

## Supporting Information

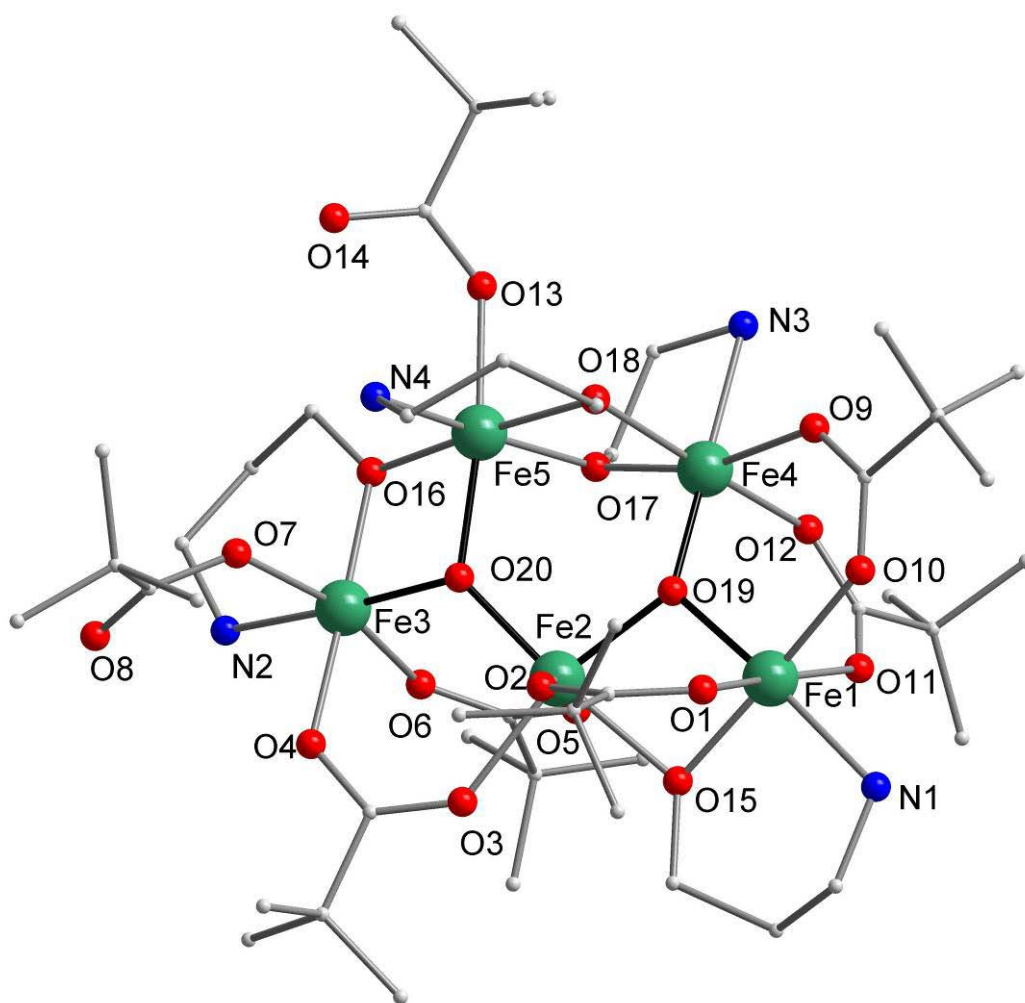
### **Pentanuclear Complexes with Unusual Structural Topologies from the Initial Use of two Aliphatic Amino-Alcohol Ligands in Fe Chemistry**

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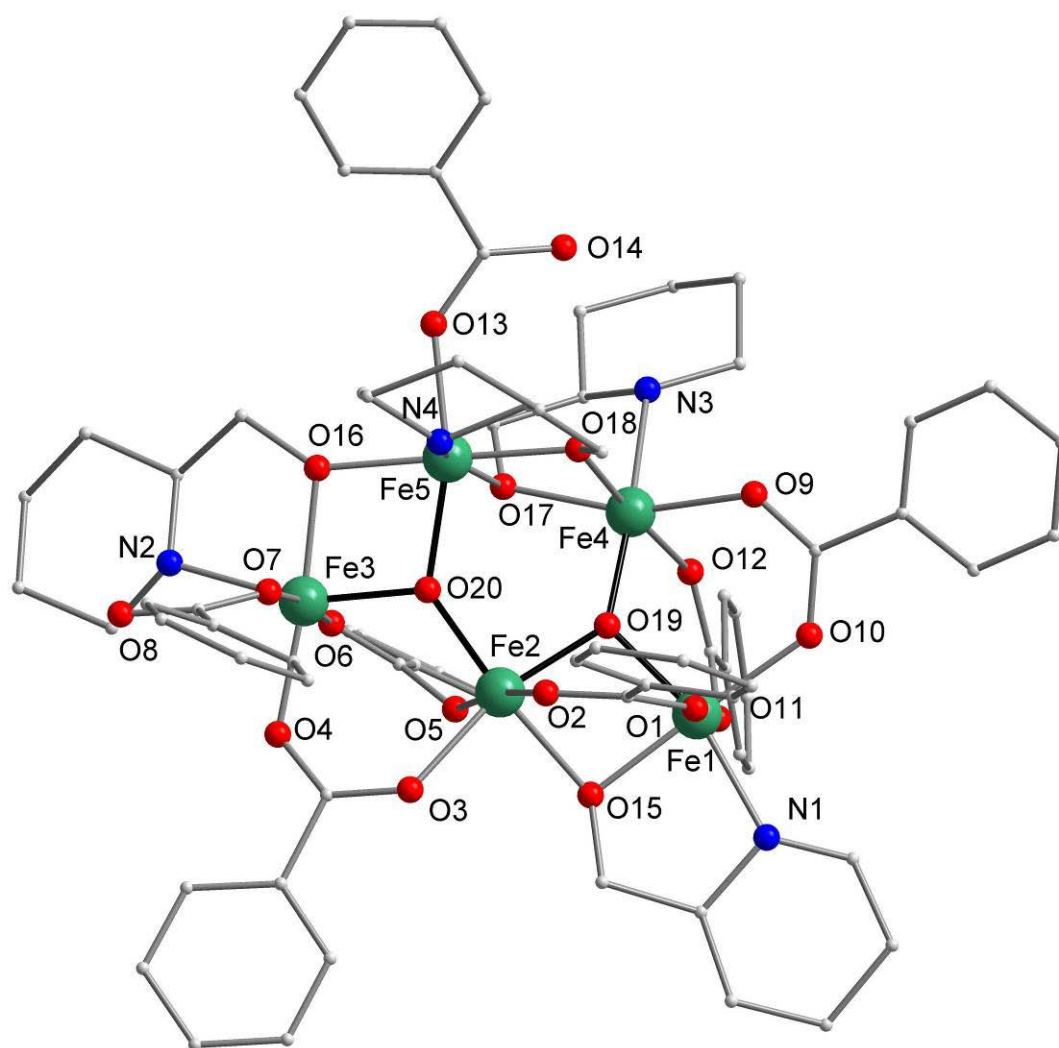
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**Fig. S1.** A partially labelled representation of the molecular structure of **2**. Colour code: Fe, green; O, red; N, blue; C, grey. H atoms are omitted for clarity.

**Table S1.** Selected interatomic distances (Å) for complex **2**

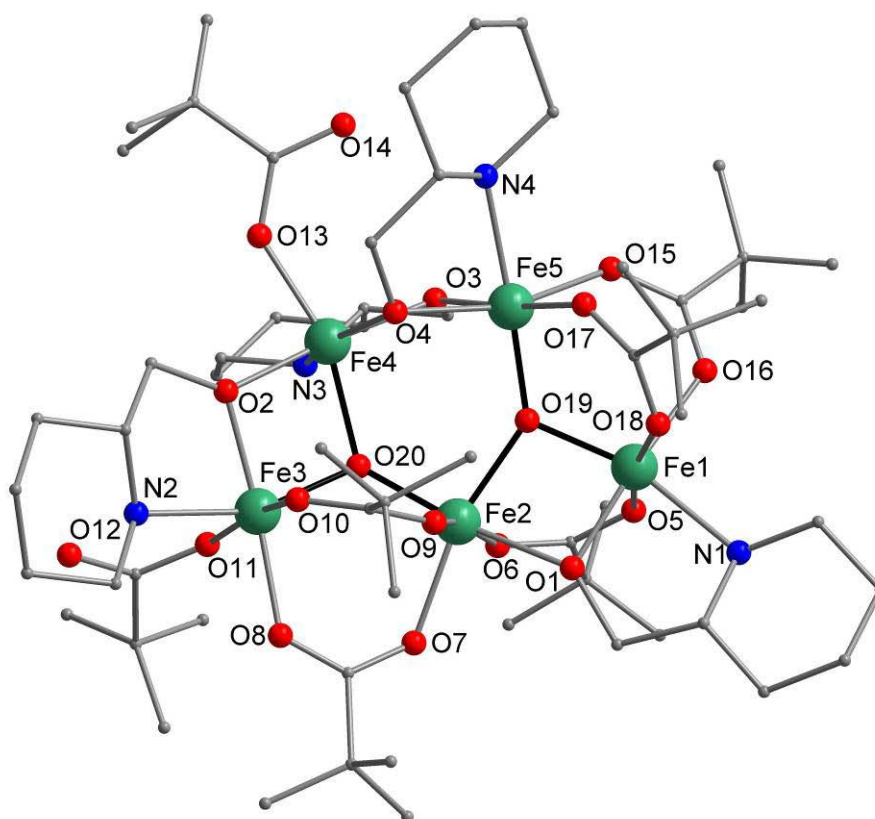
|           |          |           |          |
|-----------|----------|-----------|----------|
| Fe1...Fe2 | 2,970(1) | Fe3 - O4  | 2.015(2) |
| Fe1...Fe4 | 3,269(1) | Fe3 - O6  | 2.051(2) |
| Fe2...Fe3 | 3,265(1) | Fe3 - O7  | 2.022(2) |
| Fe2...Fe4 | 3,462(1) | Fe3 - O16 | 1.988(2) |
| Fe2...Fe5 | 3,516(1) | Fe3 - O20 | 1.904(2) |
| Fe3...Fe5 | 2,996(1) | Fe3 - N2  | 2.159(3) |
| Fe4...Fe5 | 3,045(1) | Fe4 - O9  | 2.041(2) |
| Fe1 - O1  | 2.066(2) | Fe4 - O12 | 2.030(2) |
| Fe1 - O10 | 2.066(2) | Fe4 - O17 | 1.975(2) |
| Fe1 - O11 | 2.061(2) | Fe4 - O18 | 2.020(2) |
| Fe1 - O15 | 1.946(2) | Fe4 - O19 | 1.851(2) |
| Fe1 - O19 | 1.878(2) | Fe4 - N3  | 2.181(3) |
| Fe1 - N1  | 2.124(2) | Fe5 - O13 | 2.046(2) |
| Fe2 - O2  | 2.061(2) | Fe5 - O16 | 1.987(2) |
| Fe2 - O3  | 2.065(2) | Fe5 - O17 | 1.985(2) |
| Fe2 - O5  | 2.038(2) | Fe5 - O18 | 2.017(2) |
| Fe2 - O15 | 2.117(2) | Fe5 - O20 | 2.011(2) |
| Fe2 - O19 | 1.938(2) | Fe5 - N4  | 2.132(2) |
| Fe2 - O20 | 1.889(2) |           |          |



**Fig. S2.** A partially labelled representation of the molecular structure of **3**. Colour code: Fe, green; O, red; N, blue; C, grey. H atoms are omitted for clarity.

**Table S2.** Selected interatomic distances (Å) for complex **3**·1.3MeCN·H<sub>2</sub>O

|           |          |           |          |
|-----------|----------|-----------|----------|
| Fe1...Fe2 | 2,970(9) | Fe3 - N2  | 2.168(4) |
| Fe1...Fe4 | 3,248(2) | Fe3 - O4  | 2.015(3) |
| Fe2...Fe3 | 3,214(9) | Fe3 - O6  | 2.045(3) |
| Fe2...Fe4 | 3,524(2) | Fe3 - O7  | 1.994(4) |
| Fe2...Fe5 | 3,563(2) | Fe3 - O16 | 1.993(3) |
| Fe3...Fe5 | 3,011(2) | Fe3 - O20 | 1.895(3) |
| Fe4...Fe5 | 3,041(8) | Fe4 - N3  | 2.157(4) |
| Fe1 - N1  | 2.105(4) | Fe4 - O9  | 2.023(3) |
| Fe1 - O1  | 2.077(3) | Fe4 - O12 | 2.075(3) |
| Fe1 - O10 | 2.039(3) | Fe4 - O17 | 2.039(3) |
| Fe1 - O11 | 2.032(3) | Fe4 - O18 | 1.995(3) |
| Fe1 - O19 | 1.871(3) | Fe4 - O19 | 1.848(3) |
| Fe1 - O15 | 1.981(3) | Fe5 - N4  | 2.161(4) |
| Fe2 - O2  | 2.095(3) | Fe5 - O13 | 2.006(3) |
| Fe2 - O3  | 2.066(3) | Fe5 - O16 | 1.963(3) |
| Fe2 - O5  | 2.059(3) | Fe5 - O17 | 2.012(3) |
| Fe2 - O15 | 2.064(3) | Fe5 - O18 | 1.997(3) |
| Fe2 - O19 | 1.952(3) | Fe5 - O20 | 2.011(3) |
| Fe2 - O20 | 1.875(3) |           |          |



**Fig. S3.** A partially labelled representation of the molecular structure of **4**. Colour code: Fe, green; O, red; N, blue; C, grey. H atoms are omitted for clarity.

**Table S3.** Selected interatomic distances (Å) for complex **4**·0.3H<sub>2</sub>O

|           |          |           |          |
|-----------|----------|-----------|----------|
| Fe1···Fe2 | 2,954(2) | Fe3 - N2  | 2.167(5) |
| Fe1···Fe5 | 3,230(2) | Fe3 - O10 | 2.066(4) |
| Fe2···Fe3 | 3,199(2) | Fe3 - O11 | 1.988(4) |
| Fe2···Fe4 | 3,576(2) | Fe3 - O2  | 1.983(4) |
| Fe2···Fe5 | 3,540(2) | Fe3 - O20 | 1.899(4) |
| Fe3···Fe4 | 3,038(2) | Fe3 - O8  | 2.028(5) |
| Fe4···Fe5 | 3,070(2) | Fe4 - N3  | 2.177(5) |
| Fe1 - N1  | 2.174(5) | Fe4 - O13 | 2.007(4) |
| Fe1 - O1  | 1.955(4) | Fe4 - O2  | 1.959(4) |
| Fe1 - O16 | 2.028(4) | Fe4 - O20 | 2.048(4) |
| Fe1 - O18 | 2.025(5) | Fe4 - O3  | 1.997(4) |
| Fe1 - O19 | 1.864(4) | Fe4 - O4  | 2.031(4) |
| Fe1 - O5  | 2.072(4) | Fe5 - N4  | 2.163(5) |
| Fe2 - O1  | 2.070(4) | Fe5 - O15 | 2.043(4) |
| Fe2 - O19 | 1.959(4) | Fe5 - O17 | 2.082(4) |
| Fe2 - O20 | 1.861(4) | Fe5 - O19 | 1.844(4) |
| Fe2 - O6  | 2.066(4) | Fe5 - O3  | 1.985(4) |
| Fe2 - O7  | 2.049(4) | Fe5 - O4  | 2.044(4) |
| Fe2 - O9  | 2.018(4) |           |          |