Incommensurate Crystal Structure, Thermal Expansion Study and Magnetic Properties of (dimethylimidazolium)$_2$[Fe$_2$Cl$_6$(μ-O)]

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Figure S1. Reciprocal lattice showing the main and satellite reflections.
Figure S2. Variable temperature synchrotron powder X-ray diffraction patterns collected while heating the sample in the 100-378 K range.
Figure S4. Sequential refinements against follow the evolution of the propagation vector with the temperature from 100 to 208 K.
Figure S4. Comparison of the PXRD patterns collected at 20 °C during sample solid-liquid transition in a heating and cooling cycle.
Table S1 (a). Intramolecular bond parameters for the imidazolium cation and most relevant interatomic distances of (dimim)$_2$[Fe$_2$Cl$_6$(μ-O)] at 293(2) K.

| Imidazolium bond parameters (Å, °) |
|-----------------------------------|
| N1–C2  | 1.319 |
| C2–N3  | 1.309 |
| N3–C4  | 1.369 |
| C4–C5  | 1.340 |
| C5–N1  | 1.349 |
| N1–C6  | 1.472 |
| N3–C7  | 1.460 |
| C6–N1–C2 | 126.5(8) |
| C7–N3–C2 | 125.8(7) |

| Supramolecular interactions |
|----------------------------|
| **Length (Å)** | **Angle (°)** |
|-----------------|---------------|
| **H···Cl (potential hydrogen bonds)** |
| C5–H5···Cl1      | 2.765         | 163.8(2)$^a$ |
| C6$^a$–H6$^a$···Cl2$^i$ | 2.860       | 139.1(1)$^a$ |
| C4$^i$–H4$^i$···Cl2 $^i$ | 2.846       | 146.8(8)$^a$ |
| **[FeCl]···[Dimim]$^+$ (potential π-d interactions)** |
| Fe···Centroid     | 5.60          | 163.4(3)$^b$ |
| Cl1···Centroid    | 4.788         | 167.0(7)      |
| Cl2···Centroid    | 4.536         | 135.1(4)      |

(a) Distance longer than the sum of vdw radii (2.95Å for C-H···Cl)

(b) Angle between Fe···Centroid vector and the imidazolium ring plane.

(c) Symmetry codes: $^i$: 2-x, 1-7, 2-z; $^a$: x, 1+y, 1+z
### Table S1 (b). Intramolecular bond parameters for the imidazolium cation and most relevant interatomic distances of (dimim)$_2$[Fe$_2$Cl$_6$(μ-O)] at 100(2) K.

| Bond                  | Average   | Minimum  | Maximum  |
|-----------------------|-----------|----------|----------|
| N1–C2                 | 1.317(13) | 1.304(13) | 1.331(13) |
| C2–N3                 | 1.333(12) | 1.320(12) | 1.347(12) |
| N3–C4                 | 1.370(11) | 1.354(11) | 1.386(11) |
| C4–C5                 | 1.343(17) | 1.334(17) | 1.351(17) |
| C5–N1                 | 1.377(12) | 1.363(12) | 1.391(12) |
| N1–C6                 | 1.461(14) | 1.455(14) | 1.467(14) |
| N3–C7                 | 1.467(14) | 1.451(12) | 1.471(12) |
| C6–N1–C2              | 124.8(8)  | 122.4(8)  | 127.3(8)  |
| C7–N3–C2              | 125.7(6)  | 122.9(6)  | 128.5(7)  |
| Assignment | (dimim)[FeCl₄] Frequency (cm⁻¹) | (dimim)₂[Fe₂Cl₆(μ-O)] Frequency (cm⁻¹) |
|------------|-------------------------------|-------------------------------------|
| Fe-Cl Sym-Bend | 110.9                         | 98.1                               |
| Fe-Cl Asym-Bend | 137.0                         | 128.4                              |
| Fe-Cl Sym-Stretch | 329.4                         | 302.6                              |
| Fe-Cl Asym-Stretch | 373.5                         | 408.2                              |
| **Fe-O-Fe Sym-Stretch** |                               |                                    |
| [Ring] ip sym bend, [Ring CH₃] CH₃-N stretch | 606.3                         | 604.3                              |
| [Ring] op asym bend, CH₃-N CN stretch | 622.7                         | 620.4                              |
| [Ring] ip asym bend, [Ring CH₃] CH₃-N stretch | 660.6                         |                                    |
| [Ring] ip asym bend, CH₃-N CN stretch | 713.6                         | 715.2                              |
| **Fe-O-Fe Sym-Stretch** |                               | **847.2**                         |
| [Ring] HC=CH asym bend | 858.8                         | 861.4                              |
| [Ring] ip sym stretch | 1020.2                        | 1026.1                             |
| [Ring] ip sym stretch, [Ring CH₃] CH₃-N stretch | 1080.5                        |                                    |
| [Ring] ip asym stretch, [Ring CH₃] CH₃-N twist | 1104.9                        | 1108.1                             |
| [Ring] ip asym stretch, [Ring CH₃] CH₃-N stretch | 1120.9                        | 1120.7                             |
| [Ring CH₃] H-C-H bend | 1168.3                        | 1195.4                             |
| [Ring] ip asym stretch, [Terminal CH₃] CH₃-N stretch | 1369.7                        | 1340.9                             |
| [Ring] ip asym stretch, [Ring CH₃] CH₃-N stretch | 1395.6                        | 1400.2                             |
| [Ring] ip asym stretch, CC stretch, CH₃-N CN stretch | 1426.8                        | 1435.1                             |
| [Ring] ip asym stretch, [Ring CH₃] CH₃-N stretch | 1570.2                        | 1560.4                             |
| [Terminal CH₃] H-C-H sym stretch | 2810.4                        | 2816.5                             |
| [Ring CH₃] H-C-H sym stretch | 2848.5                        | 2857.8                             |
| CH₃-N sym stretch | 2961.4                         | 2960.1                             |
| CH₃-N sym stretch | 2967.3                         |                                    |
| [Terminal CH₃] asym stretch | 2988.0                        | 2985.4                             |
| [Ring CH₃] H-C-H asym stretch | 3112.1                        | 3022.2                             |
| [Ring CH₃] H-C-H asym stretch | 3121.9                        | 3110.2                             |
| [Ring N-C(H)-N] C-H stretch | 3129.0                        | 3134.7                             |
| [Ring] HC=CH sym stretch, [Ring] sym stretch | 3151.7                        |                                    |
| [Ring] HC=CH sym stretch, [Ring] sym stretch | 3163.74                       | 3166.2                             |
