Article

Not peer-reviewed version

Single Crystal Structure Analysis of Three Novel Iron(II) Coordination Polymers with Bridging 1,3,5-Tris(1H-1,2,4-triazol-1-yl)methyl)benzene

Aysenur Limon , Dustin N. Jordan , Till Strothmann , Laure P. Cuignet , Yann Garcia , Christoph Janiak *

Posted Date: 27 September 2023

doi: 10.20944/preprints202309.1826.v1

Keywords: coordination polymers; coordination networks; triazole ligand; iron(II); self-assembly; hydrogen bonds

Article

Single Crystal Structure Analysis of Three Novel Iron(II) Coordination Polymers with Bridging 1,3,5-Tris(1*H*-1,2,4-triazol-1-yl)methyl)benzene

Aysenur Limon [1], Dustin N. Jordan [1], Till Strothmann [1], Laure P. Cuignet [1,2], Yann Garcia [2] and Christoph Janiak [1,*]

[1] Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität, 40204 Düsseldorf, Germany; aysenur.limon@uni-duesseldorf.de (A.L.); dustin.jordan@uni-duesseldorf.de (D.N.J.); till.strothmann@uni-duesseldorf.de (T.S.); laure.cuignet@sciensano.be (L.P.C.); janiak@uni-duesseldorf.de (C.J.)

[2] Institute of Condensed Matter and Nanosciences, Molecular Chemistry, Materials and Catalysis (IMCN/MOST), Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium; yann.garcia@uclouvain.be (Y.G.)

* Correspondence: janiak@uni-duesseldorf.de (C.J.)

Abstract: Three novel iron(II) coordination polymers, $[Fe(H_2O)_2(ttmb)_2](ClO_4)_2\cdot4H_2O$ (**1**), $[Fe(H_2O)_2(ttmb)_2](BF_4)_2\cdot4H_2O$ (**2**), $[Fe(ttmb)_2(NCS)_2]$ (**3**), were synthesized with the linker 1,3,5-tris(1*H*-1,2,4-triazol-1-yl)methyl)benzene (ttmb). The single-crystal structures show that all three compounds form a double chain structure with the adjacent iron atoms being bridged by two ttmb linkers. The iron(II) ions are octahedrally surrounded by four N4 donor atom from the 1,2,4-triazol-1-yl groups of four different ttmb linkers which form an equatorial plane and two trans-coordinated aqua ligands in **1** and **2** or isothiocyanato ligands in **3** in the axial positions. In view of the neutral bridging ttmb linker, there is a counter-anion in all structures; uncoordinated ClO_4^- and BF_4^-in **1** and **2** or coordinated NCS^-in **3**. Compounds **1** and **2** are isostructural. Interestingly, the ttmb linker only utilizes two of its three potentially coordinating triazole groups. All iron(II) coordination networks are colorless or have a light-yellow color, being indicative of the high-spin state.

Keywords: coordination polymers; coordination networks; triazole ligand; iron(II); self-assembly; hydrogen bonds

1. Introduction

According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), a coordination polymer is a one-, two- or three-dimensional (1D, 2D or 3D) coordination compound consisting of repeating units [1–4]. Coordination polymers are often formed by self-assembly processes and are constructed from metal ions as connectors and organic ligands as linkers [5–7]. They can provide a wide range of topologies and structures [8–11]. Self-assembly describes a process in which the molecules arrange themselves into an ordered pattern based on interactions without external forces [6,12–17]. For the construction of 2D or 3D networks, tripodal ligands with three coordinating groups are attractive linkers to connect between three metal ions as a basis for higher dimensionality [18–24]. Triazole based ligands are appropriate as linkers in coordination polymers since they can be deprotonated to the corresponding azolate anions in which the nitrogen atoms are strong donor atoms for d-metal ions [25–34]. Not only the dimensionality but also the stability of networks increases with the number of donor atoms and coordination sites [35]. The geometry of coordination polymers not only depends on the structure of the linker, it also depends on the presence of non-coordinating anions [36]. Particularly non-coordinating anions not only balance the charges of the complex, but they also function as templates [37–41]. A template provides an organized arrangement of atoms to achieve a specific linkage of atoms [39,40]. In addition to the anions, solvent molecules can act as templates and control the arrangement of a network [31,42–48]. Depending on the size and properties of the anion the effect on the geometry can vary [49,50]. Even if the anion is uncoordinated to the metal ion, then there are intermolecular interaction with the surrounding network [51], such as anion-π, hydrogen bonding or Lewis base-acid interactions [52,53]. Also, hydrogen bonds within the coordination network have an influence on the structure [7,54].

2. Materials and Methods

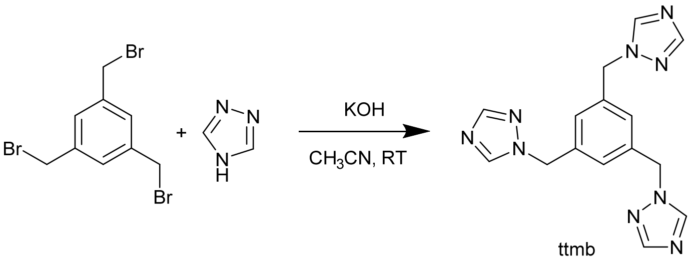
The used chemicals were all commercially obtained and no further purification was done (see Suppl. Mater., Section S1). The used water was deionized.

FT-IR measurements were carried out on a Bruker TENSOR 37 IR spectrometer (Bruker, Billerica, MA, USA) in ATR mode (Platinum ATR-QL, Diamond) in the range 4000-500 cm^{-1}. NMR spectra were collected with a Bruker Avance III – 300 (Bruker, Billerica, MA, USA) (^{1}H: 300 MHz); ^{13}C{^{1}H}: 75 MHz). Elemental analyses were measured on a PerkinElmer 2400 series II elemental analyzer (PerkinElmer, Waltham, MA, USA) (accuracy of 0.5%). Thermogravimetric analyses were carried out using a Netzsch TG209 F3 Tarsus (Netzsch, Selb, Germany) under nitrogen atmosphere with a ramp of 5 K min^{-1} up to 1000°C. X-ray powder diffraction measurements were performed on a Rigaku MiniFlex600 (Rigaku, Tokyo, Japan) (600 W, 40 kV, 15 mA) at room temperature with Cu-Kα radiation (λ = 1.54184 Å). The low-background silicon holder in the PXRD device is the cause of the rising baseline below 5° 2Theta. The highest reflex was normalized to 1. The simulated powder patterns were derived from the single crystal data using the MERCURY 2020.3.0 software [55].

Under a polarized-light Leica M80 microscope (Leica, Wetzlar, Germany) suitable single crystals were carefully selected and covered with oil on a cryo-loop. The single crystal diffraction measurement for compounds **1** and **3** were carried out on a Rigaku XtaLAB Synergy S diffractometer (Rigaku, Tokyo, Japan) with a hybrid pixel array detector and a micro-focus sealed X-ray tube, PhotonJet copper X-ray source (λ = 1.54184 Å). For cell refinement, data reduction and absorption correction CRYSALISPRO was used [56]. For compound **2** the measurement was performed on a Bruker Kappa APEX2 CCD X-ray diffractometer (Bruker, Billerica, MA, USA) with a microfocus sealed tube molybdenum X-ray source (λ = 0.71073 Å) and a multi-layer mirror monochromator. Cell refinement was performed with APEX2, data reduction with SAINT and adsorption correction with SADABS [57–59]. The crystal structures for compounds **1-3** were solved using OLEX2 with SHELXT and the refinement was done with SHELXL [60–63]. The graphics were drawn with the DIAMOND 4.0 software [64].

2.1. Synthesis

2.1.1 Synthesis of 1,3,5-tris(1*H*-1,2,4-triazol-1-yl)methyl)benzene (ttmb)



(1)

The linker ttmb was synthesized with a modified synthesis procedure of Shang *et al.* [65] as shown in Equation (1). 0.85 g (12.3 mmol) of 1,2,4-triazole and 1.32 g(23.5 mmol) of potassium hydroxide were stirred in 30 mL of acetonitrile for 30 min at room temperature. Afterwards, a solution of 1.0 g (2.8 mmol) of 1,3,5-tris(bromomethyl)benzene in 20 mL of acetonitrile was added. The resulting solution was stirred for an additional 30 min at room temperature. After filtration the solvent was removed in vacuo. Next, the resulting oil was dissolved in 20 mL of deionized water and extracted with chloroform (5 x 50 mL). Once the organic phase was dried with $MgSO_4$, the solvent was again removed using rotatory evaporation. The product crystallized over night and was then dried in vacuum at 60 °C. Yield: 0.45 g (46%). $C_{15}H_{15}N_9$: calc. C 56.1, H 4.7, N 39.2; exp. C 55.5, H 4.6, N 38.5 %. IR: ṽ [cm^{-1}]: 3114, 3096, 3034, 2994, 2955, 3034, 2993, 2956, 2849, 1798, 1757, 1711, 1609, 1503, 1466, 1445, 1430, 1373, 1338, 1298, 1270, 1207, 1170, 1137, 1096, 1018, 987, 960, 917, 895, 880, 858, 800, 742, 680, 648, 601, 570. ^{1}H-NMR (300 MHz, DMSO-d^6): δ [ppm]: 8.63 (s, 3H), 7.97 (s, 3H), 7.12 (s, 3H), 5.39 (s, 6H). ^{13}C{^{1}H}-NMR (75 MHz, DMSO-d^6: δ [ppm]: 151.81, 144.31, 137.26, 51.62.

2.1.2. Synthesis of $[Fe(H_2O)_2(ttmb)_2](ClO_4)_2{\cdot}4H_2O$ (1)

Please note, that perchlorates are potentially explosive and should be handled with care! TGA shows an explosion at around 200 °C after the sample was dried at 60 °C in vacuo beforehand. The amount of 49 mg (0.19 mmol) of $Fe(ClO_4)_2{\cdot}xH_2O$ and 84 mg (0.26 mmol) of ttmb were dissolved in 3 mL of H_2O and stored in an pre-heated oven at 60 °C for 20 h. After cooling down to room temperature over a period of 4 h, yellow crystals were obtained. The crystals were washed with water (3 x 3 mL) and stored in H_2O. Yield: 73 mg (38%). $C_{30}H_{42}Cl_2FeN_{18}O_{14}$: calc. C 40.2, H 3.4, N 28.0; exp. C 39.5, H 3.6, N 27.8 %. IR: $\tilde{\nu}$ [cm^{-1}]: 3509, 3455, 3357, 3269, 3126, 3036, 2357, 1767, 1679, 1632, 1612, 1517, 1466, 1438, 1373, 1359, 1340, 1302, 1283, 1218, 1179, 1163, 1134, 1078, 1026, 989, 977, 962, 915, 886, 853, 778, 765, 747, 693, 677, 654, 621, 577.

2.1.3. Synthesis of $[Fe(H_2O)_2(ttmb)_2](BF_4)_2{\cdot}4H_2O$ (2)

For the synthesis of **2** two solutions were prepared. The first solution contained 122.1 mg (0.36 mmol) of $Fe(BF_4)_2{\cdot}6H_2O$ and 62.9 mg (0.36 mmol) of ascorbic acid in 1.5 mL of H_2O. The second solution was composed of 57.9 mg (0.18 mmol) of ttmb dissolved in 1.5 mL of EtOH. Both solutions were heated up to 80 °C and then combined. The mixture was stored in the preheated oven at 60 °C for 24 h and cooled down for 4 h. The resulting colorless crystals were washed with a 1:1 (v:v) mixture of H_2O:EtOH (3 x 3 mL) and later stored in that mixture as well. Yield: 68.5 mg (56 %). $C_{30}H_{42}B_2F_8FeN_{18}O_{14}$: calc. C 36.8, H 4.3, N 25.8; exp. C: 36.9, H 4.2, N 25.4 %. IR: $\tilde{\nu}$ [cm^{-1}]: 3537, 3460, 3264, 3129, 3033, 2360, 1766, 1634, 1612, 1518, 1469, 1439, 1374, 1360, 1341, 1284, 1218, 1180, 1163, 1144, 1133, 1047, 1023, 990, 977, 913, 884, 852, 795, 778, 765, 747, 693, 677, 654, 577.

2.1.4. Synthesis of $[Fe(ttmb)_2(NCS)_2]$ (3)

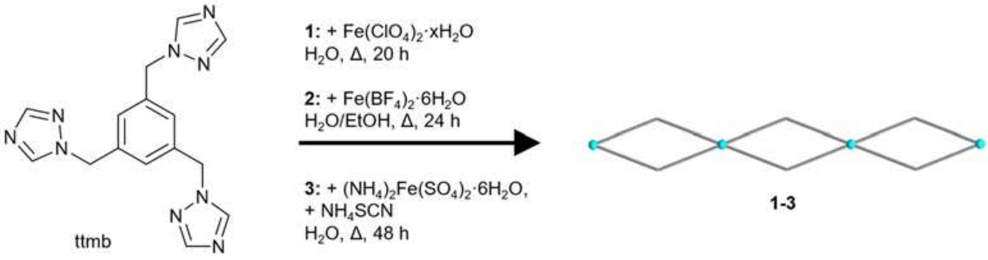
A modified procedure of Garcia *et al*. [66] was used. Three solutions were prepared. Solution 1 contained 19.6 mg (0.05 mmol) of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 32 mg (0.18 mmol) of ascorbic acid in 1 mL of H_2O. The second solution embodied 7 mg (0.09 mmol) of NH_4SCN in 1 mL H_2O. Solution 3 was composed of 29 mg (0.09 mmol) of ttmb in 1 mL of deionized water. After heating each solution near its boiling point, solution 2 was added to solution 1. Solution 3 was then added dropwise to this combined solution. After 48 h at 60 °C colorless crystals were obtained. The crystals were washed with water (3 x 3 mL) and stored in H_2O. Yield: 26 mg (65%). $C_{32}H_{30}FeN_{20}S_2$: calc.: C = 47.2, H = 3.7, N = 34.4; exp.: C = 46.5, H = 3.8, N = 33.9. IR: $\tilde{\nu}$ [cm^{-1}]: 3580, 3436, 3140, 3126, 3110, 2961, 2845, 2338, 2162, 2046, 1779, 1757, 1611, 1522, 1502, 1466, 1430, 1359, 1340, 1311, 1298, 1275, 1202, 1178, 1159, 1131, 1019, 988, 974, 956, 923, 884, 847, 789, 759, 747, 682, 673, 652, 633, 583, 569.

3. Results and Discussion

The linker 1,3,5-tris(1*H*-1,2,4-triazol-1-yl)methyl)benzene (ttmb) was synthesized by a nucleophilic substitution reaction between 1*H*-1,2,4-triazole and 1,3,5-tris(bromomethyl)benzene in acetonitrile (see Equation (1)). The authentification was done by ^{1}H, ^{13}C NMR and IR spectroscopy. The results of thermographic analysis show a thermal stability up to 310 °C (see Supplementary Materials, Section S2).

A schematic presentation of the synthesis of the complexes **1-3** is given in

Scheme **1**. The compounds had to be prepared with different molar metal:ligand ratios, which were optimized beforehand, in order to obtain crystals of sufficient quality for single crystal X-ray analysis. The molar M:L ratio for **1** was 2:3, for compound **2** it was 2:1 and for **3** it was 1:2. The synthesis for the crystals of **1** was carried out by combining the metal salt and the linker in water. For compound **2** the preparation was different: Two separate warm solutions were assembled and later combined. The first solution contained the metal salt with ascorbic acid and the second one contained the linker. This approach was chosen to avoid rapid precipitation as powders. A similar synthesis was done for **3**: Additionally, a third warm solution with NH_4NCS was prepared and in order to form the intermediate product, ferrous nitrate, the solution of the metal salt and ascorbic acid were combined with this solution first. After that the solution of the linker was added [67]. The crystals have a colorless or a light-yellow color and the microscopic images of the crystals can be found in the Supplementary Materials, Section S5.



Scheme 1. Schematic presentation of the synthesis of the coordination polymers **1-3** with their double chain structures. The blue spheres represent Fe(II) atoms.

The IR spectra of the coordination polymers **1-3** (see Supplementary Materials, section S3) show their indicative bands for the ttmb linker at around 977 cm^{-1} for ν(C=C) and 1519 cm^{-1} for ν(C=N). Additionally, the characteristic bands for the anions of the compounds can be detected for the ClO_4^- of **1** at ν(Cl–O) = 621 cm^{-1}, 1078 cm^{-1}. The band of the anion BF_4^- of **2** can be observed at ν(B–F) = 1047 cm^{-1} and the anion of **3** at ν(NCS) = 2046 cm^{-1} [68].

Thermogravimetric analysis (at a heating rate of 5 K min^{-1}, see Supplementary Materials, Section S4) revealed that the decomposition for compounds **1** and **2** already starts at around 70 °C due to the loss of crystal water. The main decomposition starts for compound **1** at 190 °C and for **2** at 250 °C. Compound **3**, which does not contain solvent of crystallization, is thermally stable up to 300 °C where the decomposition of the ligand starts.

The experimental powder X-ray diffraction patterns of **1-3** could be positively matched to the simulated pattern from the single-crystal X-ray analysis which indicated a high the phase purity for the crystalline part of each compound (see Supplementary Materials, Section S8). At the same time, light microscopy images of the batches of compound **1-3** showed almost exclusively crystalline matter (see Supplementary Materials, Section S5).

3.1. Crystal structure of $[Fe(H_2O)_2(ttmb)_2](X)_2{\cdot}4H_2O$ *(1: X =* ClO_4*; 2: X =* BF_4*)*

Single crystal X-ray analysis reveals that the isostructural complexes **1** and **2** crystallize in the monoclinic space group $P2_1/n$. The asymmetric unit consists of one half of an Fe(II) atom (on an inversion center), one ttmb ligand, one coordinated and two uncoordinated water molecules, and one uncoordinated ClO_4^- or BF_4^- anion (Figure 1). Due to the steric hindrance of the ttmb ligand and the interactions with the anions, the metal center possesses a somewhat distorted octahedral geometry with a FeO_2N_4 coordination environment (see Supplementary Materials, Section S7).

The equatorial positions are occupied by four nitrogen atoms which are provided by four pyrazole groups of four ttmb units. The oxygen atoms of the water molecules are trans-positioned around the Fe(II) atom (Figure 1).

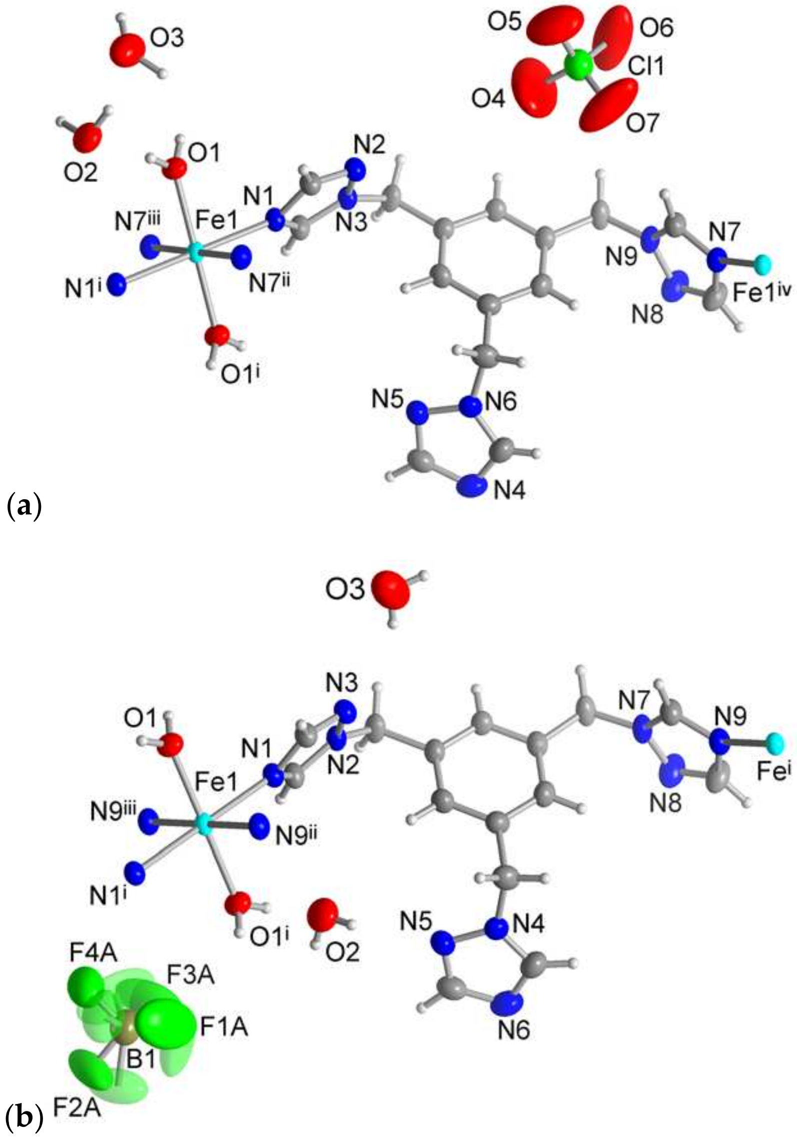


Figure 1. Extended asymmetric unit of (**a**) **1** and (**b**) **2** (50 % thermal ellipsoids and H atoms with arbitrary radii). The distorted F atoms of the BF_4^- anion of compound **2** are presented as transparent atoms. Symmetry transformation: (**a**): i=-x+1, -y+1, -z; ii=-x+1, -y+1, -z+1; iii=x, y, z-1; iv=x, y, z+1; v=-x+2, -y+1, -z+1; vi=x-1/2, -y+3/2, z-1/2; vii=-x+3/2, y-1/2, -z+3/2, viii=x+1, y, z+1. (**b**): i = −x+2, −y+1, −z+2; ii = −x+2, −y+1, −z+1; iii = x, y, z+1; iv = x, y, z−1; v = −x+1, −y+1, −z+1; vi = −x+3/2, y+1/2, −z+3/2.

For compound **1** the distances of the Fe—N bonds range from 2.14 and 2.22 Å. The Fe—N bond lengths for comound **2** are close to the ones in **1** with distances from 2.08 to 2.22 Å. The Fe–O length is about 2.07 Å for **1** and 2.08 Å for **2**.

Every ttmb ligand functions as a twofold bridge and connects two Fe(II) atoms with an anti-conformation of the coordinating pyrazole groups. The spanned distance between the Fe atoms is 13.46 Å. Every Fe(II) atom is connected to its neighbor by two ttmb linkers in a double chain structure (Figure 2). Since the perchlorate and tetrafluoroborate anion have similar sizes, similar geometries and also similar chemical hardness, it was expected that both compounds **1** and **2** have the same structure [69]. The ionic radius of ClO_4^- is 2.37 Å the one of BF_4^- is 2.29 Å [36].

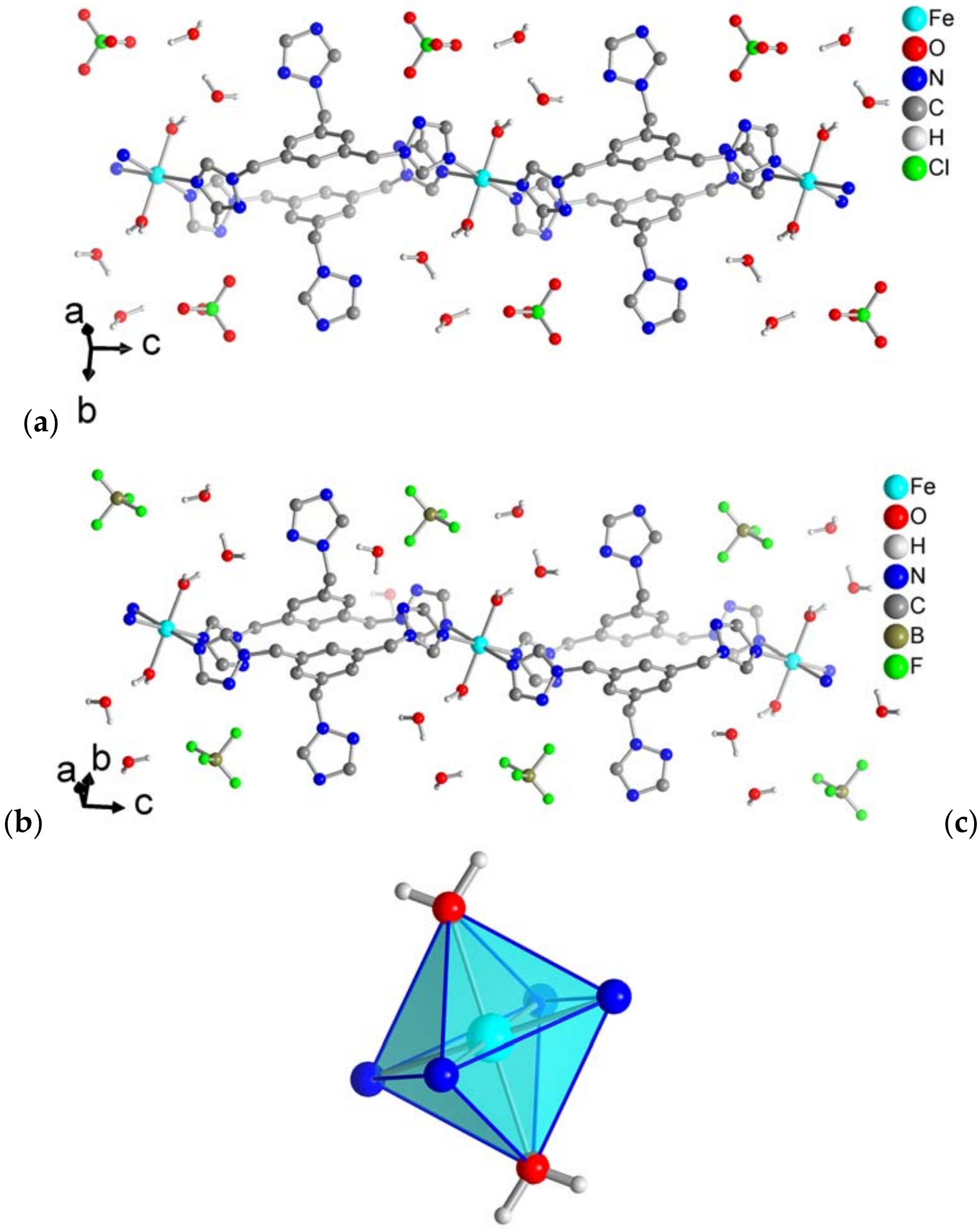


Figure 2. View of the double chain of (**a**) **1** and (**b**) **2** with the surrounding crystal water and anions. For clarity the H atoms have been omitted on the ttmb linkers. (**c**) Presentation of the octahedral iron(II) environment in **1** (identical to **2**).

The ClO_4^- and BF_4^- anions have C–H···O and C–H···F, respectively, hydrogen bond interactions from the triazole groups of the ttmb linker [69]. For compound **1** Figure 3 shows that a ClO_4^- anion interacts with one C-H of each triazole ring of the ttmb linker. For the C–H···O interactions in **1** the hydrogen bond lengths range from 2.44 to 2.65 Å (Supplementary Materials, Table S4). The C–H···F contacts in **2** are in the range of 2.45–2.55 Å (Supplementary Materials, Table S4).

doi:10.20944/preprints202309.1826.v1

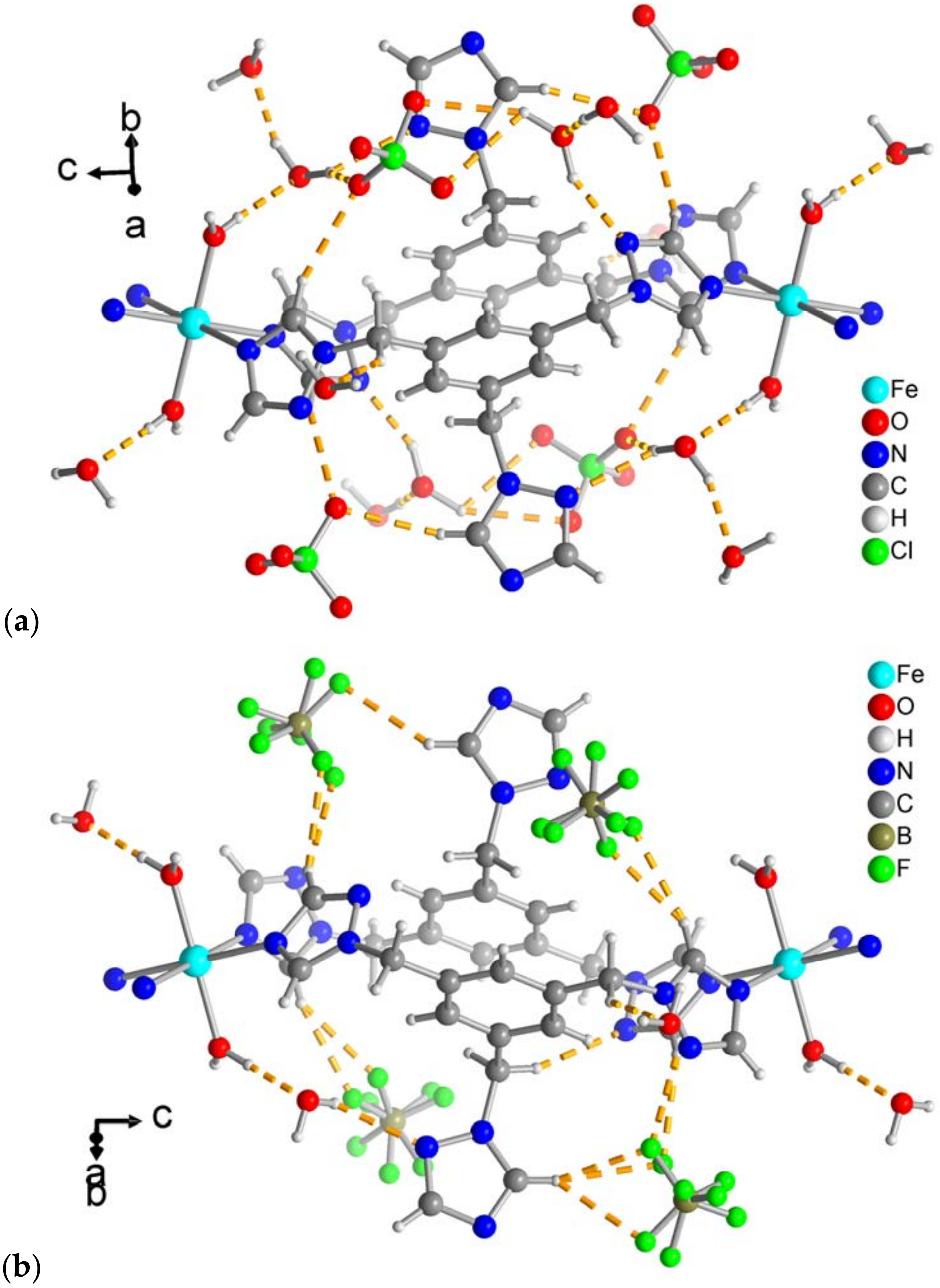


Figure 3. Hydrogen-bonding interactons in (**a**) 1 and (**b**) **2** as orange dashed lines. See Supplementary Materials, Table S4 for distances and angles.

3.2. Crystal Structure of [Fe(ttmb)$_2$(NCS)$_2$] (3)

The X-ray crystallographic analysis reveals that compound **3** crystallizes in the triclinic space group P$\bar{1}$. The asymmetric unit is composed one half of an Fe(II) atom (on an inversion center), one ttmb ligand and one coordinated NCS$^-$ anion, as shown in Figure 4. The Fe(II) metal is octahedrally coordinated by six nitrogen donor atoms from four triazole rings in the equatorial plane and two trans-coordinated NCS$^-$ in the axial positions.

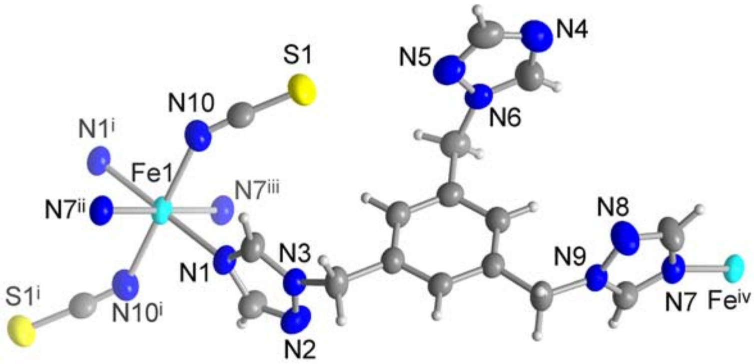


Figure 4. Extended asymmetric unit of **3** (50 % thermal ellipsoids and H atoms with arbitrary radii). Symmetry transformations: i = -x+1, -y+2, -z; ii = x, y+1, z-1; iii = -x+1, -y+1, -z+1; iv = x, y-1, z+1; v = -x, -y+1, -z+1; vi = x, y-1, z.

The distances of the Fe–N bonds lie between 2.07 and 2.23 Å. Similar to the structures of **1** and **2**, two Fe(II) atoms are linked by two ttmb linkers in an anti-conformation to form a double chain structure (**Figure 5**). The distance between two Fe(II) atoms is 13.79 Å.

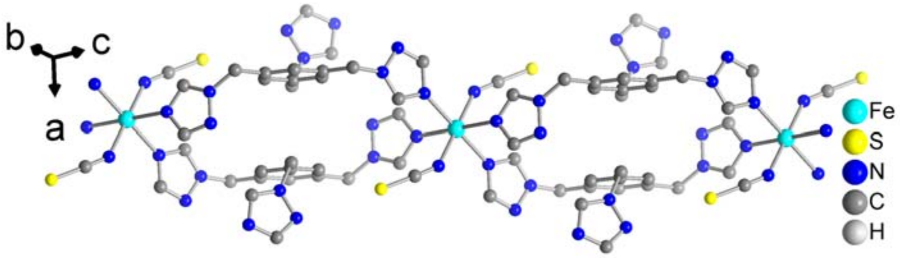


Figure 5. The double chain of 3. For the sake of clarity the H atoms have been omitted.

4. Conclusions

The new iron(II) coordination polymers $[Fe(H_2O)_2(ttmb)_2](ClO_4)_2 \cdot 4H_2O$ (**1**), $[Fe(H_2O)_2(ttmb)_2](BF_4)_2 \cdot 4H_2O$ (**2**), $[Fe(ttmb)_2(NCS)_2]$ (**3**) with the linker 1,3,5-tris(1*H*-1,2,4-triazol-1-yl)methyl)benzene (ttmb) were structurally characterized by single-crystal X-ray diffraction. It was hoped for that the potentially tritopic ttmb linker would utilize its three triazole N-donor groups for metal coordination to form at least 2D if not even 3D coordination networks. Somewhat to a surprise, only two of the triazole groups coordinated to iron. This could have still given a 2D framework if each of the four ttmb linkers around an iron atom would connect to a different iron. Yet, two ttmb linkers each did connect to the same iron atom through a double bridge. Subsequently, 1D coordination polymers with a double chain structure and a 1:2 Fe:ttmb stoichiometry resulted. We note that the metal ions were even offered in excess during the optimized synthesis with a molar M:L ratio of 2:3 for **1** and 2:1 for **2**. We hypothesize that it is not so much the counter anions which exert a templating effect in the structures of **1-3** but the water solvent (or water/ethanol for **2**) from which the compounds were crystallized. Future work using different solvents and also other metal ions for the crystallization should try to invoke the coordination of all triazole groups of the ttmb linker.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Section S1: Used Chemicals; Section S2: Ligand analyses; Section S3: Infrared spectra of **1-3**; Section S4: Thermogravimetric analyses of **1-3**; Section S5: Crystal images of **1-3**; Section S6: Crystal data of **1-3**; Section S7: Distortion of the coordination polyhedron of **1-3**; Section S8: Powder X-ray diffraction patterns of **1-3**; Section S9: References.

Author Contributions: Conceptualization, A.L., D.N.J., L.P.C., Y.G. and C.J.; methodology, A.L., D.N.J. and L.P.C.; validation, A.L., D.N.J. and L.P.C.; formal analysis, A.L, D.N.J., T.S. and L.P.C.; investigation, A.L, D.N.J., T.S. and L.P.C.; resources, C.J.; data curation, A.L., D.N.J. and T.S.; writing—original draft preparation, A.L.;

writing—review and editing, C.J.; visualization, A.L. and C.J.; supervision, C.J.; project administration, C.J.; funding acquisition, C.J. and Y.G. All authors have read and agreed to the published version of the manuscript.

Funding: Fonds De La Recherche Scientifique—FNRS (PDR T.0095.21, CDR J.0064.23) and by the Deutsche Forschungsgemeinschaft (DFG) under grant 440366605 (for the Rigaku diffractometer), grant INST 208/589-1 (for the Bruker diffractometer) and within the Priority Program SPP 1928/2 COORNETs (C.J. grant Ja466/43-1).

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The CCDC numbers 2297073-2297075 for **1**–**3**, respectively, contain the supplementary crystallographic data reported in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 25 September 2023).

Acknowledgments: The authors thank Birgit Tommes for IR measurements.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Batten, S.R.; Neville S.M.; Turner, D.R. *Coordination polymers. Design, analysis and application*; Royal Society of Chemistry: Cambridge, UK, 2009. ISBN: 978-0-85404-837-3.
2. Batten, S.R.; Champness, N.R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Öhrström, L.; O'Keeffe, M.; Suh, M.P.; Reedijk, J. Coordination polymers, metal–organic frameworks and the need for terminology guidelines. *CrystEngComm* **2012**, *14*, 3001. doi:10.1039/c2ce06488j.
3. Batten, S.R.; Champness, N.R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Öhrström, L.; O'Keeffe, M.; Paik Suh, M.; Reedijk, J. Terminology of metal–organic frameworks and coordination polymers (IUPAC Recommendations 2013). *Pure Appl. Chem.* **2013**, *85*, 1715–1724. doi:10.1351/PAC-REC-12-11-20.
4. Kuznetsova, A.; Matveevskaya, V.; Pavlov, D.; Yakunenkov, A.; Potapov, A. Coordination Polymers Based on Highly Emissive Ligands: Synthesis and Functional Properties. *Materials* **2020**, *13*. doi:10.3390/ma13122699.
5. Leong, W.L.; Vittal, J.J. One-dimensional coordination polymers: complexity and diversity in structures, properties, and applications. *Chem. Rev.* **2011**, *111*, 688–764. doi:10.1021/cr100160e.
6. Kitagawa, S.; Kitaura, R.; Noro, S. Functional porous coordination polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375. doi:10.1002/anie.200300610.
7. Robin, A.Y.; Fromm, K.M. Coordination polymer networks with O- and N-donors: What they are, why and how they are made. *Coord. Chem. Rev.* **2006**, *250*, 2127–2157. doi:10.1016/j.ccr.2006.02.013.
8. Naik, A.D.; Dîrtu, M.M.; Railliet, A.P.; Marchand-Brynaert, J.; Garcia, Y. Coordination Polymers and Metal Organic Frameworks Derived from 1,2,4-Triazole Amino Acid Linkers. *Polymers* **2011**, *3*, 1750–1775. doi:10.3390/polym3041750.
9. Hoskins, B.F.; Robson, R. Infinite polymeric frameworks consisting of three dimensionally linked rod-like segments. *J. Am. Chem. Soc.* **1989**, *111*, 5962–5964. doi:10.1021/ja00197a079.
10. Horike, S.; Shimomura, S.; Kitagawa, S. Soft porous crystals. *Nat. Chem.* **2009**, *1*, 695–704. doi:10.1038/nchem.444.
11. Kitagawa, S.; Noro, S.; Nakamura, T. Pore surface engineering of microporous coordination polymers. *Chem. Commun.* **2006**, 701–707. doi:10.1039/b511728c.
12. Lehn, J.-M. Supramolecular chemistry: Concepts and perspectives : a personal account built upon the George Fisher Baker lectures in chemistry at Cornell University [and] Lezioni Lincee, Accademia nazionale dei Lincei, Roma; *VCH*: Weinheim, New York, **1995**, ISBN 3527293124.
13. Mu, Y.; Han, G.; Ji, S.; Hou, H.; Fan, Y. Coordination polymers based on a flexible bis(triazole) ligand and aromatic polycarboxylate anions: syntheses, topological structures and photoluminescent properties. *CrystEngComm* **2011**, *13*, 5943. doi:10.1039/c1ce05129f.
14. Du, M.; Bu, X.-H.; Huang, Z.; Chen, S.-T.; Guo, Y.-M.; Diaz, C.; Ribas, J. From metallacyclophanes to 1-D coordination polymers: role of anions in self-assembly processes of copper(II) and 2,5-bis(3-pyridyl)-1,3,4-oxadiazole. *Inorg. Chem.* **2003**, *42*, 552–559. doi:10.1021/ic025851h.
15. Chand, D.K.; Biradha, K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. A molecular sphere of octahedral symmetry. *Chem. Commun.* **2002**, 2486–2487. doi:10.1039/B206625B.
16. Friese, V.A.; Kurth, D.G. From coordination complexes to coordination polymers through self-assembly. *Current Opinion in Colloid & Interface Science* **2009**, *14*, 81–93. doi:10.1016/j.cocis.2008.11.001.

17. Li, W.; Kim, Y.; Li, J.; Lee, M. Dynamic self-assembly of coordination polymers in aqueous solution. *Soft Matter* **2014**, *10*, 5231–5242. doi:10.1039/c4sm01068j.
18. Liu, H.-L.; Sun, W.-Y.; Zhu, H.-L.; Yu, K.-B.; Tang, W.-X. A two-dimensional network constructed via 72-membered heart-shaped macrocycles, a copper(II) complex with 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene and diethylenetriamine ligands. *Inorg. Chim. Acta* **1999**, *295*, 129–135. doi:10.1016/S0020-1693(99)00332-1.
19. Shi, X.; Tan, D.; Liu, Y.; Liang, G.; Zhang, X. Syntheses, structures and fluorescence properties of two novel polymers based on a flexible tripodal ligand 1,3,5-tris((1H-1,2,4-triazol -1-yl)methyl)benzene. *J. Mol. Struct.* **2014**, *1074*, 134-139. doi:10.1016/j.molstruc.2014.05.058.
20. Shi, X.; Zhang, X.; Li, X.; Hou, H.; Fan, Y. Structure analysis and catalytic property of a microporous framework based on a flexible tripodal ligand with novel conformations. *J. Mol. Struct.* **2011**, *996*, 110-114. doi: 10.1016/j.molstruc.2011.04.027.
21. Yin, X.-J.; Zhou, X.-H.; Gu, Z.-G.; Zuo, J.-L.; You, X.-Z. Syntheses and physical properties of three-dimensional coordination polymers with the flexible tripodal ligand 1,3,5-tris(1,2,4-triazol-1-ylmethyl)benzene. *Inorg. Chem. Commun.* **2009**, *12*, 548-551. doi:10.1016/j.inoche.2009.04.012.
22. Shi, Z.; Pan, Z.; Zhang, C.; Zheng, H. Syntheses, structures, and properties of six cobalt(II) complexes based on a tripodal tris(4-(1H-1,2,4-triazol-1-yl)phenyl)amine ligand. *Dalton Trans.* **2015**, *44*, 16854–16864. doi:10.1039/c5dt02774h.
23. Li, B.Z.; Liu, X.G.; Wang, Z.H.; Li, B.L.; Zhang, Y. A novel two-dimensional network cadmium(II) coordination polymer containing one 1,4-bis(1,2,4-triazol-1-yl)butane and double dicyanamide bridges. *Acta Crystallogr. C* **2006**, *62*, m10-2. doi:10.1107/S0108270105038102.
24. Woschko, D.; Millan, S.; Ceyran, M.-A.; Oestreich, R.; Janiak, C. Synthesis of a Chiral 3,6T22-Zn-MOF with a T-Shaped Bifunctional Pyrazole-Isophthalate Ligand Following the Principles of the Supramolecular Building Layer Approach. *Molecules* **2022**, *27*, 5374. https://doi.org/10.3390/molecules27175374.
25. Aromí, G.; Barrios, L.A.; Roubeau, O.; Gamez, P. Triazoles and tetrazoles: Prime ligands to generate remarkable coordination materials. *Coordination Chemistry Reviews* **2011**, *255*, 485–546. doi:10.1016/j.ccr.2010.10.038.
26. Haasnoot, J.G. Mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivates as ligands. *Coord. Chem. Rev.* **2000**, *200-202* , 131-185. doi:10.1016/S0010-8545(00)00266-6.
27. Garcia, Y.; Adarsh, N.N.; Naik, A.D. Crystal engineering of Fe(II) spin crossover coordination polymers derived from triazole or tetrazole ligands. *Chimia (Aarau)* **2013**, *67*, 411–418. doi:10.2533/chimia.2013.411.
28. Ding, B.; Yi, L.; Cheng, P.; Liao, D.-Z.; Yan, S.-P. Synthesis and characterization of a 3D coordination polymer based on trinuclear triangular CuII as secondary building units. *Inorg. Chem.* **2006**, *45*, 5799–5803. doi:10.1021/ic060030o.
29. Ouellette, W.; Liu, H.; O'Connor, C.J.; Zubieta, J. Solid-state coordination chemistry of copper(II) tetrazolates: anion control of frameworks constructed from trinuclear copper(II) building blocks. *Inorg. Chem.* **2009**, *48*, 4655–4657. doi:10.1021/ic9003802.
30. Ouellette, W.; Hudson, B.S.; Zubieta, J. Hydrothermal and structural chemistry of the zinc(II)- and cadmium(II)-1,2,4-triazolate systems. *Inorg. Chem.* **2007**, *46*, 4887–4904. doi:10.1021/ic062269a.
31. Zhang, J.-P.; Chen, X.-M. Crystal engineering of binary metal imidazolate and triazolate frameworks. *Chem. Commun.* **2006**, 1689–16990. doi:10.1039b516367f.
32. Wang, H.-P.; Wang, H.-L.; Li. B.-L. Synthesis, Structure, Lumiescence and Thermal Stability Properties of a New (3,4)-Connected 2D Zn Coordination Polymer. *J. Struct. Chem.* **2020**, *10*, 1835-1840. doi: 10.14102/j.cnki.0254 5861.2011 2708.
33. Li, H.; Liu, G.; Liu, T.T.; Zhang, H.Y.; Yue, F.; Wang, J.D. Syntheses of triazole-bridged cadmium coordination polymer with luminescence properties. *Russ J Coord Chem* **2011**, *37*, 8–11. doi:10.1134/S1070328411010088.
34. Lin, H.-Y.; Luan, J.; Wang, X.-L.; Zhang, J.-W.; Liu, G.-C.; Tian, A.-X. Construction and properties of cobalt(ii)/copper(ii) coordination polymers based on N-donor ligands and polycarboxylates mixed ligands. *RSC Adv* **2014**, *4*, 62430–62445. doi:10.1039/C4RA12367K.
35. Schweifer, J.; Weinberger, P.; Mereiter, K.; Boca, M.; Reichl, C.; Wiesinger, G.; Hilscher, G.; van Koningsbruggen, P. J.; Koojiman, H.; Grunert, M.; Linert, W. *catena*-[μ-Tris(1,2-bis(tetrazol-1-yl)ethane-N4,N4′)iron(II)] bis(tetrafluoroborate): synthesis, structure, spectroscopic and magnetic characterization of

a chain-type coordination polymer spin-crossover compound. *Inorg. Chim. Acta* **2002**, *339*, 297-306. doi:10.1016/S0020-1693(02)00934-9.

36. Absmeier, A.; Bartel, M.; Carbonera, C.; Jameson, G.N.L.; Werner, F.; Reissner, M.; Caneschi, A.; Létard, J.-F.; Linert, W. Mutual Influence of Spacer Length and Noncoordinating Anions on Thermal and Light-Induced Spin-Crossover Properties of Iron(II)–α,ω-Bis(tetrazol-1-yl)alkane Coordination Polymers. *Eur J Inorg Chem* **2007**, *2007*, 3047–3054. doi:10.1002/ejic.200601096.
37. Li, D.-P.; Zhou, X.-H.; Liang, X.-Q.; Li, C.-H.; Chen, C.; Liu, J.; You, X.-Z. Novel Structural Diversity of Triazolate-Based Coordination Polymers Generated Solvothermally with Anions. *Crystal Growth & Design* **2010**, *10*, 2136–2145. doi:10.1021/cg9012894.
38. Schottel, B.L.; Chifotides, H.T.; Shatruk, M.; Chouai, A.; Pérez, L.M.; Bacsa, J.; Dunbar, K.R. Anion-pi interactions as controlling elements in self-assembly reactions of Ag(I) complexes with pi-acidic aromatic rings. *J. Am. Chem. Soc.* **2006**, *128*, 5895–5912. doi:10.1021/ja0606273.
39. Busch, D.H. Structural Definition of Chemical Templates and the Prediction of New and Unusual Materials. *Am. Chem. Soc.* **1992**, *12*, 389–395. doi: 10.1007/978-94-011-2532-1_25.
40. Anderson, S.; Anderson, H.L.; Sanders, J.K.M. Expanding roles for templates in synthesis. *Acc. Chem. Res.* **1993**, *26*, 469–475. doi:10.1021/ar00033a003.
41. Zhu, X.; Wang, L.-Y.; Liu, X.-G.; Wang, J.; Li, B.-L.; Li, H.-Y. Structural versatility of seven copper(ii) coordination polymers constructed with the long flexible ligand 1,4-bis(1,2,4-triazol-1-yl)butane. *CrystEngComm* **2011**, *13*, 6090. doi:10.1039/c1ce05466j.
42. Tanaka, D.; Kitagawa, S. Template Effects in Porous Coordination Polymers. *Chem. Mater.* **2008**, *20*, 922–931. Doi:10.1021cm7031866.
43. Halper, S.R.; Do, L.; Stork, J.R.; Cohen, S.M. Topological Control in Heterometallic Metal-Organic Frameworks by Anion Templating and Metalloligand Design. *J. Am. Chem. Soc.* **2006**, *128*, 15255–15268. doi: 10.1021/ja0645483.
44. Beer, P.D.; Gale, P.A. Anion Recognition and Sensing: The State of the Art and Future Perspectives. *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516. doi:10.1002/1521-3773(20010202)40:3<486:AID-ANIE486>3.0.CO;2-P.
45. Huang, X.-C.; Zhang, J.-P.; Chen, X.-M. A new route to supramolecular isomers via molecular templating: nanosized molecular polygons of copper(I) 2-methylimidazolates. *J. Am. Chem. Soc.* **2004**, *126*, 13218–13219. doi:10.1021/ja045249l.
46. Huang, X.-C.; Zhang, J.-P.; Lin, Y.-Y.; Chen, X.-M. Triple-stranded helices and zigzag chains of copper(I) 2-ethylimidazolate: solvent polarity-induced supramolecular isomerism. *Chem. Commun.* **2005**, 2232–2234. doi:10.1039/b501071c.
47. Vilar, R. Anion-templated synthesis. *Angew. Chem. Int. Ed Engl.* **2003**, *42*, 1460–1477. doi:10.1002anie.200200551.
48. Wang, H.; Feng, Y.; Liang, N.; Li, B.; Zhang, Y. Two nickel coordination polymers with flexible ligand 1,3,5-tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene. *Inorg. Chem. Commun.* **2009**, *12*, 1161–1163. doi:10.1016/j.inoche.2009.09.012.
49. Gimeno, N.; Vilar, R. Anions as templates in coordination and supramolecular chemistry. *Coordination Chemistry Reviews* **2006**, *250*, 3161–3189, doi:10.1016/j.ccr.2006.05.016.
50. Kim, H.-J.; Zin, W.-C.; Lee, M. Anion-directed self-assembly of coordination polymer into tunable secondary structure. *J. Am. Chem. Soc.* **2004**, *126*, 7009–7014. doi:10.1021/ja049799v.
51. Vilar, R. Anion-templated synthesis. *Angew. Chem. Int. Ed Engl.* **2003**, *42*, 1460–1477. doi:10.1002/anie.200200551.
52. Wang, H.; Feng, Y.; Liang, N.; Li, B.; Zhang, Y. Two nickel coordination polymers with flexible ligand 1,3,5-tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene. *Inorganic Chemistry Communications* **2009**, *12*, 1161–1163. doi:10.1016/j.inoche.2009.09.012.
53. Lankshear, M.D.; Beer, P.D. Strategic anion templation. *Coordination Chemistry Reviews* **2006**, *250*, 3142–3160. doi:10.1016/j.ccr.2006.04.018.
54. Shi, Q.; Cao, R.; Sun, D.-F.; Hong, M.-C.; Liang, Y.-C. Solvothermal syntheses and crystal structures of two metal coordination polymers with double-chain structures. *Polyhedron* **2001**, *20*, 3287-3293. doi:10.1016/S0277-5387(01)00945-7.
55. Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; Wood, P.A. Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.* **2020**, *53*, 226–235. doi:10.1107/S1600576719014092.

56. *Agilent*; Agilent Technologies Ltd, Yarnton, Oxfordshire, England, 2014.
57. APEX2, *data collection program for the CCD area-detector system, Version 2.1-0*, Bruker Analytical X-ray Systems, Madison (WI), USA,1997–2014.
58. SAINT, data reduction and frame integration program for the CCD area-detector system, Bruker Analytical X-ray Systems, Madison(WI), USA, 1997–2014.
59. Sheldrick, G.M. SADABS: *Area-Detector Absorption Correction*, University of Göttingen, Göttingen, Germany, 1996.
60. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2 : a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. doi:10.1107/S0021889808042726.
61. Sheldrick, G.M. SHELXT - integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71*, 3–8. doi:10.1107/S2053273314026370.
62. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71*, 3–8. doi:10.1107/S2053229614024218.
63. Sheldrick, G.M. SHELXT - integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8. doi:10.1107/S2053273314026370.
64. Brandenburg, K., Diamond (Version 4.5), Crystal and Molecular Structure Visualization, Crystal Impact – K. Brandenburg & H. Putz Gbr, Bonn, Germany, 2009–2022.
65. Shang, Q.; Zeng, T.; Gao, K.; Liu, N.; Cheng, Q.; Liao, G.; Pan, Z.; Zhou, H. A novel nitrogen heterocyclic ligand-based MOF: synthesis, characterization and photocatalytic properties. *New J. Chem.* **2019**, *43*, 16595–16603. doi:10.1039/C9NJ04371C.
66. Garcia, Y.; Bravic, G.; Gieck, C.; Chasseau, D.; Tremel, W.; Gütlich, P. Crystal structure, magnetic properties, and 57Fe Mössbauer spectroscopy of the two-dimensional coordination polymers M(1,2-bis(1,2,4-triazol-4-yl)ethane)2(NCS)2 (MII = Fe, Co). *Inorg. Chem.* **2005**, *44*, 9723–9730. doi:10.1021/ic050971l.
67. Lavrenova, L.G.; Yudina, N.G.; Ikorskii, V.N.; Varnek, V.A.; Oglezneva, I.M.; Larionov, S.V. Spin-crossover and thermochromism in complexes of iron(II) iodide and thiocyanate with 4-amino-1,2,4-triazole. *Polyhedron* **1995**, *14*, 1333–1337. doi: https://doi.org/10.1016/0277-5387(94)00398-X.
68. Hesse, M.; Meier, H.; Zeeh, B.; Bienz, S.; Bigler, L.; Fox, T. Spektroskopische Methoden in der Organischen Chemie; 8 Auflage; Georg Thieme Verlag: Stuttgart, Germany, 2012; ISBN 9783135761084.
69. Jordan, D.N.; Straßburg, P.G.; Woschko, D.; Carrella, L.M.; Cuignet, L.P.; Eickmeier, K.; Dronskowski, R.; Garcia, Y.; Rentschler, E.; Janiak, C. Interpenetration Phenomena via Anion Template Effects in Fe(II) and Co(II) Coordination Networks with a Bis-(1,2,4-triazole) Ligand. *Polymers* **2023**, *15*, 3286. https://doi.org/10.3390/polym15153286.