169/160Au and HS_208Ag), all of them showing clearly stretching character.

Comparison of electronic effects of trzH and trz^- ligands

In this section we discuss the effects that lead to the observed shortening of the Fe-N_{trz} bonds compared to Fe-N_{trz} ones in the HS isomer of the title system (**1**). We begin with the comparison of the molecular orbitals of the trzH and trz^- ligands. Fig. 9 shows the graphic representation of the four highest occupied molecular orbitals (HOMO) of both ligands, together with the corresponding LUMO orbital.

Figure 9

The inspection of the shapes of the obtained MO's reveals that for the triazole ligand the HOMO and LUMO are of σ - and π -type, respectively, implying its σ -donor and π -acceptor character, typically for common aromatic nitrogen containing ligands. For the deprotonated trz^- ligand the HOMO orbital displays π -character, while the σ -orbital, corresponding to HOMO of the trzH ligand lies below it. This, together with a 10 % larger HOMO-LUMO gap for the anionic ligand, points to a somewhat weaker both σ -donor and π -acceptor properties of the deprotonated trz^- ligand compared to the trzH one.

In order to model the difference between the electronic effects of the trzH and trz^- ligands we performed calculations for the mononuclear model structures [$\text{Fe}(\text{trzH})_6$]²⁺ and [$\text{Fe}(\text{trzH})_4(\text{trz}^-)_2$]. It is important to note that the polyazole 1D systems like (**1**) or its 4-amino-1,2,4-triazole analogues reveal the ideal S_6 symmetry rather than the O_h one. As a consequence the d-orbital of d_{z^2} shape is of π -character and lies on the long axis of the 1D chain. The shapes and

the orientations of the iron d-orbitals for the model $[(\text{H}_2\text{O})_3\text{Fe}(\text{atrz})_3\text{Fe}(\text{OH}_2)_3]\text{Cl}_6^{20}$ complex are discussed and given in Supplementary Materials (Figs. S8-11). The corresponding orientation of Cartesian coordinates are shown in Fig. 10.

Figure 10

The DFT calculations show that above coordinate system and the d-orbital pattern is the same in mononuclear $[\text{Fe}(\text{trzH})_6]^{2+}$ and $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$. The first one allows the highest symmetry of D_{3d} for both spin isomers, while the latter was optimised with the C_{2h} symmetry. The MO orbitals of d-character for the two LS isomers are shown in Figure 11. Figure 12 shows the relative energies of the above 3d-orbitals for the LS and HS isomers of both complexes.

Figure 11

Figure 12

One may observe that the z-axis (that of the d_{z^2} orbital) in the $[\text{Fe}(\text{trzH})_6]^{2+}$ corresponds to the threefold axis of D_{3d} symmetry group and the pattern of occupied and virtual d-orbitals in its LS isomer are the same as in the above discussed polynuclear complex of S_6 symmetry. Again the a_g d_{z^2} -orbital is the lowest-lying one for the LS isomer, while the two pairs of e_g orbitals of σ - and π -character lie over it. For the C_{2h} symmetric $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$ the d_{z^2} orbital (a_g) lies on the energy scale between the $d_{x^2-y^2}$ and d_{xy} ones (a_g), for both isomers. The highest lying d_{xz} and d_{yz} (b_g) orbitals reveal the same spatial pattern as in the corresponding homoleptic complexes of D_{3d} and S_6 symmetry. Again, the z-axis lies along the apparent threefold axis of the FeN_6 core. The admixture of ligand π - to the d- π -orbitals in LS $[\text{Fe}(\text{trzH})_6]^{2+}$ is rather limited while for $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$ it is clear that the HOMO orbital 85 (see Fig. 12) is a combination of $d_{x^2-y^2}$ orbital and two occupied π -orbitals of the trz^- anion. This effect of π - donation is reflected in the obtained Fe-N distances. While, as stated above, the DFT calculations predict no significant difference between $\text{Fe-N}_{\text{trzH}}$ and $\text{Fe-N}_{\text{trz}^-}$ distances for the oligonuclear complexes, for the mononuclear LS $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$ the corresponding distances are 1.997 and 2.018 Å, respectively, compared to 2.015 Å in $[\text{Fe}(\text{trzH})_6]^{2+}$. The analysis of the results shown in Figure 11 and 12 shows additionally that in the HS isomer there is a significant splitting of e_g orbitals on going from the D_{3d} symmetric $[\text{Fe}(\text{trzH})_6]^{2+}$ to the C_{2h} symmetric $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$. Particularly, the σ -d-orbital interacting with the trz^- σ -orbitals is destabilized. A decrease in the ligand field splitting in the HS $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$, compared to its heteroleptic analogue, may be inferred.

The calculated (B3LYP*/CEP-31G) spin transition energies in both mononuclear models yield the values of 19 and 33 kJ/mol for $[\text{Fe}(\text{trzH})_6]^{2+}$ and $[\text{Fe}(\text{trzH})_4(\text{trz}^-)_2]$, respectively. This implies that the change in the effective ligand field change splitting on going from LS to HS isomer is larger for the complex with anionic triazole. This effect is supposedly more pronounced in the polynuclear chains, where the presence of the negative charge of the ligands leads to the compensation of the electrostatic repulsion within the iron ion chain (cf. Ref. 8a, 11b and 17).

Taking into account all above observations the shortening of the HS Fe-N bonds on going from the trzH to the trz^- ligand with no effect for LS complexes may be assigned to electrostatic effects.

These are predominant for the more elastic HS isomer, while the higher radial rigidity of the LS centres, probably together with stronger π -donor effects compensates the effect of the charged ligand.

Conclusions

In conclusion the DFT calculations performed in this work show that the iron centres in the one-dimensional SCO molecular chain $[\text{Fe}(\text{trzH})_2(\text{trz}^-)](\text{BF}_4)$ (**1**) have a stoichiometric coordination of two non-charged trzH and one charged trz^- -ligand per iron based on the consideration of calculated ground state energies of heptameric model systems. As found also in earlier work for the aminotriazole chain, $[\text{Fe}(\text{atrz})_3]$, the iron-ligand modes of both the LS and the HS state do not depend on the type of counter ion. The presented DFT simulations show that the relative distribution of non-charged and charged ligands has only a minor effect on the energies of the iron ligand-modes. What is effected by introducing the charged trz^- -ligands is the symmetry of the iron nitrogen bonds in the HS state. Here the negative ligand charge leads to shorter iron nitrogen bonds between the iron and the trz^- -ligands in comparison to the uncharged trzH ligands. This effect is not observed in the LS state due to the higher flexibility of the LS state. Yet, the introduction of a charged trz^- -ligand leads to an increased iron ligand bond strength. This is even more evident for the iron ligand bonds of the LS iron with its HS neighbours in a HS matrix as shown by investigating the Zn diluted compound **2**. Compared to $[\text{Fe}(\text{atrz})_3]$ an upshift of the iron ligand stretching modes of $\sim 30 \text{ cm}^{-1}$ was observed.

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Figures

Figure 1: Experimental pDOS of the LS state of a) $[^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ at 80 K, b) $[^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{CH}_3\text{SO}_3)$ at 20 K and c) $[^{57}\text{Fe}(\text{atrz})_3](\text{CH}_3\text{SO}_3)_2$ at 80 K¹³.

Figure 2: Experimental pDOS of $[\text{Zn}_{0.9}^{57}\text{Fe}_{0.1}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ obtained at a) room temperature and at b) 20 K.

Figure 3: Graphic representation of the heptameric model molecule used for DFT calculations in this study

Figure 4. Comparison of the crystal packing in LS $[\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ (Ref. 10d) (left) and the optimised (B3LYP*/CEP-31G) (right) structure of its nonameric model (*vide infra*). Fe-Fe distances: 3.671 Å (exp.) and 3.719 Å (calc. av. Value); Fe-N distances: 1.827(5) and 1.981(6) Å (exp.) (two values) and 1.999 and 1.983 Å (Fe-N_{trzH}), 1.987 Å (Fe-N_{trz}), both for Fe in symmetry centre (calc. av. Value). Closest Fe-B distances: 5.789 and 5.875 Å (exp.) and 5.63-5.99 Å (calc.).

Figure 5: Comparison of a) experimental (T = 80 K) and b)-c) calculated (B3LYP*/CEP-31G) pDOS of the LS $[\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$. The calculated results are given for three different anions distributions a) 111111, b) 012210 and c) 003300 as discussed in the text. A similar comparison for the HS isomer is given in Suppl. Materials (Fig 4S).

Figure 6: Comparison of a) experimental ($T = 80$ K) and calculated (B3LYP*/CEP-31G) pDOS of b) heptameric and c) nonameric models of $[\text{}^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ in the LS state. The vibrational amplitudes of all LS iron centres are taken into account.

Figure 7: Comparison of the effects of dilution in zinc matrix on the pDOS in 1D chains of triazole and 4-amino-1,2,4-triazole complexes of Fe(II). a) experimental pDOS of $[\text{}^{57}\text{Fe}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ at 80 K, b) experimental pDOS of $[\text{}^{57}\text{Fe}(\text{atrz})_3](\text{CH}_3\text{SO}_3)_2$ at 80 K (ref. 13) c) experimental pDOS of $[\text{Zn}_{0.9}\text{}^{57}\text{Fe}_{0.1}(\text{atrz})_3(\text{CH}_3\text{SO}_3)_2]$ at 80 K. The peaks around 250 cm⁻¹ are due to residual HS centres (ref. 13) d) experimental pDOS $[\text{Zn}_{0.9}\text{}^{57}\text{Fe}_{0.1}(\text{trzH})_2(\text{trz})](\text{BF}_4)$ in the LS state (20K) e). Calculated (B3LYP*/CEP-31G) pDOS of the model HHHLHHH system, only the vibrations involving the central LS iron were taken into account when calculating the pDOS. Calculations applying models with other distributions of LS centres in the HS-matrix predict essentially the same pDOS pattern (see Suppl. Materials, Fig. S1)

Figure 8: pDOS of the HS centre obtained as the difference spectrum of (1) (a) and in zinc-diluted (2) (b) and the simulation of the HS state in the heptameric model for three different anion distributions based on the DFT calculations (c)-(e). The difference spectrum shown in a) is obtained by subtracting the experimental LS data from the experimental HS data as mentioned before. The pDOS below (b, zinc diluted sample) is calculated from the NIS spectrum with a binning of 1 meV after subtracting a constant background. (Further information about the data processing in Suppl. Materials). This measures had to be taken because of insufficient statistics and a high noise level. Due to the calculation algorithm of pDOS which is highly sensitive to big changes in the higher energy area and the noise level, the energy area over 340 cm⁻¹ is not reliable. As the simulation for the HS state ((c)-(e)) shows, bands in this area shall not appear.

Figure 9: Comparison of four highest lying occupied MO's and LUMO (top orbital for trzH (left) and trz- ligands (right). The calculations were performed with B3LYP* functional and CEP-31G basis set. The calculated HOMO-LUMO gaps are ca. 1900 cm⁻¹ and 2100 cm⁻¹, for trzH and trz-, respectively.

Figure 10: Coordinate system of the model linear Fe(II)-azole linear polynuclear complexes. The z-axis corresponds to the S_6 axis, the y-axis lies in the plane of the two trans coordinated rings (the Fe-N bonds shown with thinner line), the x-axis lies in the plane defined by four remaining coordinated N-atoms.

Figure 11: The occupied (three lowest) and virtual (two highest) MO's of the predominantly d-character for LS $[\text{Fe}(\text{trzH})_6]^{2+}$ (left) and $[\text{Fe}(\text{trzH})_4(\text{trz}')_2]$ (right). The numbers indicate the orbital number as calculated by DFT.

Figure 12: Relative energies of the orbitals with predominantly d-character for LS and HS $[\text{Fe}(\text{trzH})_6]^{2+}$ and $[\text{Fe}(\text{trzH})_4(\text{trz}')_2]$ as calculated for the structural model displayed in Fig. 10.