Supporting Information

Spin-State Dependent Pressure Responsiveness of Fe(II)-based Triazolate Metal-Organic Frameworks

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1. Material synthesis

Materials

N,*N*-dimethylformamide (DMF, 99.8% analytical grade; VWR/ extra dry 99.8%; Acros), methanol (MeOH, 99.8% analytical grade; VWR), iron(II)chloride (99.999% Sigma Aldrich/ 98%; abcr), 4-methylbenzenesulfonohydrazide (97%; Alfa Aesar), ammonia (7M in methanol, Acros), and 1,1-dimethoxypropan-2-one (97%; Alfa Aesar) were used without further purification as obtained from the commercial supplier. 1*H*-1,2,3-triazole (**H-ta**, 98%, BLDpharm) was degassed and stored over molecular sieves under an argon atmosphere.

Synthetic procedures – Linker synthesis

The **1,4,5,6-tetrahydrocyclopenta-1***H***-1,2,3-triazole** (**H**-**cta**) ligand was prepared following a literature procedure¹ and purified further *via* sublimation, while **methyl-1***H***-1,2,3-triazole** (**H**-**mta**) was synthesised by a protocol adapted from literature² and purified *via* distillation.

4-methyl-1*H*-1,2,3-triazole (H-mta)

In the first step, 1,1-dimethoxypropan-2-one (20 g, 20.2 mL, 169 mmol) and 4-methylbenzenesulfonohydrazide (30.8 g, 165 mmol) were dissolved in 250 mL MeOH in an ACE round-bottomed pressure flask (400 mL inner volume, sealed with a silicone o-ring). After 5 min OF stirring the solution, ammonia (7M in methanol; 52 mL, 364 mmol) was added and the resulting mixture was heated to 110 °C. The solution was concentrated *under reduced pressure* and cooled to room temperature. The resulting oil was separated from the crystallised by-products *via* decantation, followed by two washing cycles with CH_2Cl_2 (10 mL). The solvent was evaporated, and the resulting mixture was distilled under reduced pressure to yield a fraction of the colourless product as an oil at approximately 130 °C (4.31 g, 1.61 mmol, 32% yield).

¹**H NMR** (400 MHz, CDCl₃) δ [ppm]: 11.9 (br. s, 1H, N-H) 7.45 (s, 1H), 2.3 (s, 3H);

Synthetic procedures – MOF synthesis

 $Fe(ta)_2$ was prepared according to a previously reported synthesis route, and the $Fe(cta)_2$ and $Fe(mta)_2$ coordination frameworks were synthesised in a similar fashion³.

 $Fe(cta)_2$ was synthesised by combining $FeCl_2$ (64.5 mg, 0.509 mmol) and H-cta (164.1 mg, 1.504 mmol) in dry DMF (3 mL) under an argon atmosphere in a DURAN® culture tube and sealed with a teflon-lined screw cap. The vial was placed in a heating block and heated to 120 °C. After 3 d heating at this temperature, the resulting product was centrifuged and washed three times with DMF (3 mL) and

three times with MeOH (3 mL). After drying for 4 h *in vacuo* at room temperature, a phase pure product as a greyish powder (55 mg, 40%) was yielded.

FT-IR (ATR) 4000 – 400 cm⁻¹: 2974 (m), 2924 (w), 2859 (m), 1604 (w), 1533 (m), 1500 (w), 1441 (w), 1265 (w), 1212 (s), 1156 (s), 1126 (w), 1074 (s), 1028 (m), 900 (m), 727 (m), 677 (w), 574 (s); **EDX** Fe:Cl ratio: 1 : 0.066.

 $Fe(mta)_2$ -as (as-synthesised) was synthesised by combining $FeCl_2$ (316.9 mg, 2.5 mmol) and H-mta (623.3 mg, 7.5 mmol) in dry DMF (15 mL) under an argon atmosphere in an ACE pressure tube (38 mL inner volume, sealed with a silicone o-ring). After 3 d heating at 120 °C in a heating block, the resulting product was centrifuged and washed with DMF (5 mL) and three times with MeOH (5 mL). After drying *in vacuo* at room temperature, a phase pure product of $Fe(mta)_2$ -as as a yellow powder (117 mg, 21%) was yielded. The as-synthesised Fe(mta)_2 was then activated *in vacuo* at 280 °C for 2 h to obtain $Fe(mta)_2$.

FT-IR (ATR) 4000 – 400 cm⁻¹: 2930 (w), 1620 (w), 1532 (m), 1455 (w), 1374 (m), 1306 (w), 1222 (m), 1178 (m), 1069 (m), 1013 (m), 825 (s), 718 (w), 677 (m); **EDX** Fe:Cl ratio: 1: 0.114.

2. NMR spectroscopy

To confirm the chemical composition of the triazole-based **H-mta** linker, we performed liquid state ¹H NMR measurements. The ¹H NMR spectrum (400 MHz) was recorded on a *Mercury plus 400 high-resolution (Fa. Varian Deutschland GmbH)* spectrometer at room temperature.



Figure S1: ¹H NMR of the 4-methyl-1*H*-1,2,3-triazole (H-mta) ligand in CDCl₃.

3. Infrared spectroscopy

We used Fourier transform infrared (FT-IR) spectroscopy to characterise the vibrational spectrum of $Fe(ta)_2$, $Fe(mta)_2$, and $Fe(cta)_2$ to compare all synthesised triazole-based MOFs. We measured in the range of 4000 – 400 cm⁻¹ on a *Bruker Equinox 55 FT-IR* spectrometer equipped with the *PLATINUM ATR* unit.



Figure S2: IR spectra comparison for $Fe(ta)_2(red)$, $Fe(mta)_2(blue)$, and $Fe(cta)_2(black)$. $Fe(ta)_2$ shows a small signal at 3150 cm⁻¹ for its hydrogen atoms at the triazole ring, which is barely visible for $Fe(mta)_2$, featuring only one of such hydrogen atoms.



Figure S3: IR spectra recorded for as-synthesised (black) and activated (blue) $Fe(mta)_2$, showing the loss of the band around 1700 cm⁻¹ associated with residual solvent (DMF).

4. Thermogravimetric analysis

We performed thermogravimetric analysis (TGA) of the Fe(ta)₂, Fe(mta)₂, and Fe(cta)₂ samples with a *TA Instruments Q500* thermogravimetric analyser in a nitrogen atmosphere at a heating rate of 5 K min⁻¹ after a 5 min isothermal step in the temperature range of 25 - 800 °C.



Figure S4: TGA curves of as-synthesised Fe(mta)₂-as (dotted) and activated (solid) Fe(mta)₂, showing the loss of approx. 2 wt% residual DMF from Fe(mta)₂-as as red traces, indicating the thermal derivative of the relative mass changes (red) shows the decomposition onset at 400 °C and the peak at approximately 470 °C.



Figure S5: TGA curve of $Fe(cta)_2$ (black) and thermal derivative of the relative mass changes (red), showing the decomposition onset at 400 °C and the corresponding peak at approximately at 470 °C.

5. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments of the powder $Fe(ta)_2$ and $Fe(mta)_2$ samples were performed in a DSC (*NETZSCH DSC 214*) under constant nitrogen purging flow (40 mL min⁻¹) and a heating rate of 10 K min⁻¹ in the temperature range between 193.15 – 383.15 K. The *NETZSCH-Proteus*[®] software was used to analyse the heat flow signals.



Figure S6: Cycling DSC measurement of the of activated $Fe(mta)_2$, showing a reversible phase transition. Note here that signals below 220 K are measurement artifacts. Running the DSC measurement with a heating rate of 20 K min⁻¹ splits the broad heat signal into two signals. This underlines the complexity about the temperature dependent behaviour and presumably the pressure-induced phase transition.



Figure S7: Cycling DSC measurement of the as-synthesised Fe(mta)₂-as, showing a phase transition shifted to lower temperatures. Note here that the phase transition goes down to the signals below 220 K, which are measurement artifacts.



Figure S8: Cycling DSC measurement of $Fe(ta)_2$, showing a broad phase transition shifted to higher temperatures in the first heating curve, as well as the loss of some water residues in the initial heating run.

6. Magnetic susceptibility measurements

A superconducting quantum interference device (SQUID) magnetometer (*Quantum Design, MPMS5*), working in the temperature range of 2 K \leq T \leq 700 K and in magnetic fields -5 T $\leq \mu$ 0H ≤ 5 T, was used to measure the magnetization M of the powder MOF samples. A heating and cooling rate of 2 K min⁻¹ was applied, and the temperature dependence of the magnetic susceptibility at a given magnetic field was determined as $\chi = M/H$.



Figure S9: Thermal variation of the molar susceptibility, comparing the spin-crossover behaviour of $Fe(ta)_2$ (green), $Fe(mta)_2$ -as (light blue), $Fe(mta)_2$ dry (blue), and $Fe(cta)_2$ (pink) in χ MT representation taken on increasing and decreasing temperatures in the corresponding colour based on the respective sum formulas considering the different iron sites ([FeFe₂(X)₆]).



Figure S10: Temperature dependence of the magnetic susceptibility $\chi = M/H$ of Fe(cta)₂ based on the reduced form to one metal ion taken at an external field of H = 1000 Oe (left ordinate) and its inverse (right ordinate). Insert: temperature dependence of the product χT . The pink solid lines indicate the fit curves.



Figure S11: Temperature dependence of the magnetic susceptibility $\chi = M/H$ of Fe(mta)₂ based on the reduced form to one metal ion taken at an external field of H = 1000 Oe (left ordinate) and its inverse (right ordinate). Insert: temperature dependence of the product χT . The blue solid lines indicate the fit curves.



Figure S12: Temperature dependence of the magnetic susceptibility $\chi = M/H$ of Fe(mta)₂-as based on the reduced form to one metal ion taken at an external field of H = 1000 Oe (left ordinate) and its inverse (right ordinate). Insert: temperature dependence of the product χT . The blue solid lines indicate the fit curves.

Figure S9 shows the temperature dependence of the molar susceptibility of $Fe(ta)_2$ already described in detail in the literature³ in comparison to its new derivatives $Fe(cta)_2$ and $Fe(mta)_2$ in a χT plot. In general, the $Fe(ta)_2$ showed the classical behaviour of a spin-crossover (SCO) transition at elevated temperatures, exhibiting the largest hysteresis observed for such a material so far.⁴ In contrast, depending on the steric demand of the respective ligands resulting in larger unit cell constants (Table S3), the SCO takes place in a step-wise fashion and is shifted to lower temperatures for $Fe(mta)_2$, and only partially for $Fe(cta)_2$ down to temperatures of 4 K.

The course of $Fe(mta)_2$ -as starts with $\chi T = 0.3$ emu Kmol⁻¹, rises steeply up to 40 K, and then changes to a slightly rising plateau up to 240 K. The starting value, exceeding pure low-spin Fe(II), can be explained by an incomplete transition, or impurities, as already described in the literature.⁵ The plateau starts at $\chi T = 1.5$ emu Kmol⁻¹ (0.5 HS Fe(II)) and goes up to $\chi T = 3$ emu Kmol⁻¹ (1 HS Fe(II)). It then goes into a steep transition to 280 K, ending at $\chi T = 9$ emu Kmol⁻¹, which corresponds well to 3 HS Fe(II). This course is in fair agreement with a stepwise transition of the different iron sites in the framework with a Fe1: Fe2 1:2 ratio, suggesting that with increasing temperature, first all "Fe1" (central Fe ion of the Kuratowski unit) iron atoms go into the high spin state in a relatively long temperature range before the "residual Fe2" (peripheral Fe ions of the Kuratowski unit) follow at higher temperatures with a cooperative phase transition. Removal of residual DMF occluded in the structure at 553 K does not change the general behaviour but shifts the spin transition of the Fe2 sites by approximately 15 K to higher temperatures. This indicates that not only steric strain from bulky ligands but also solvent molecules in the voids significantly influence the SCO transition behaviour in such frameworks, which could be exploited to further influence the behaviour *via* the incorporation of sterically demanding molecules. Both $Fe(mta)_2$ samples showed no signs of hysteresis in contrast to $Fe(ta)_2$.

Starting from $\chi T = 1.3$ emu Kmol⁻¹, the susceptibility of $Fe(cta)_2$ at 4 K is larger than expected for a pure Fe (II) low spin compound ($\chi T = 0$ emu Kmol⁻¹) indicating that the material is already in a transition state and the χ^{-1} plot (Figure S10) suggests from its slope that approximately half of the Fe ions in $Fe(cta)_2$ are already in the high-spin state at this temperature. The flat low-temperature range of $Fe(cta)_2$ cannot be represented because it is below 0 K. Upon heating, the χ T-curve increases until it flattens out at 150 K at $\chi T = 9$ emu Kmol⁻¹ in a complete high spin state for all 3 Fe(II) ions. Here, the transition from low- to high-spin state seems to occur continuously, foreclosing a cooperative behaviour.

7. Laboratory powder X-ray diffraction

Powder X-ray diffraction (PXRD) data was collected at ambient temperature using the *Malvern Panalytical* Empyrean diffractometer equipped with a Bragg–Brentano^{HD} mirror and a *PIXcel*^{3D} 2×2 detector. For the variable temperature PXRD data, a CHC+ reaction chamber was used with N₂ gas flow for cooling control.



Figure S13: Collection of laboratory PXRD data ($\lambda = 1.54$ Å) of Fe(mta)₂, and Fe(cta)₂ compared to the calculated patterns of the high-spin and low-spin Fe(ta)₂.



Figure S14: Variable Temperature PXRD data ($\lambda = 1.54$ Å) of Fe(mta)₂.



Figure S15: Variable Temperature PXRD data ($\lambda = 1.54$ Å) of Fe(cta)₂. The measurement at -180°C was performed under vacuum instead of using N₂.

8. High-pressure powder X-ray diffraction

High-pressure powder X-ray diffraction (HPPXRD) data at variable pressure points was collected at the Diamond Light Source (UK), beamline (I15) within beamtime CY30815-2. We used a monochromatic X-ray beam $\lambda = 0.4246$ Å (with a fixed operating beam energy 29.2 keV), equipped with a Pilatus3 X CdTe 2M area detector for HPPXRD data collection. The finely grounded MOF powders were handled in the glove box and filled into soft plastic capillaries (Makrolon, inside diameter 1.8 mm), together with Silicone oil AP100 (polyphenyl-methylsiloxane) as pressure transmitting medium to maintain hydrostatic conditions up to 0.4 GPa, and sealed with adhesive epoxy paste (Araldyte-2014-1) by heating up to 60 °C for 20 min. We used a hydraulic high-pressure cell as described in more detail in the literature.⁶ Therefore, the samples were loaded into a chamber filled with water to transmit the hydrostatic pressure, and a hydraulic gauge pump was used to apply and release water pressure. HPPXRD measurements were performed through two diamond windows in the high-pressure chamber (metal block) along beam direction in the pressure range from ambient to 0.4 GPa in 0.02 GPa step size (Δp) with an estimated error of $\sigma p = \pm 0.003$ GPa.

Stack plot of the ambient pressure data



Figure S16: Collection of the normalised PXRD patterns of each MOF, *i.e.* Fe(ta)₂, Fe(mta)₂, and Fe(cta)₂ recorded at ambient pressure.

Stack plots of the HPPXRD data



Figure S17: HPPXRD patterns for Fe(ta)₂ collected in the pressure range from ambient to 0.4 GPa.



Figure S18: HPPXRD patterns for Fe(mta)₂ collected in the pressure range from ambient to 0.4 GPa.



Figure S19: HPPXRD data for Fe(cta)₂ collected in the pressure range from ambient to 0.4 GPa.

9. PXRD analysis

The collected 2D detector images were integrated by DAWN software.⁷ Profile fits (Pawley method)⁸ of the collected pressure-dependent PXRD data sets were performed using routines implemented in TOPAS V6⁹ to obtain unit cell parameters and cell volume (*a* and *V*) with standard deviations. The representative profile fits of the PXRD data collected at ambient pressure show a good fit using the published cubic crystal structure of Fe(ta)₂.^{3,10} Additionally, Rietveld refinements¹¹ against high-resolution HPPXRD data were performed using TOPAS V6⁹ to obtain bond lengths (Fe-N) as a function of increasing hydrostatic pressure. Therefore, the single crystal structure of the cubic Fe(ta)₂.^{3,10} and 3D electron diffraction data (Chapter 14) were used as the starting model, and Pawley fits provided unit cell and background parameters for the refinement. The peak shapes were refined using the macro "PVII_Peak_Type" (with *ha*, *hb*, *hc*, *lora*, *lorb*, *lorc* as refined parameters), and we performed zero point refinement to account for a zero shift due to misalignment using "Zero_Error". The zero error was refined for the first pressure point and then kept constant for subsequent pressure points. We described the structure models using atom coordinate sites and parameters as given below.

Rietveld refinements



Figure S20: Rietveld refinement of $Fe(mta)_2$ at ambient pressure. Experimental data is shown as dark blue line and the calculated data from Rietveld refinement as light transparent blue line, and the difference curve (fit – data) as grey line. Reflection positions are shown as black vertical tick marks.

Atom coordinates of $Fe(ta)_2$ used in the Rietveld refinement with fixed cell parameter a = 16.5969 Å extracted from Pawley refinement of the ambient PXRD data; Wyckoff position (site symmetry) for the crystallographic Fe^{II}: Fe²⁺ (16c) and Fe²⁺ (8a)

site H1	x = H1x;	y 0.817810	z 0.580600
site Fel	x 0.00000	y 0.00000	z 0.00000
site Fe2	x 0.12500	y 0.12500	z 0.12500
site N1	x 0.67090	y 0.290360	z 0.579100
site C1	x 0.65421	y = C1y;	z 0.595790

site N2 x 0.62500 y 0.244960 z 0.62500 prm H1x 0.93219`_0.01460 min 0.932190 max 0.932191 prm C1y 0.36780`_0.00291 min 0.3678 max 0.36781 R_{Bragg} 4.9143 R_{wp} 6.8140

Atom coordinates of Fe(mta)₂ used in the Rietveld refinement with fixed cell parameter a = 17.3175Å extracted from Pawley refinement of the ambient PXRD data; Wyckoff position (site symmetry) for the crystallographic Fe^{II}: Fe²⁺ (16d) and Fe²⁺ (8b)

site Fe1 x 0.375000 y 0.375000 z 0.375000 site Fe2 x 0.500000 y 0.250000 z 0.250000 site N1 x 0.375000 y 0.375000 z 0.24820 site N2 x = C1x + dc2x + dn2x; y = 0.75 - C1x - dc2x - dn2x; z = 0.20580site $C1 \quad x = C1x;$ y = 0.75-C1x; z 0.13010site C2 x = C1x+dc2x; $y C2y 0.31967^{-0.00868} z 0.05720 \text{ prm } C1z 0.13025^{-0.01022} \text{ min } 0.1301 \text{ max } 0.13025$ prm C1x 0.40294`_0.00125 min 0.375 prm dc2x 0.01794`_0.00792 min 0 max 0.03 prm dn2x 0.00265`_0.00801 min 0 max 0.03 Flatten(N1 0 0 0 0 N2 0 0 0 0 N2 33 0 0 0 C1 0 0 0 0 C1 33 0 0 0, 0`, 0.2, 1000) Distance_Restrain(N1 0 N2 0 0 0 0, 1.30656, 1.39690`_0.23615, 0.15, 1000) Distance_Restrain(N2 0 C1 0 0 0 0, 1.37385, 1.40454`_0.09905, 0.15, 1000) Distance_Restrain(C1 0 C1 33 0 0 0, 1.3692, 1.36837`_0.06146, 0.15, 1000) Distance_Restrain(C1 0 C2 0 0 0 0, 1.43927, 1.38393`_0.05619, 0.15, 1000) Angle_Restrain(N2 11 C1 11 C2 11,120, 135.02828`_13.70031, 5, 0.001) Angle_Restrain(N2 11 C1 11 C2 88,120, 92.29834`_0.49327, 5, 0.001) R_{Bragg} 1.1806

 $R_{wp} 2.8995$

Atom coordinates of $Fe(cta)_2$ used in the Rietveld refinement with fixed cell parameter a = 18.2301 Å extracted from Pawley refinement of the ambient PXRD data; Wyckoff position (site symmetry) for the crystallographic Fe^{II}: Fe²⁺ (16c) and Fe²⁺ (8a)

site Fe1 x 0.125000	y 0.625000	z 0.625000
site Fe2 x 0.250000	y 0.750000	z 0.750000
site N1 x 0.092750	y 0.705470	z 0.705470
site N2 x 0.135260	y 0.750000	z 0.750000
site C1 x 0.023380	y = C1y;	z = C1y;
site C2 x -0.050130	y = C2y;	z 1.200660
site C3 x 0.000000	y = C3y;	z 1.000000
site H1 $x = -1x$;	y 0.141570	z = H1z;
site $H2a x = H2ax$;	y = H2ay;	z = 1 + H2ax;
prm C1y 0.72430`_0.0	00188 min 0.72	24 max 0.7243

prm C2y 0.20100`_0.00355 min 0.200 max 0.201 prm C3y 0.65000`_0.00377 min 0.650 max 0.651 prm H1x 0.05840`_0.00605 min 0.058 max 0.0584 prm H1z 1.21290`_0.01172 min 1.2128 max 1.2129 prm H2ay 0.61680`_0.01112 min 0.6168 max 0.6169 prm Fe1beq 2.03690`_1.09329 min 0.1 max 5 prm Fe2beq 2.87588`_1.37744 min 0.1 max 5 prm N1beq 1.00000`_1.98487 min 1 max 2 prm N2beq 2.00000`_2.28288 min 1 max 2 prm C1beq 1.00000`_3.04254 min 1 max 2 prm C2beq 2.00000`_1.89394 min 1 max 2 prm C3beq 2.00000`_8.37352 min 1 max 2 R_{Bragg} 1.6689 R_{wp} 2.6856

p / GPa	$R_{_{ m wp}}$	<i>Fe1-N1</i> /Å	<i>Fe2-N2</i> /Å
ambient	6.8140	1.97360	1.99082
0.0194	6.6503	1.97374	1.99096
0.0398	7.0890	1.97358	1.99080
0.0598	7.5883	1.97309	1.99030
0.0797	7.8771	1.97257	1.98978
0.0995	7.9865	1.97208	1.98928
0.1199	7.9965	1.97170	1.98890
0.1399	7.9905	1.97114	1.98834
0.1593	7.7592	1.97058	1.98777
0.1793	7.7794	1.97024	1.98743
0.1996	7.7105	1.96972	1.98691
0.2196	7.7578	1.96934	1.98653
0.2397	7.7167	1.96895	1.98613
0.2597	7.7362	1.96857	1.98575
0.2797	7.6352	1.96807	1.98524
0.2997	7.6308	1.96774	1.98491
0.3198	7.6966	1.96713	1.98429
0.3397	7.8345	1.96673	1.98389
0.3598	7.7522	1.96619	1.98335
0.3798	7.9929	1.96576	1.98291
0.3998	7.8943	1.96538	1.98253

Table S1: Overview of the Fe-N bond lengths of $Fe(ta)_2$ derived from Rietveld refinements of the HPPXRD data.

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Table S2: Overview of the Fe-N bond lengths of Fe(cta)₂ derived from Rietveld refinements of the HPPXRD data.



Figure S21: The evolution of the bond distances (Fe1-N1 and Fe2-N2) as a function of pressure up to 0.4 GPa of $Fe(ta)_2$ (a) shown in green and $Fe(cta)_2$ (b) in purple.

Pawley profile fits



Figure S22: Pawley fit for $Fe(ta)_2$ at ambient pressure. Experimental data is shown as dark green line, Pawley fit as light green line, and the difference curve (fit – data) as grey line.



Figure S23: Pawley fit for $Fe(mta)_2$ at ambient pressure. Experimental data is shown as dark blue line, Pawley fit as light blue line, and the difference curve (fit – data) as grey line.



Figure S24: Pawley fit for $Fe(cta)_2$ at ambient pressure. Experimental data is shown as dark pink line, Pawley fit as light pink line, and the difference curve (fit – data) as grey line.



Figure S25: Pawley fit for $Fe(mta)_2$ at 0.4 GPa. Experimental data is shown as dark blue line, Pawley fit as light blue line, and the difference curve (fit – data) as grey line.

Table S3: Structural parameters (lattice parameter a, volume V, and space group S.G.) for all studied triazolebased Fe(II) MOFs obtained from Pawley refinement of the ambient pressure PXRD data.

Fe(x) ₂	Fe(ta) ₂	Fe(mta) ₂	Fe(cta) ₂
<i>a</i> / Å	16.5969(6)	17.3175(7)	18.2301(4)
$V/ m \AA^3$	4571.8(5)	5193.5(7)	6058.6(4)
S.G.	Fd-3m	Fd-3m	Fd-3m

p / GPa	$R_{_{ m wp}}$	<i>a</i> / Å	$V/ m \AA^3$
ambient	2.73774	16.5969(6)	4571.8(5)
0.0194	2.73552	16.5969(6)	4571.8(5)
0.0398	2.45438	16.5955(6)	4570.6(5)
0.0598	2.58785	16.5914(6)	4567.2(5)
0.0797	2.75515	16.5870(6)	4563.6(5)
0.0995	2.81962	16.5829(6)	4560.2(5)
0.1199	2.83131	16.5797(6)	4557.5(5)
0.1399	2.82163	16.5750(6)	4553.7(5)
0.1593	2.81628	16.5703(6)	4549.8(5)
0.1793	2.78023	16.5674(7)	4547.4(5)
0.1996	2.77953	16.5631(7)	4543.9(5)
0.2196	2.71871	16.5599(6)	4541.3(5)
0.2397	2.68595	16.5566(6)	4538.5(5)
0.2597	2.70596	16.5534(6)	4535.9(5)
0.2797	2.73582	16.5492(7)	4532.4(5)
0.2997	2.76427	16.5464(7)	4530.1(5)
0.3198	2.78284	16.5413(7)	4526.0(5)
0.3397	2.81206	16.5379(7)	4523.2(5)
0.3598	3.10945	16.5334(7)	4519.5(6)
0.3798	2.86024	16.5298(7)	4516.5(5)
0.3998	2.87148	16.5266(7)	4513.9(5)

Table S4: Overview of the unit cell parameters and volumes of $Fe(ta)_2$ derived from Pawley fits of the HPPXRD data.

p / GPa	$R_{_{ m wp}}$	<i>a</i> / Å	$V/ m \AA^3$
ambient	2.66004	18.2301(4)	6058.6(4)
0.0194	1.57839	18.2315(9)	6060.0(9)
0.0398	1.5153	18.2232(8)	6051.7(8)
0.0598	1.53717	18.2125(6)	6041.1(6)
0.0793	2.33418	18.2095(9)	6038.1(9)
0.0995	1.40499	18.2086(7)	6037.2(7)
0.1198	1.49129	18.2063(7)	6034.9(7)
0.1399	1.51052	18.2023(7)	6030.9(7)
0.1594	1.54993	18.1959(9)	6024.5(8)
0.1794	1.55415	18.1936(9)	6022.3(9)
0.1996	1.51402	18.1863(8)	6015.1(8)
0.2196	1.548	18.1829(8)	6011.6(8)
0.2397	1.54349	18.1797(7)	6008.5(7)
0.2597	1.56373	18.1770(7)	6005.8(7)
0.2798	1.57277	18.1734(7)	6002.2(7)
0.2998	1.56371	18.1688(8)	5997.6(7)
0.3198	1.57561	18.1655(7)	5994.4(7)
0.3397	1.55788	18.1617(7)	5990.6(7)
0.3598	1.59253	18.1579(8)	5986.9(7)
0.3798	1.56215	18.1543(7)	5983.3(7)
0.3998	1.61549	18.1520(7)	5981.0(7)

Table S5: Overview of the unit cell parameters and volumes of $Fe(cta)_2$ derived from Pawley fits of the HPPXRD data.



Figure S26: Fwhm extracted from Pawley profile fits for $Fe(ta)_2(a)$ and $Fe(cta)_2(b)$ as a function of increasing hydrostatic pressure up to 0.4 GPa.

10. Bulk moduli (EOSFit)

The unit cell volume changes obtained by HPPXRD data analysis were fitted to 2^{nd} order Birch-Murnaghan (B-M) equation of state using EoSFitGui to estimate the bulk moduli of Fe(ta)₂ and Fe(cta)₂.¹² The standard deviations of the volumes extracted by Pawley profile fitting and a standard pressure error ($\sigma p = \pm 0.003$ GPa) were included in the B-M fitting routine. For both studied MOFs, variable pressure unit cell volumes across the *p* range between ambient – 0.4 GPa were used for fitting. In addition, we present 2^{nd} and 3^{rd} order calculations of the bulk moduli for completeness (Table S6).



Figure S27: The evolution of the unit cell volume of $Fe(ta)_2$ is fitted using 2^{nd} order B-M equation of state shown as green line in the V(p)-plot (a) and F(f)-plot (b), confirming the applicability of the 2^{nd} order fit to calculate the bulk modulus.



Figure S28: The evolution of the unit cell volume of $Fe(cta)_2$ is fitted using 2^{nd} order B-M equation of state shown as pink line in the V(p)-plot (a) and F(f)-plot (b), confirming the applicability of the 2^{nd} order fit to calculate the bulk modulus.

Table S6: Overview of bulk moduli (*B*) determined by using 2^{nd} and 3^{rd} order B-M equation of state calculations for the unit cell volume at ambient pressure (V_0 at zero pressure and temperature) with standard deviations.

	Fe(ta)2	Fe(cta) ₂
$B(2^{\rm nd})/{\rm GPa}$	28.2	29.5
$\sigma B (2^{\rm nd}) / {\rm GPa}$	0.2	0.5
$V_0(2^{ m nd})/{ m \AA}^3$	4576.5	6057.9
$\sigma V_{0}\left(2^{\mathrm{nd}} ight)/\mathrm{\AA}^{3}$	0.3	0.8
<i>B</i> (3 rd) / GPa	27.3	26.8
$\sigma B(3^{\mathrm{rd}}) / \mathrm{GPa}$	0.9	0.5
$V_{0}\left(3^{\mathrm{rd}} ight)/\mathrm{\AA}^{3}$	4576.9	6058.8
$\sigma V_0(3^{ m rd})/{ m \AA}^3$	0.5	0.8

11. Standard material for high-pressure PXRD analysis

To validate the high-pressure cell setup, we used Ni(dmgH)₂ (Nickel dimethylglyoxime) as reference material with literature-known variable pressure behaviour.^{13,14} The sample was prepared in a similar fashion as described above in the HPPXRD experimental details (Chapter 8). The HPPXRD data was collected in the pressure range (ambient pressure to 0.4 GPa) with a defined pressure step size (0.02 GPa). Pawley refinement of the PXRD data at ambient pressure reveals unit cell parameters a = 16.5717(6) Å, b = 10.4331(3) Å, c = 6.4621(2) Å, and V = 1117.28(6) Å³ is in great accordance across variable pressure PXRD data with the reported structure.¹⁵ The calculated bulk moduli, *i.e.* $B = 8.43 \pm 0.15$ GPa (derived from the B-M 3rd order equation of state fit) and $B = 9.57 \pm 0.09$ GPa (derived from the B-M 2nd order equation of state fit) are in line with literature data, confirming the applicability of the setup.¹³



Figure S29: Normalised HPPXRD data of the standard material Ni(dmgH)₂ recorded in the pressure range from ambient pressure up to 0.4 GPa.

p / GPa	$R_{ m wp}$	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	$V/ m \AA^3$
ambient	2.95280	16.5717(6)	10.4331(3)	6.4621(2)	1117.28(6)
0.0197	3.58596	16.5718(9)	10.4265(5)	6.4539(4)	1115.16(10)
0.0398	2.99285	16.5677(7)	10.4105(4)	6.4483(3)	1112.21(8)
0.0598	2.96639	16.5690(8)	10.4004(4)	6.4412(3)	1109.99(9)
0.0793	2.97736	16.5615(9)	10.3890(5)	6.4345(3)	1107.11(10)
0.0999	2.87619	16.5635(8)	10.3808(6)	6.4283(3)	1105.31(10)
0.1199	2.95232	16.5562(6)	10.3677(5)	6.4217(4)	1102.29(9)
0.1399	2.49250	16.5566(6)	10.3571(4)	6.4157(3)	1100.16(7)
0.1594	3.03165	16.5552(8)	10.3482(6)	6.4108(2)	1098.30(11)
0.1795	2.52741	16.5501(6)	10.3387(4)	6.4045(2)	1095.86(7)
0.1996	3.04075	16.5497(8)	10.3310(5)	6.3991(4)	1094.11(10)
0.2196	2.55868	16.5480(6)	10.3221(4)	6.3934(2)	1092.07(7)
0.2397	2.66187	16.5446(6)	10.3129(4)	6.3890(3)	1090.12(7)
0.2597	2.66473	16.5418(8)	10.3073(6)	6.3828(3)	1088.29(9)
0.2798	2.61754	16.5367(7)	10.2969(4)	6.3774(3)	1085.93(8)
0.2997	2.37638	16.5330(7)	10.2919(5)	6.3722(3)	1084.28(9)
0.3198	2.96540	16.5287(7)	10.2873(6)	6.3673(3)	1082.68(9)
0.3397	2.72334	16.5242(9)	10.2765(6)	6.3609(4)	1080.17(10)
0.3598	2.86385	16.5198(7)	10.2708(5)	6.3565(3)	1078.52(9)
0.3798	2.57641	16.5161(6)	10.2624(5)	6.3514(3)	1076.54(8)
0.3998	2.58556	16.5147(6)	10.2581(4)	6.3463(2)	1075.14(7)

Table S7: Unit cell parameters and the corresponding R_{wp} values for Ni(dmgH)₂ derived from Pawley profile fitting of the HPPXRD data.



Figure S30: Change in volume (a), relative changes of the lattice parameters a, b, and c (b), and fwhm (c) for Ni(dmgH)₂ as a function of increasing hydrostatic pressure up to 0.4 GPa.



Figure S31: 2^{nd} order -BM equation of state fit of Ni(dmgH)₂ shown as blue line in the V(p)-plot (a) and F(f)-plot (b), confirming the applicability of the 2^{nd} order fit to derive the bulk modulus.



Figure S32: 3^{rd} order B-M equation of state fit of Ni(dmgH)₂ shown as blue line in the V(p)-plot (a) and F(f)-plot (b), confirming the applicability of the 3^{rd} order fit to derive the bulk modulus.

12. PASCal calculations

To verify the bulk moduli calculations as described above (Chapter 10), we performed additional calculations of the bulk moduli using the web-based software tool PASCal to fit the HPPXRD data of $Fe(ta)_2$ and $Fe(cta)_2$ with a 2nd and 3rd order B-M equation of states.¹⁶ The calculated bulk moduli of Ni(dmgH)₂ using PASCal, *i.e.* $B = 9.26 \pm 0.12$ GPa (derived from 2nd order B-M equation of state fit) and $B = 7.89 \pm 0.28$ GPa (derived from 3rd order B-M equation of state fit) are in line with the bulk moduli obtained *via* EOSFit, see Chapter 11.

		Fe(ta) ₂	Fe(cta) ₂	
	<i>B</i> (2 nd) / GPa	28.9	29.4	
	$\sigma B (2^{\rm nd}) / {\rm GPa}$	0.4	0.6	
	$V_0(2^{ m nd})/{ m \AA}^3$	4575.5	6058.1	
_	$\sigma V_{0}\left(2^{\mathrm{nd}} ight)/\mathrm{\AA}^{3}$	0.5	1.0	
	<i>B</i> (3 rd) / GPa	30.7	23.3	
	$\sigma B(3^{\mathrm{rd}})/\mathrm{GPa}$	1.4	2.1	
	$V_{0}\left(3^{\mathrm{rd}} ight)/\mathrm{\AA}^{3}$	4574.9	6060.9	
	$\sigma V_0(3^{ m rd})/{ m \AA}^3$	0.6	1.5	

Table S8: Bulk moduli (*Bs*) determined from 2nd and 3rd order B-M equation of states fits to the HPPXRD data using PASCal.

13. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Scanning electron microscopy (SEM) images were obtained with a *Zeiss Crossbeam 550* electron microscope, and subsequent energy-dispersive X-ray spectroscopy (EDX) of $Fe(mta)_2$ was performed using this device equipped with a *EDAX SiLi* detector. The EDX spectra of $Fe(cta)_2$ were collected using the *Philips XL 30 FEG* with an *EDAX SiLi* detector. The Fe:Cl ratios were determined as average from measurements on sample squares of at least 5×5 µm and applying an operating voltage of 20 kV.



Figure S33: SEM micrograph of Fe(mta)₂.



Figure S34: SEM micrographs of Fe(cta)₂.

14. 3D electron diffraction data

3D electron diffraction (3DED) data of Fe(mta)₂ and Fe(cta)₂ was collected using a Rigaku XtaLAB Synergy-ED system¹⁷ equipped with a Rigaku HyPix-ED detector and LaB₆ electron source operating at 200 keV ($\lambda = 0.0251$ Å) in a vacuum at different temperatures using Gatan's Elsa cryo-transfer holder. Data collection and processing, *i.e.* structure refinements, data reductions, and analysis were performed using the Rigaku Oxford Diffraction CrysAlis^{Pro} program package.¹⁸ The shutterless data was recorded in continuous crystal rotation mode at the 645 mm detector distance using the selected area configuration. The samples were placed on a standard amorphous carbon on a Cu grid and transferred to a holder at 233 K. The initial object search, electron beam sensitivity tests, selection and centering of crystal, and first measurements were performed at the transfer temperature. Next, the continuous grid was cooled down to 173 K, and the same crystal was located again and measured with the same scan conditions. In the last step, the grid was heated to 373 K, and measurements were repeated for the same crystals. Due to the high symmetry of the crystal structures, dataset merging was not required. The collected data was processed and finalised with frame scaling and empirical absorption correction up to 0.8 Å resolution. The structure was solved, and the space group Fd-3m was determined by the ShelXT 2018/219 structure solution program using Intrinsic Phasing and refined in the kinematic approximation model using atomic electron scattering factors²⁰ by Least Squares using ShelXL 2018/3.²¹ An extinction parameter has been refined to mitigate the effect of dynamic intensity data. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. A static disorder of ligand molecules around the symmetry elements in both crystal structures can be observed and refined with constrained atom occupancies and RIGU/SIMU restrains.

Compound	data_M-173	data_M-233	data_M-293	data_M-373	
Fe(mta) ₂					
Formula	C.oH.oFeaN.o				
D_{calc} / g cm ⁻³	1.820	1.760	1.688	1.690	
Formula weight	654.00	654.00	654.00	654.00	
<i>T</i> / K	173(1)	233(1)	293(2)	373(1)	
Crystal system	cubic	cubic	cubic	cubic	
Space group	Fd-3m	Fd-3m	Fd-3m	Fd-3m	
a/Å	16.84(8)	17.0(4)	17.26(9)	17.26(8)	
$V / Å^3$	4773(68)	4936(316)	5146(78)	5140(74)	
Ζ			8		
Z'		1/	/24		
Wavelength / Å		0.0	251		
Radiation type		elec	trons		
$Q_{min}/°$	0.074	0.073	0.072	0.072	
$Q_{max}/°$	0.896	0.898	0.897	0.898	
Measured refl.	4981	1808	5776	4510	
Independent refl.	270	267	291	291	
Reflections with I	188	134	208	251	
> 2(I)					
R _{int}	0.5094	0.2492	0.4135	0.2358	
Parameters	31	30	30	31	
Restraints	0	0	30	0	
Largest peak	0.710	0.350	0.250	0.212	
Deepest hole	-0.230	-0.098	-0.177	-0.274	
GoF	1.310	1.117	1.268	1.285	
wR_2 (all data)	0.3978	0.3815	0.3803	0.3491	
wR_2	0.3804	0.3236	0.3453	0.3406	
R_{l} (all data)	0.1904	0.1702	0.1420	0.1288	
R_{I}	0.1779	0.1198	0.1209	0.1218	
CCDC Deposition	2311804	2311805	2311806	2311807	
number					

Table S8: Crystal structure and refinements details for $Fe(mta)_2$.



Figure S35: Image of Fe(mta)₂, showing suitable crystals used for ED.

Fe(mta) ₂ at 173 K			
Atom	Atom	Length / Å	
Fe1	N3	2.083(14)	
Fe1	N31	2.083(14)	
Fe1	N3 ²	2.083(14)	
Fe1	N3 ³	2.083(14)	
Fe1	N3 ⁴	2.083(14)	
Fe1	N3 ⁵	2.083(14)	
Fe2	N46	2.048(14)	
Fe2	N4	2.048(14)	
Fe2	N4 ⁷	2.048(14)	
Fe2	N4 ⁸	2.048(14)	
Fe2	N49	2.048(14)	
Fe2	N4 ¹⁰	2.048(14)	
N3	N4	1.303(12)	
N3	N4 ¹¹	1.303(12)	
N4	C5	1.322(16)	
C5	C511	1.39(3)	
C5	C6	1.44(3)	

 $^{1}\text{-}1/2\text{+}z,3/4\text{-}x,5/4\text{-}y;$ $^{2}\text{-}1/2\text{+}z,1/2\text{+}x,+y;$ $^{3}3/4\text{-}y,+z,3/4\text{-}x;$ $^{4}1/4\text{-}x,5/4\text{-}y,+z;$ $^{5}\text{-}1/2\text{+}y,+z,1/2\text{+}x;$ $^{6}1\text{-}y,1/4\text{+}z,1/4\text{+}x;$ $^{7}\text{-}1/4\text{+}z,1\text{-}x,-1/4\text{+}y;$ $^{8}\text{-}1/2\text{+}y,5/4\text{-}z,3/4\text{-}x;$ $^{9}1/2\text{-}x,3/2\text{-}y,1\text{-}z;$ $^{10}3/4\text{-}z,1/2\text{+}x,5/4\text{-}y;$ $^{11}\text{+}x,5/4\text{-}y,5/4\text{-}z$

Atom	Atom	Length / Å
Fe1	N1 ¹	2.198(15)
Fe1	$N1^2$	2.198(15)
Fe1	N1 ³	2.198(15)
Fe1	$N1^4$	2.198(15)
Fe1	N1 ⁵	2.198(15)
Fe1	N1 ⁶	2.198(15)
Fe2	$N2^2$	2.117(14)
Fe2	N2 ⁵	2.117(14)
Fe2	N2 ⁷	2.117(14)
Fe2	N2 ⁸	2.117(14)
Fe2	N2 ⁹	2.117(14)
Fe2	N2 ¹⁰	2.117(14)
N1	N2	1.302(11)
N1	N2	1.302(11)
N2	C1	1.369(15)
C1	C1	1.338(19)
C1	C3	1.43(3)

¹⁺z,x+1/2,y+1/2; ²-y+3/4,-z+1/4,x+1/2; ²z+3/4,-x+1/4,y+1/2; ⁴-x+3/4,z+1/2,-y+1/4; ⁵y+3/4,x+1/2,-z+1/4; ⁶-x+3/4,-y+1/4,z+1/2; ⁷ y+1/4,-x+1/2,z+3/4; ⁸-z+3/4,x+1/2,-y+1/4; ⁹ y+1/4,z+3/4,-x+1/2; ¹⁰ z+1/4,-x+1/2,y+3/4

Fe(mta) ₂ at 233 K			
Atom	Atom	Length / Å	
Fe2	N4	2.08(5)	
Fe2	N41	2.08(5)	
Fe2	N4 ²	2.08(5)	
Fe2	N4 ³	2.08(5)	
Fe2	N4 ⁴	2.08(5)	
Fe2	N4 ⁵	2.08(5)	
Fe1	N36	2.15(5)	
Fe1	N3	2.15(5)	
Fe1	N3 ⁷	2.15(5)	
Fe1	N3 ⁴	2.15(5)	
Fe1	N3 ⁸	2.15(5)	
Fe1	N3 ²	2.15(5)	
N3	N4	1.29(3)	
N3	N49	1.29(3)	
N4	C5	1.33(3)	
C5	C59	1.33(4)	
C5	C6	1.54(5)	

¹1-z,1-x,1-y; ²+z,+x,+y; ³1-y,1-z,1-x; ⁴+y,+z,+x; ⁵1-x,1-y,1-z; ⁶3/4-y,+z,3/4-x; ⁷+z,3/4-x,3/4-y; ⁸3/4-x,3/4-y,+z; ⁹3/4-x,+y,3/4-z

Fe(mta) ₂ at 373 K			
Atom	Atom	Length / Å	
Fe1	N3 ¹	2.198(13)	
Fe1	N3 ²	2.198(13)	
Fe1	N3 ³	2.198(13)	
Fe1	N3 ⁴	2.198(13)	
Fe1	N3 ⁵	2.198(13)	
Fe1	N3	2.198(13)	
Fe2	N4	2.129(13)	
Fe2	N46	2.129(13)	
Fe2	N4 ⁷	2.129(13)	
Fe2	N4 ⁸	2.129(13)	
Fe2	N4 ⁴	2.129(13)	
Fe2	N4 ³	2.129(13)	
N3	N49	1.285(10)	
N3	N4	1.285(10)	
N4	C5	1.331(14)	
C5	C59	1.39(2)	
C5	C6	1.38(3)	

 $^{1}+y,3/4-z,3/4-x;\ ^{2}3/4-z,3/4-x,+y;\ ^{3}+z,+x,+y;$ $^{4}+y,+z,+x;\ ^{5}3/4-x,+y,3/4-z;\ ^{6}1-x,1-y,1-z;\ ^{7}1-z,1-x,1-y;\ ^{8}1-y,1-z,1-x;\ ^{9}3/4-x,3/4-y,+z$

Figure S36: Bond lengths for $Fe(mta)_2$ as determined at different temperatures (a-d).

Compound	data_C-173	data_C-233	data_C-293	data_C-373
Fe(cta) ₂				
T 1			E N	
Formula		C ₃₀ H ₃	$_{6}Fe_{3}N_{18}$	
$D_{calc.}$ / g cm ⁻³	1.840	1.836	1.802	1.828
Formula weight	816.28	816.28	816.28	816.28
T/K	173(1)	233(1)	293(2)	373(1)
Crystal system	cubic	cubic	cubic	cubic
Space group	Fd-3m	Fd-3m	Fd-3m	Fd-3m
<i>a</i> / Å	18.06(7)	18.08(16)	18.19(10)	18.10(10)
V / Å ³	5893(65)	5907(158)	6017(99)	5932(99)
Ζ	8			
Z'	1/24			
Wavelength / Å	0.0251			
Radiation type	electrons			
$Q_{min}/°$	0.069	0.069	0.068	0.069
$Q_{max}/°$	0.896	0.896	0.898	0.899
Measured refl.	6138	6134	4041	4241
Independent refl.	327	327	333	328
Reflections with I	310	306	306	250
> 2(I)				
R _{int}	0.3114	0.2070	0.1988	0.4731
Parameters	39	42	31	39
Restraints	27	45	0	27
Largest peak	0.233	0.249	0.492	0.256
Deepest hole	-0.157	-0.164	-0.319	-0.155
GoF	1.255	1.352	1.844	1.238
wR_2 (all data)	0.3649	0.3568	0.4424	0.3659
wR_2	0.3605	0.3535	0.4358	0.3380
R_I (all data)	0.1530	0.1491	0.2025	0.1734
R_{I}	0.1479	0.1434	0.1950	0.1434
CCDC Deposition	2311808	2311809	2311810	2311811
number				

Table S9: Crystal structure and refinements details for Fe(cta)₂.



Figure S37: Image of Fe(cta)₂, showing suitable crystals used for ED.

Atom	Atom	Length / Å
Fe1	N3 ¹	2.191(14)
Fe1	N3 ²	2.191(14)
Fe1	N3 ³	2.191(14)
Fe1	N3	2.191(14)
Fe1	N3 ⁴	2.191(14)
Fe1	N3 ⁵	2.191(14)
Fe2	N4 ⁶	2.205(12)
Fe2	N4	2.205(12)
Fe2	N4 ³	2.205(12)
Fe2	N4 ⁵	2.205(12)
Fe2	N47	2.205(12)
Fe2	N4 ⁸	2.205(12)
N4	N3	1.327(12)
N4	C5	1.322(14)
C5	C59	1.41(2)
C5	C6	1.456(16)
C6	C7	1.43(5)

 $^{1}3/4-y,+z,3/4-x;\ ^{2}+z,3/4-x,3/4-y;\ ^{3}+z,+x,+y;\ ^{4}3/4-x,3/4-y,+z;\ ^{5}+y,+z,+x;\ ^{6}1-y,1-z,1-x;\ ^{7}1-x,1-y,1-z;\ ^{8}1-z,1-x,1-y;\ ^{9}3/4-x,+y,3/4-z$

Atom	Atom	Length / Å
Fe1	N5 ¹	2.223(18)
Fe1	N5 ²	2.223(18)
Fe1	N5 ³	2.223(18)
Fe1	N5 ⁴	2.223(18)
Fe1	N5 ⁵	2.223(18)
Fe1	N56	2.223(18)
Fe2	N3 ⁷	2.231(15)
Fe2	N3 ⁸	2.231(15)
Fe2	N3 ⁹	2.231(15)
Fe2	N3 ¹⁰	2.231(15)
Fe2	N3 ¹¹	2.231(15)
Fe2	N3 ¹²	2.231(15)
N5	N3	1.319(13)
N5	N3	1.319(13)
N3	C4	1.325(16)
C4	C4	1.39(2)
C4	C6	1.460(19)
C6	C7	1.549(18)

$$\label{eq:spherical_states} \begin{split} ^{1} &+ y, z \!+\! 1/2, x \!+\! 1/2; \, ^{2} z \!+\! 1/2, -x \!+\! 3/4, -y \!+\! 1/4; \, ^{3} \!+\! x \!+\! 3/4, \\ &- y \!+\! 1/4, \, z \!+\! 1/2; \, ^{4} \!-\! y \!+\! 1/4, \, z \!+\! 1/2, -x \!+\! 3/4; \, ^{5} \!-\! z \!+\! 3/4, \\ &- x \!+\! 3/4, \!+\! y; \, ^{6} \!-\! z \!+\! 3/4, \!+\! y, -\! x \!+\! 3/4; \, ^{7} \!-\! x \!+\! 1/2, \\ &z \!+\! 1/4, \! y \!+\! 3/4; \, ^{8} \!-\! y \!+\! 1/4, \, x \!+\! 1/2, \, -\! z \!+\! 3/4; \, ^{9} \!x \!+\! 1/2, - \\ &z \!+\! 3/4, \!-\! y \!+\! 1/4; \, ^{10} \!x \!+\! 1/2, \!-\! y \!+\! 1/4, \!-\! z \!+\! 3/4; \, ^{11} \!y \!+\! 3/4, \!- \\ &x \!+\! 1/2, \! z \!+\! 1/4; \, ^{12} \!x \!+\! 1/2, \! y \!+\! 3/4, \!-\! x \!+\! 1/4; \end{split}$$

Fe(cta) ₂ at 233 K		
Atom	Atom	Length / Å
Fe1	N3 ¹	2.18(2)
Fe1	N3 ²	2.18(2)
Fe1	N3 ³	2.18(2)
Fe1	N3	2.18(2)
Fe1	N3 ⁴	2.18(2)
Fe1	N3 ⁵	2.18(2)
Fe2	N4	2.20(2)
Fe2	N4 ⁵	2.20(2)
Fe2	N4 ⁶	2.20(2)
Fe2	N4 ⁷	2.20(2)
Fe2	N4 ⁸	2.20(2)
Fe2	N4 ³	2.20(2)
N4	N3	1.339(16)
N4	C5	1.328(18)
C5	C6	1.45(2)
C6	C7	1.49(4)

 $^{1}3/4\text{-}y,+z,3/4\text{-}x;\ ^{2}+z,3/4\text{-}x,3/4\text{-}y;\ ^{3}+z,+x,+y;\ ^{4}3/4\text{-}x,3/4\text{-}y,+z;\ ^{5}+y,+z,+x;\ ^{6}1\text{-}z,1\text{-}x,1\text{-}y;\ ^{7}1\text{-}y,1\text{-}z,1\text{-}x;\ ^{8}1\text{-}x,1\text{-}y,1\text{-}z$

Fe(cta) ₂ at 373 K			
Atom	Atom	Length / Å	
Fe1	N3 ¹	2.188(16)	
Fe1	N3 ²	2.188(16)	
Fe1	N3 ³	2.188(16)	
Fe1	N3 ⁴	2.188(16)	
Fe1	N3 ⁵	2.188(16)	
Fe1	N3	2.188(16)	
Fe2	N4 ⁶	2.212(15)	
Fe2	N4	2.213(15)	
Fe2	N4 ³	2.212(15)	
Fe2	$N4^4$	2.212(15)	
Fe2	N4 ⁷	2.212(15)	
Fe2	N4 ⁸	2.212(15)	
N3	N49	1.332(13)	
N3	N4	1.332(13)	
N4	C5	1.328(13)	
C5	C59	1.35(2)	
C5	C6	1.463(16)	
C6	C7	1.58(5)	

 $^{1}3/4\text{-}y,+z,3/4\text{-}x;$ $^{2}+z,3/4\text{-}x,3/4\text{-}y;$ $^{3}+z,+x,+y;$ $^{4}+y,+z,+x;$ $^{5}3/4\text{-}x,3/4\text{-}y,+z;$ $^{6}1\text{-}y,1\text{-}z,1\text{-}x;$ $^{7}1\text{-}x,1\text{-}y,1\text{-}z;$ $^{8}1\text{-}z,1\text{-}x,1\text{-}y;$ $^{9}+x,3/4\text{-}y,3/4\text{-}z$

Figure S38: Bond lengths for Fe(cta)₂ as determined at different temperatures (a-d).

15. Note to the structural chemistry of Fe(mta)₂

The crystal structure of $Fe(mta)_2$ was obtained by 3DED at four different temperatures (173 K, 233 K, RT and 373 K). In addition, a Rietveld-based structure refinement was performed based on the PXRD data at ambient pressure (s. S-20). Due to the aromaticity of triazolate linker, one would expect that - CH_3 groups of (mta)⁻ are disordered between two sites (50% occupancy) and located within the plane of the trizolate ligand. During structure solution and refinement of 3DED and PXRD data, a significantly better structural model was obtained when moving the - CH_3 group out of the triazolate plane, leading to a 25% occupancy of carbon atoms. Since this leaves some open questions related to the final structure of Fe(mta)₂ and translates to ambiguities when analyzing the pressure-induced phase transition of Fe(mta)₂, we decided focus on the comparison of the high-pressure behaviour of Fe(ta)₂ and Fe(cta)₂ in this work and address the high-pressure behaviour of Fe(mta)₂ in a follow-up study.

16. **References**

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