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Evidence of ligand elasticity occurred in thermally, light and pressure induced spin crossover in 1D coordination polymers $[Fe(3ditz)_3]X_2$ (X=ClO₄⁻, BF₄⁻)

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Abstract: The complexes $[M(3ditz)_3]X_2$ (X=ClO₄, M=Fe(II) (1), Zn(II) (2) and X=BF₄, M=Fe(II) (3), Zn(II) (4)) were prepared. Disordering of the propylene chain in 3ditz is not affected by thermally induced spin crossover in 1 (T_{1/2} \downarrow =149 K, T_{1/2} \uparrow =150 K) and **3** ($T_{1/2}^{\downarrow}$ =158, $T_{1/2}^{\uparrow}$ =161 K). Low spin to high spin (LS \rightarrow HS) switching triggered by laser light irradiation (520 nm) also does not influence on the disordering of the ligand, leading to restoration of initial HS phase. Pressurization of crystals involves reduction of Fe-N distances of about 0.19 Å which indicates practically complete SCO. Also in this case disordering of the ligand remains unchanged. Although thermally and pressure induced SCO is accompanied by different changes of 3ditz molecules. Upon thermally induced SCO, perturbation resulted from reduction of Fe-N distances involves slight elongation of bridging ligand. In contrast, in the range 0.25-0.55GPa, the pressure induced SCO is associated with shrinkage of 3ditz molecule. Further elevation of pressure involves inversion of structural changes and - similarly to temperature induced spin crossover - a slight elongation of ligand molecule takes place.

Introduction

Spin crossover phenomenon (SCO) occurs usually in octahedral complexes of metal ions with $3d^4-3d^7$ electronic configuration.^[1] High spin (HS, S=2)→low spin (LS, S=0) transition in octahedral iron(II) complexes can be obtained through the change of temperature, pressure,^[2] pulsing magnetic field^[3] or by the light irradiation^[4] and it is accompanied by the alteration of magnetic, optical, dielectric^[5] and conducting^[6] properties. A variety of methods which permits switching/reading of spin state allows the complexes exhibiting SCO to be considered for potential applications as memory devices,^[7] sensors,^[8] switches or in

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medical diagnostics.^[9] HS→LS transition is associated with shortening of the Fe-N bond lengths from approx. 2.2 to 2.0 Å. The change of the spin state involves reduction of the volume of the coordination octahedron at about 25% (~3 Å³). This effect causes also the shrinkage of a complex molecule.^[10] Usually such alteration results in less distorted [FeN₆] coordination octahedron, however presence of bulky and rigid ligand molecules may induce steric hindrance involving an increase of the distortion of coordination octahedron.^[1f] The shrinkage of the coordination octahedron may also lead to a misfit between coordination geometry of the ligand molecule and the coordination geometry of a metal ion. Among them one can find Fe(II) complexes based on flexible chelating ligands.^[11] In this family of structurally related complexes, the differences in ligands strain arise from various sizes of chelate rings. The resulting trigonal distortion of coordination octahedra corresponds to the shift of SCO temperature.^[12] The appearance of strain can be compensated by occurrence of more pronounced changes related to the conformational freedom of chelate ring.^[13] Finally, a misfit between coordination geometry of the ligand molecule and metal ion may result in serious structural alterations associated with a change of coordination number of metal ion.^[14] The last is a very interesting and important phenomenon because it may cause an extraordinary stabilization of light induced HS state in which coordination number of Fe(II) ion differs from that observed in the initial high temperature HS phase. Depending on the structure of the coordinated ligand molecule, SCO can also trigger other alterations in the first coordination sphere for example related to reorientation of small coordinated molecules like thiocyanate

anion^[15] or nitriles^[16] as well as to conformational changes.^[17] Spin crossover phenomenon is of molecular nature but in solid state the perturbation produced by the change of spin state spreads progressively over the whole crystal lattice. Thus it may affect a network of intermolecular contacts. In coordination polymers the perturbation produced by SCO can also influence molecules linking metal ions. In polymeric complexes based on small and rigid moieties like pyrazine, SCO can be accompanied by their reorientation. In the three-dimensional (3D) network of [Fe(pyz)Pt(CN)₄] spin crossover triggers turning of the pyrazine ring.^[18] Also in the one-dimensional (1D) network of [Fe(pyz)(CH₃CN)₄](ClO₄)₂·2CH₃CN a three step SCO is associated with rotation of bridging pyrazine molecules.^[19] In the two-dimensional (2D) network of [Fe(44btr)₃](ClO₄)₂ (44btr = 4,4'-bis(1,2,4-triazole) the change of spin state triggers reorientation of 1,2,4-triazole rings. [20] Incorporation of an alkyl spacer, separating the donor groups, becomes an another factor

increasing the elasticity of the bridging molecule. In the 1D coordination polymer of [FeL1(bppa)₂] [L1 = chelating N₂O₂ Schiff base type ligand, bppa = 1,3-bis(4-pyridyl)propane)] SCO is accompanied by the adjustment of bppa dimensions to structural changes.^[21]

Investigations of Fe(II) complexes based on di(tetrazolyl)- and di(1,2,3-triazolyl)alkane - type ligands revealed that SCO can be accompanied by conformational changes of bridging ligands, occurring without significant structural alteration of [Fe(azole)₆] cores. The most sophisticated structural alterations were observed in a 3D coordination network of [Fe(qbtr)₃](ClO₄)₂ (qbtr = 1,5-di(1,2,3-triazol-1-yl)pentane) in which the change of temperature as well as SCO trigger sequence of consecutive conformational changes accompanied by crystallographic phase transitions P-1(HS, HS)→P-1(HS, HS, HS)→P-1(HS,LS) with intermediary phase (2a+2b,2a-2b,c).[22] An occurrence of conformational changes of the bridging ligands were noticed also in 2D and 3D coordination polymers in which azole rings are joined by a propylene spacer. In 2D network of $[Fe(ptrtz)_3](CIO_4)_2 \cdot CH_3CN$ (ptrtz = 1-(tetrazol-1-yl)-3-(1,2,3triazol-1-yl)propane) a two step SCO is associated with partial vanishing of ligand disorder and formation of superstructure in intermediate phase.^[23] In the 3D network the of $[Fe(pbtz)_3](CIO_4)_2 \cdot C_2H_5OH$ (pbtz = 1,3-di(tetrazol-2-yl)propane), the HS iron(II) ions are bridged only by disordered pbtr molecules and during the gradual SCO the disorder of ligands in LS phase disappeared.^[24] Conformational changes of the bridging ligand, which compensate perturbation resulted from reduction of Fe-N distance, may be responsible for gradual SCO in this complex. In contrast, 1D network of [Fe(3ditz)₃](BF₄)₂, based on regioisomerical ligand 1,3-di(tetrazol-1-yl)propane (3ditz), exhibits an abrupt, one step and complete SCO, with all ligand molecules disordered in both the HS and LS phases.^[25] It should be added that substantial conformational differences of ligand molecules in HS and LS forms were also found in molecular complex $[Fe(L)_2](CIO_4)_2$ (L = 2,6-bis[5-{2hydroxyphenyl}pyrazol-3-yl]pyridine)^[1f,26] and in 2D coordination polymer of [Fe(entz)₂](BF₄)₂ (entz = tris[2-{tetrazol-1yl}ethylene]amine). ^[27] The overview of structures of $1,\omega$ di(azolyl)alkane-type ligands and its coordination networks was presented previously.^[23]

Taking into account that in [Fe(3ditz)₃](BF₄)₂ the central carbon atom of the propylene spacer of a potentially flexible/elastic 3ditz molecule (Scheme 1) can occupy two alternative positions, we have decided to test if chemical or physical stimuli can affect on structural liability of bridging ligand. For this purpose we have exchanged tetrafluoroborate on slightly larger perchlorate anion. SCO properties were characterized by measurements of temperature dependence of magnetic susceptibility. The possibility of structural alterations in $[Fe(3ditz)_3]X_2$, complexes caused by the change of temperature, light irradiation ($X = BF_4$, CIO_4) or pressurization (X = CIO_4) was investigated by carrying out comprehensive diffraction studies. Thus multi-temperature single crystal X-ray diffraction studies for HS and LS forms were carried out. Afterward, it has been examined how LS→HS switching achieved by light irradiation (LIESST) may perturb a crystal structure. Finally, taking into account that an application of pressure might affect the crystal structure in different way than by changing of temperature^[28], the crystal structures of $[Fe(3ditz)_3](CIO_4)_2$ complex at different pressures in the range from atmospheric pressure up to 1.13GPa have been determined.



Scheme 1. Structure of 3ditz ligand.

Results and Discussion

1-substituted tetrazoles are easily accessible in the reaction of primary amines with sodium azide and triethyl orthoformate carried out in acetic acid.^[29] This reaction proceeds with very good yields (60-90%) and allows to obtain regioisomerically pure products. However the synthesis of 1,3-di(tetrazol-1-yl)propane performed according mentioned above procedure failed. It is worth mentioning that an application of 1,3-diamino-2-propanol also leads to abnormally low yield of synthesis of suitable bistetrazole derivative.^[30] Therefore a more efficient method was used to preparation of bistetrazoles containing 1,3-propylene spacer based on alkylation of tetrazoles with suitable 1,3dibromo- or 1,3-dichloropropane derivatives. Successful synthesis of 3ditz was carried out by Müller et al. in the reaction of tetrazole with 1,3-dibromopropane in presence of tetrabutylammonium bromide in methanol.^[25] We have modified the above mentioned procedure alkylating sodium tetrazolate by 1,3-dibromopropane in water, without addition of a phase transfer catalyst. 1,3-di(tetrazol-1-yl)propane was obtained with comparable yield of 10%. This low yield is most probably due to formation of products resulting from substitution at the N2 atom of tetrazole ring.^[31] 3ditz crystallizes as colorless needles soluble in acetonitrile, methanol, ethanol and insoluble in CCl₄ and aliphatic hydrocarbons.

Recently the complex $[Fe(3ditz)_3](BF_4)_2$ was prepared by Müller *et al.* in the reaction of $Fe(BF_4)_2 \cdot 6H_2O$ with 3ditz in hot methanol, followed by evaporation of the solvent and washing of obtained solid residue by dichloromethane.^[25] In order to prepare its perchlorate analogue we have reacted $Fe(CIO_4)_2 \cdot 6H_2O$ with 3ditz (metal to ligand molar ratio 1:3) in the acetonitrile. $[Fe(3ditz)_3](CIO_4)_2$ (1) crystallizes in the form of hexagonally shaped colourless crystals. Applying similar reaction conditions the complex $[Zn(3ditz)_3](CIO_4)_2$ (2) and tetrafluoroborate analogues $[Fe(3ditz)_3](BF_4)_2$ (3) and $[Zn(3ditz)_3](BF_4)_2$ (4). were also prepared. Magnetic and diffraction studies presented in the further part were carried out for complexes 1-4 prepared from acetonitrile.

Magnetic and photomagnetic studies. The temperaturedependent magnetic susceptibility measurements for the complex [Fe(**3ditz**)₃](ClO₄)₂ were carried out in the 10-300 K range. Thermal dependence of $\chi_M T$ is shown in the Figure 1a (χ_M , molar susceptibility; *T*, temperature). In the temperature

range from 300 to 170 K the $\chi_M T$ is almost constant adopting value of 3.7 cm³K/mol which is characteristic for the high-spin form of the iron(II) ion. Further lowering of temperature involves very rapid decrease of the $\chi_M T$ value with $T_{1/2}^{\downarrow}=149$ K ($\chi_M T$ = 1.85 cm³Kmol⁻¹, γ_{HS} =0.50; γ_{HS} = [($\chi_M T$)_T - ($\chi_M T$)_{LS}]/[($\chi_M T$)_{HS} - $(\chi_M T)_{LS}$], where $(\chi_M T)_T$ represents $\chi_M T$ at temperature T, $(\chi_M T)_{LS}=0.2 \text{ cm}^3 \text{Kmol}^{-1}$ and $(\chi_M T)_{HS}=3.7 \text{ cm}^3 \text{Kmol}^{-1}$). At 100 K the $\chi_M T$ reaches the value of 0.2 cm³K/mol. This magnetic behavior is characteristic for the thermally induced SCO. In the heating mode the $T_{1/2}^{\uparrow}$ is equal to 150 K. The abruptness of the spin transition is practically the same as in the cooling mode. Spin crossover in [Fe(3ditz)₃](BF₄)₂ is very abrupt in the cooling mode and shifted if compared to 1 towards slightly higher temperature with $T_{1/2}^{\downarrow}=158$ K (Figure 1b). Below 150 K the $\chi_{\rm M}T$ is almost constant reaching at 100 K the value of ca. 0.15 cm³K/mol which points at the complete spin crossover. In the heating mode $T_{1/2}$ is equal to 161 K indicating the presence of a more pronounced thermal hysteresis loop.



Figure 1. Changes of $\chi_M T$ vs. T for $[Fe(3ditz)_3](CIO_4)_2$ (a) and for $[Fe(3ditz)_3](BF_4)_2$ (b) upon thermally induced SCO in cooling (filled blue triangles) and heating (filled red triangles) modes. Increasing of $\chi_M T$ upon laser light irradiation (520 nm) are marked by filled green triangles (LIESST). Changes of $\chi_M T$ during laser light irradiation were measured in heating (open red triangles) and cooling (open blue triangles) cycles (LITH experiments).

After cooling of [Fe(**3ditz**)₃](ClO₄)₂ sample to 10 K the LS phase was switched to HS phase using green laser light. Afterwards the laser light was switched off and the temperature increased at a rate 0.3K/min. The optically induced HS phase is unstable and starts to decay abruptly with increasing temperature. The temperature value of T_{LIESST} = 48 K (estimated from minima of d_{XM}T/dT derivative). The T_{LIESST} value for **3** is equal to 46 K. A comparison of T_{1/2} and T_{LIESST} values shows that according to relationship T_{LIESST} = T₀-0.3T_{1/2} the estimated T₀ values for **1** and **3** are close to T₀ = 100 K line.^[32]

Photomagnetic studies (LIESST) were performed for $[Fe(3ditz)_3]X_2$ (X = CIO₄⁻ and BF₄⁻) complexes using laser light irradiation with wavelength of 520 nm (Figure 1). A crystalline sample of [Fe(3ditz)₃](ClO₄)₂ was cooled from 300 to 10 K (1K/min). Next the sample was illuminated with laser light (3 mW for about 90 minutes) until saturation at $\chi_{\rm M}T = 3.0 \ {\rm cm}^3{\rm Kmol}^{-1}$ was reached. With the laser light on, the temperature was increased at a rate 0.3K/min. After initial elevation of $\chi_M T$ (probable resulted from zero-field splitting of Fe(II) ions) to maximum value of 3.8 cm³Kmol⁻¹ at 41 K, further increasing in temperature involves an abrupt HS-LS relaxation. The experiment carried out for [Fe(3ditz)₃](BF₄)₂ showed that HS phase remaining under continuous irradiation is stable up to 41 K ($\chi_{M}T$ = 3.6 cm³Kmol⁻¹) too. For both complexes after reaching the temperature 70 K measurements were carried out in the cooling mode (Figure 1).

Multitemperature single crystal X-ray diffraction studies. The crystal structures of **1** were determined at temperature range 100-250 K (Table S1a and S1b). The lattice parameters for Fe(II) complexes give a clear evidence for occurrence of SCO (Figure 2). The complexes **1**, **2**, **4** crystallize in the trigonal P-3c1 space group and are isostructural with tetrafluoroborate analogue **3** (Tables S2a, S3a and S4a).^[25] Iron(II) ion is surrounded by six symmetry equivalent tetrazole rings (Figure 3) which coordinate through exodentate nitrogen atoms N4 and form an almost regular octahedron. In temperature range 250-160 K the Fe-N4 distances change from 2.1882(29) to 2.1677(22) Å and these values are characteristic for the high spin form of Fe(II) ions in FeN₆ chromophore. Two neighboring Fe(II) ions, separated at distance 7.4267(6) Å (250 K), are linked by three ligand molecules.

The central atom of propylene spacer of ligand molecule is disordered with occupancies equal to 0.5 (Figure 3) what is forced by the space group symmetry (P-3c1). However the refinement of the crystal structure for the lower symmetry (P-3 space group) confirmed that during SCO the symmetry does not change and the disordering of the ligand remains unchanged (Tables S1c, S2b, S3b, S4b).

The bridging mode is propagated in the *c* direction leading to the formation of the 1D polymeric unit (Figure 3). Each chain is surrounded by six parallel oriented ones which affords hexagonal arrangement of the polymeric units in the crystal. There are no hydrogen bonds or other strong intermolecular interactions between chains. Only two distant contacts C3-H3A···N2(x-y+1, -y+1, -z+1/2) of 3.299(8) Å and C2-H2B···N2(1-

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Figure 3. Fragment of the polymeric chain showing the coordination environment and bridging fashion of iron(II) ions in $[Fe(3ditz)_3](CIO_4)_2$ with labeling scheme of atoms. Hydrogen atoms were omitted for clarity.





y, 1+x-y, z) of 3.354 (6) Å (250 K) are present (Figures 4, S1 and S2). The reduction of temperature to 160 K involves only a slight shortening of them to 3.264(6) and 3.326(4) Å, respectively. In the HS form the shortest distance between iron(II) ions from neighboring chains is equal to 11.0848(5) at 250 K and 11.0792(4) Å at 160 K. The noncoordinated perchlorate anions are placed in channels between polymeric units (Figure 4). Anions are disordered, occupying two alternative positions with probability 0.67 and 0.33. They are engaged in the formation of C_{tetrazole}-H···O(CIO₄⁻) and C_{alkyl}-H···O(CIO₄⁻) intermolecular contacts.

Reduction of temperature triggers in **1** an abrupt HS \rightarrow LS transition associated with shortening of the Fe-N distance from 2.1599(22) (155 K) to 2.0023(21) Å (150 K) (Figure 5a, Table S1a and S1b). For the comparison on Figure 5a there is also shown the temperature dependence of Zn-N distance. After further cooling, the geometry of the coordination octahedron is practically the same; the N4-Fe-N4(x, y, 0.5-z) angle remains practically unchanged adopting value of 90.53(8)°. In spite of the direct linkage of Fe(II) ions in the polymeric chain, the HS \rightarrow LS transition involves only a small reduction of iron…iron intrachain





c)

Figure 2. Temperature dependence of unit cell parameters (a and b) and unit cell volumes (c) for $[M(3ditz)_3]X_2$ (M = Fe²⁺ and X = ClO₄⁻ - up/down triangles; M = Zn²⁺ and X = ClO₄⁻ - left/right triangles; M = Fe²⁺ and X = BF₄⁻ - squares; M = Zn²⁺ and X = BF₄⁻ - circles) complexes in cooling (blue), heating (red) modes and after LIESST (green).

distance at about 0.05 Å. The temperature dependence of N4…N4(x, y, 0.5-z) is shown on Figure 5b. After transition from HS to LS the intermolecular distances C3-H3A…N2(x-y+1, -y+1, -z+1/2) and C2-H2B…N2(1-y, 1+x-y, z) slightly increase from 3.264(6) and 3.326(4) Å to 3.337(6) and 3.353(4) Å, respectively (Figures S1 and S2). The disordering scheme of the perchlorate anion remain unchanged after the HS→LS transition.

The structural changes associated with HS->LS transition in 3 are very similar to those found in 1. SCO is very abrupt and going from 163 to 161 K results in a shortening of Fe-N distance at 0.17 Å. In this temperature range a reduction of intra- and interchain iron…iron separations by 0.05 Å and 0.14 Å respectively occur. SCO is accompanied by small changes of N2-N1-C2-C3 and N1-C2-C3-C3(x, y, 0.5-z) torsion angles comparable with those observed for 1 (ESI). The analogous C3-H3A…N2(x-y+1, -y+1, -z+1/2) and C2-H2B…N2(-y+1, x-y+1, z) intermolecular distances slightly increase after HS→LS transition as observed in **1**. In the heating mode abrupt LS→HS transition occurs between 164 and 165 K leading to restoration of the HS structure of 3. Temperature dependence of the Fe-N distance (Figure 5a) confirms the presence of a narrow hysteresis loop of width about 3 K being consistent with temperature dependences of $\chi_M T$ and lattice parameters.

Single crystal X-ray diffraction studies under continuous laser light irradiation. Photomagnetic studies revealed that iron(II) complexes cannot be switched to the persistent light induced HS phase. Therefore we have decided to trap light induced HS phase under continuous laser light irradiation to determine the crystal structure.^[33] LIESST experiments were carried out at continuous irradiation of single crystals with laser light (520 nm) at 15 K for both 1 and 3 (Tables S5a and S5b). In the light induced HS phase of [Fe(3ditz)₃](ClO₄)₂ the lattice parameter a (Figure 2a) reaches the value observed in the starting HS phase at 200K. The lattice parameter c, related to iron…iron intrachain separation, increases slightly by 0.04 Å, whereas, upon a thermally induced LS→HS transition its value increases by about 0.1 Å. Inspection of geometrical parameters of the polymeric chain revealed that the elasticity of bridging ligands is responsible for that difference. One can observe that spin state switching, triggered by light irradiation, leads to a reduction of N4…N4' distance at 0.18 Å (Figure 5b), whereas upon thermally induced SCO this separation changes at about 0.13 Å. It means that at very low temperature light induced spin state switching involves slightly greater structural alterations in the closest vicinity of Fe(II) ion. Similar behavior has been noticed for the 2D coordination polymer of [Fe(hbtz)₂(allyl cyanide)₂](CIO₄)₂.^[17] In this complex appearance of HS iron(II) ions after light induced LS $\rightarrow \! \text{HS}$ switching is compensated by a few structural changes of bridging ligand resulting in an increase of deformation of corrugated polymeric layer.

LIESST experiment on a $[Fe(3ditz)_3](BF_4)_2$ single crystal have shown that similarly to 1, in which the Fe-N distance increases from 1.9892(13) to 2.1721(13) Å, the Fe-N bond lengths in 3 increase from 1.9861(15) to 2.1766(16) Å which indicates complete LS \rightarrow HS switching (Figure 5a). The remaining structural changes associated with light induced spin state switching are quite similar to those in **1**.

Single crystal X-ray diffraction studies of pressure induced spin crossover. The diffraction patterns for $[Fe(3ditz)_3](CIO_4)_2$ were collected from ambient pressure up to 1.13 GPa (Tables S6a and S6b). Reduction of the crystal lattice parameters as well as unit cell volume is usually a convenient tool to follow a course of SCO. A rough inspection of the pressure dependence of *a* and *c* lattice parameters, for $[Fe(3ditz)_3](CIO_4)_2$ does not give a direct evidence for the presence of a pressure induced SCO (Figure 6).



b)

Figure 5. Temperature dependence of the M-N distances (a) and N4...N4' (b) for $[M(3ditz)_3]X_2$ complexes (M = Fe²⁺ and X = ClO₄⁻ - up/down triangles; M = Zn²⁺ and X = ClO₄⁻ - left/right triangles; M = Fe²⁺ and X = BF₄⁻ - squares; M = Zn²⁺ and X = BF₄⁻ - circles) complexes in cooling (blue), heating (red) modes and after LIESST (green).



a)



c)

Figure 6. Pressure dependence of unit cell parameters and volume for $[Fe(\textbf{3ditz})_3](ClO_4)_2.$

2,20 2,15 Fe-N distance / A 2,10 2,05 2,00 Б 1,95 0.0 0.2 0,4 0.6 0.8 1.2 1.0 pressure / GPa

Figure 7. Pressure dependence of Fe-N bond lengths of [Fe(3ditz)₃](ClO₄)₂.

The compressibility is monotonic and without clearly noticeable anomalies, which is commonly observed for many other molecular solids.^[34] If compressed up to 1 GPa, the volume of crystal decreases to 91% (Figure 6c). Pressure of about 1 GPa reduces the closest iron…iron interchain distances (along [100] direction) of about 0.307 Å (Figure 6a). The hydrostatic compression enforces also a shortening of Fe…Fe distances in a polymer chain (along [001] direction) at 0.33 Å (0.282 ÅGPa⁻¹) (Figure 6b). In contrast, a marked reduction of Fe-N bond lengths clearly indicates the occurrence of a pressure induced SCO. With increasing pressure from 0.01 MPa up to 1.13 GPa the Fe-N distances drop gradually from 2.200(5) Å to 1.998(7) Å, a value characteristic for the LS state. (Figure 7).

The temperature induced SCO in 1 is associated with an abrupt compression of crystal lattice in a and c directions on passing the SCO region in the cooling mode (Figures 2a and 2b) and directly correlate with the observed changes of the Fe-N bond distances. The abrupt change of spin state in the cooling modes accompanied also by an abrupt increase of the is N4…N4(x,y,0.5-z) distance at 0.13 Å corresponding to a significant stretch of the ligand molecule (Figure 5b). For comparison, analysis of ligand behaviour in reference crystal of $[Zn(3ditz)_3](ClO_4)_2$ reveals that cooling brings contraction of c crystal lattice parameter, too. But for 2 the observed decrease of c is associated with a shrinkage of the ligand molecule - the N4…N4' distance decreases between 240 and 140 K at 0.09 Å. Thus comparing the results obtained for 1 and 2 indicate that ligands elasticity manifests itself in different ways as a result of internal disturbance (SCO) as well as an action of external perturbation on cooling.

The ability of **3ditz** molecules to demonstrate their elasticity is reflected in the pressure induced SCO (Figure 8a). Analysis of ligand structure shows that in the range 0-0.55 GPa a larger reduction of N4···N4' distance, if compared with that resulting in thermally induced SCO, takes place (Figure 8b). Moreover, a comparison of the Fe-N distance vs. volume of the unit cell (Figure 9) shows that a combination of SCO and ligands shrinkage causes a more gradual reduction of γ_{HS} (which can be estimated from [d_{(Fe-N)T} - d_{(Fe-N)LS}]/[d_{(Fe-N)LS}]) if compared with that observed for temperature induced SCO. Hence, a

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0.2

0.4

0.6

pressure / GPa

0.8

0.0

5,0

4,9

4.8

N4...N4(x, y, 0.5-z) distance / A

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change of *c* lattice parameter does not follow the decrease of the Fe-N distance upon SCO.

a)



1.0

1,2

b)

Figure 8. Dependences of N4···N4' distances vs pressure (a) and vs Fe-N distances (b) for $[Fe(3ditz)_3](CIO_4)_2$.



Figure 9. Dependences of N4···N4' distances vs pressure (a) and vs Fe-N distances (b) for $[Fe(3ditz)_3](CIO_4)_2$

A similarity of structural changes of ligand molecules triggered by pressure induced SCO in **1** as well as caused by lowering of temperature for **2** leads to an important conclusion that when a disturbance competitive to SCO appears (resulting of an application of pressure) the change of spin state cannot effectively influence the closest surrounding of Fe(II), that is the ligands structure. Consequently, the presence of a competitive disturbance influences the efficiency of perturbation spreading on the crystal lattice too.

Further increase of pressure, above 0.55 GPa ($\gamma_{HS} \approx 0.75$), results in the slope of Fe-N distance vs. volume of the unit cell dependence (Figure 9) becoming comparable to the one found for temperature induced SCO. It appears that above 0.55 GPa an inversion of the N4…N4' distance vs. pressure dependence occurs - starting to stretch **3ditz** molecule. Thus, in the range 0.55-1.0 GPa the structural mechanism of SCO, comprising structural changes of ligand molecules, becomes similar to the one observed for temperature induced SCO. It is worth to note that the N4…N4' separation under high pressure does not achieve values observed upon thermally induced SCO.

The network of intermolecular contacts is another structural element which is sensitive to this kind of disturbance. Thermally induced SCO in $[Fe(3ditz)_3](CIO_4)_2$ leads to a very small increase of C3-H3A···N2(x-y+1, -y+1, -z+1/2) and C2-H2B···N2(1-y, 1+x-y, z) intermolecular distances whereas increasing of pressure results in a continuous slight shortening of them.

Although an application of pressure involves different structural changes of ligand molecules, as well as intermolecular contacts, if compared with those resulting from thermally induced SCO, the disordering scheme of perchlorate anions and alkyl spacer remain unchanged

Concluding remarks

This paper is concerned with studies on thermally, light and pressure induced SCO in two 1D Fe(II) coordination polymers based on potentially flexible bridging ligand 1,3-di(tetrazol-1-yl)propane (**3ditz**). The isostructural complexes [M(**3ditz**)₃]X₂ (X=CIO₄⁻, M=Fe(II) (1), Zn(II) (2) and X=BF₄⁻, M=Fe(II) (3), Zn(II) (4)) were prepared were obtained by reacting **3ditz** and corresponding metal perchlorates or tetrafluoroborates in acetonitrile. **1** exhibits an abrupt and complete thermally induced spin crossover (T_{1/2}[↓] = 149 K, T_{1/2}[↑]=150). An abrupt spin crossover in **3** is accompanied by a more pronounced hysteresis loop (T_{1/2}[↓] = 158 K, T_{1/2}[↑]=161 K).

The characteristic feature of complexes studied is the presence of triple bridges established between iron(II) ions by **3ditz** molecules in which central atom of the propylene spacer is disordered. Thermally induced HS \rightarrow LS transition does not influence the disordering of the ligand. Iron(II) complexes were also switched from the LS to HS state at 15 K using laser light irradiation of wavelength 520 nm. Light induced switching leads to reconstruction of the high temperature HS phase where the ligands disorder still observed. Results of high pressure single crystal X-ray diffraction studies revealed the occurrence of

practically complete change from HS to LS form and also in this case disordering of propylene spacer is preserved.

Subtle differences were found in the ligand structure in HS and LS forms which result from elasticity of bridging molecules and depends on the kind of perturbation triggering spin crossover. Thermally induced spin crossover involves compression of the crystal lattice, however, the ligand molecules accommodate their structure to the ongoing reduction of Fe-N distances - a lengthening of bridging ligand takes place. On the other hand, an absence of SCO active centers in Zn(II) analogue leads to a condition where the thermal contraction of the crystal lattice involves a shrinkage of ligands molecules. During pressure induced SCO the picture of ligands structural changes is more complicated. Initially an application of pressure triggers shortening of the ligand molecule, similarly to the changes noticed during cooling of the crystal of the Zn(II) analogue. But this ligand contraction is more pronounced if compared to that observed in thermally induced SCO. Further increase of pressure causes an inversion of this tendency and elongation of the ligand molecules occurs as it was found as result of thermally induced SCO in 1.

Experimental Section

Materials and Methods. 1,3-dibromopropane, metal(II) salts hexahydrates were purchased from Aldrich and used without purification. Acetonitrile was dried by a distillation over calcium hydride. Tetrazole was prepared in the reaction of sodium azide with ammonium chloride and trimethylorthoformate in presence of glacial acetic acid (J.T.Baker) according to the procedure described previously.^[35] Syntheses of iron(II) complexes were carried out under nitrogen atmosphere using the standard Schlenk technique. *Caution! Even though no problems were encountered it is worth to mention that complexes containing perchlorates and tetrazole derivatives are potentially explosive and should be synthesized in milligram scale and handled with care.*

¹H NMR and ¹³C NMR spectra were recorded on AMX Bruker NMR 500 MHz spectrometer at room temperature in CD₃CN solutions. IR spectra of ligand and complexes were recorded with a Bruker IFS66 IR FTIR spectrometer in the range 400-4000 cm⁻¹ as KBr pellets. Elemental analyses for carbon, hydrogen and nitrogen were performed on Perkin Elmer 240C analyzer. Temperature dependences of magnetic susceptibility were measured with a Quantum Design SQUID magnetometer in the range 5-300 K at rate 1 K/min (1T). Light irradiation experiments on Fe(II) complexes were performed on a thin layer of polycrystalline sample, placed on gelatin plate inside a polyethylene tube (5 mm diameter), and using as light source a diode laser of wave length 520 nm. The laser output was adjusted to 3 mW (according to laser power meter Carl Zeiss Jenna LM-1). The weight of irradiated samples were obtained by comparison of the thermal SCO curve with that one of accurately weighted sample of the same compound. Data have been corrected for the signal of the empty holder and for diamagnetism of the sample.

Synthesis of 1,3-di(tetrazol-1-yl)propane (3ditz). A solution of NaOH (0.12 mol, 4.80 g) in water (15 mL) was added in few portions to tetrazole (0.12 mol, 8.40 g) dispensed in water (15 mL). To the obtained colorless solution, 1,3-dibromopropane (0.05 mol) was added, and the reaction mixture stirred and refluxed for 6 hours. After cooling the reaction mixture was extracted with CCl₄ (8x25 mL) and CH₂Cl₂ (2x25 mL). The water

solution was then concentrated under reduced pressure. The obtained solid mass was extracted using boiling acetonitrile (3x20 mL). Acetonitrile was removed to dryness using rotary evaporator. The solid obtained was crystallized from ethanol and then recrystallized from water giving colorless needles. Yield 1.8 g (10%). Anal. calc. %C 33.8, %H 4.5, %N 61.5; Found. %C 33.3, %H 4.3, %N, 62.1. M.p. 158 °C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ: 2.47(q, 2H, -CH₂-CH₂-, ³*J* = 6.9Hz), 4.51(t, 4H, -CH₂-CH₂-, CH₂-, ³*J* = 6.9Hz), 9.32(s, 1H, CH of tetrazol-1-yl) ppm. ¹³C NMR (500 MHz, CD₃CN, 298 K) δ: 29.30, 45.26, 144.41 ppm.

Synthesis of complexes [Fe(3ditz)₃]X₂ (X = BF₄⁻, ClO₄⁻). Syntheses of complexes were performed under nitrogen atmosphere using the standard Schlenk technique. FeX₂·6H₂O (1.0 mmol), dissolved in water (1.0 mL), was added to the solution of 3ditz (3.0 mmol) in acetonitrile (25 mL). The resulted reaction mixture was filtered to Schlenk flask and stream of nitrogen was passed over the solution. After the reduction of solution volume to one fourth of the starting one, the product begins to crystallize. Then the resulted reaction mixture was allowed to stand in a closed Schlenk flask. Next day the colorless crystalline product was filtered off, washed with acetonitrile and dried in a stream of nitrogen. [Fe(3ditz)₃](ClO₄)₂ was isolated with yield of 88%. Anal. calc. for FeC₁₅H₂₄N₂₄Cl₂O₈: %C 22.6; %H, 3.0, %N, 42.3; Found. %C, 22.8, %H, 3.1, %N, 42.5.

Applying similar reaction conditions [Fe(**3ditz**)₃](BF₄)₂ was isolated with yield of 81%. Anal. calc. for FeC₁₅H₂₄N₂₄B₂F₈: %C 24.1; %H, 3.2, %N, 43.6; Found, %C, 24.1, %H, 3.0, %N, 43.7.

Synthesis of complexes [Zn(3ditz)₃]X₂ (X = BF₄⁻, ClO₄⁻). Syntheses were carried out according to procedure described previously for [Fe(3ditz)₃]X₂. (X = BF₄⁻, ClO₄⁻) complexes. 3ditz (0.0778 mmol) dissolved in MeCN (2.0 ml) was added to a solution of ZnX₂·6H₂O (0.026 mmol) in MeCN (1.0 ml). The resulted clear solution was left in 10ml vial. After 24 hours the colourless crystals were filtered off and dried on air. Yield 88 % (X = ClO₄⁻) and 82% (X = BF₄⁻). Anal calcd for ZnC₁₅H₂₄N₂₄Cl₂O₈: C, 22.4; H, 3.0; N, 41.8 Found: C, 22.6; H, 3.3; N, 41.6%. Anal calcd for ZnC₁₅H₂₄N₂₄B₂F₈: C, 23.1; H, 3.1; N, 43.1 Found: C 22.8; H, 3.3; N, 43.0%.

X-ray data collection and structure determination. Single crystals of the complexes were obtained according with aforementioned synthesis procedure. Structural studies of the complexes in the temperature range from 100 to 250 K were performed with SuperNova X-ray diffractometer with microfocus X-ray tube, optimized multi-layer optics for Mo- K_{α} ($\lambda = 0.71073$ Å) radiation and an Atlas CCD detector. An Oxford Cryosystem cooling device was used for low-temperature measurements. The temperature stability was 0.1 K. The LIESST measurements in 15K were performed on the same diffractometer, but using a Helijet cooling device (Agilent Technologies).

After the structural measurement at 15K, the LIESST experiments were carried out at the same temperature using a laser emitting at λ = 520nm. The single crystal was continuously irradiated during the X-ray structural measurement. The laser light was delivered to the crystal by the system of the optical fibers. The system of the lenses was used to connect the laser with the optical fiber. The output power in the optical fiber was adjusted to 10 mW.

The controlling of the measurement procedure and data reduction was performed by CrysAlis^{Pro} software [Version 1.171.36.32, Agilent Technologies, Wrocław, 2013]. The same program was used to determine and refine the lattice parameters.

The structures were solved using the SHELXS-2013 program and refined with the SHELXL-2014/7 program.^[36] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced to the structure by appropriate rigid body constraints (AFIX 3 or AFIX 43) with temperature factors $U_{\rm iso}(\rm H) = 1.2U_{eq}(\rm C)$.

High pressure diffraction experiments. High-pressure single-crystal diffraction experiments for 1 have been performed at High Pressure ID09A beamline at the European Synchrotron Radiation Facility (ESRF) using parallel monochromatic X-ray beam (E = 30 keV, λ = 0.414 Å) focused to 30 \times 30 μm^2 on the sample. High-pressure membrane Diamond Anvil Cells (mDACs) equipped with Boehler-Almax seats and diamond-anvil design with an opening angle of 64° was used for all of the diffraction measurements. $^{[37]}$ The culet size was 600 μm and the samples were loaded together with silicon oil as pressure transmission medium into a hole in a stainless-steel gasket preindented to ${\sim}90~\mu\text{m}$ with an initial diameter of 300 µm. The pressure was gradually increased using PACE6000 Modular Pressure Controller. Crystals of the complex and a small ruby sphere (pressures were measured with fluorescence method using the nonlinear hydrostatic calibration by Mao et $al^{(37)}$) were loaded into the membrane mDAC, topped with silicon oil as pressure transmitting medium and closed between two diamond anvils. All data have been collected by a vertical-acting ω -axis rotation with an integrated step scan of 0.5° and a counting time of 1 s per frame. Diffraction intensities have been recorded with a Mar555 flat-panel detector. Diffraction data have been processed and analyzed with CrysAlisPro-171.37.35 software. Experimental data have not been corrected for absorption because of the high energy of the X-ray beam.

Single crystals of $[Fe(3ditz)_3](CIO_4)_2$ with the highest dimension not exceeding 50 microns have been selected and loaded into Diamond Anvil Cell with a small ruby chip and pressure transmitting medium. Single-crystal diffraction data were collected at ambient pressure and 0.07 GPa, 0.17 GPa, 0.26 GPa, 0.44 GPa, 0.54 GPa, 0.64 GPa, 0.78 GPa, 0.95 GPa and 1.13 GPa.

CCDC 1515864-1515959 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: N ligand • iron • spin crossover • structure elucidation

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Entry for the Table of Contents

FULL PAPER

Elastic bridging ligand 1,3-di(tetrazol-1-yl)propane (**3ditz**) adjusts its structure due to thermally (TIST), light (LIESST) and pressure (PIST) induced SCO in 1D system [Fe(**3ditz**)₃](CIO₄)₂.



Spin crossover*

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Evidence of ligand elasticity occurred in thermally, light and pressure induced spin crossover in 1D coordination polymers [Fe(3ditz)₃]X₂