# Supporting information

## Strategies for Synthesis of Prussian Blue Analogues

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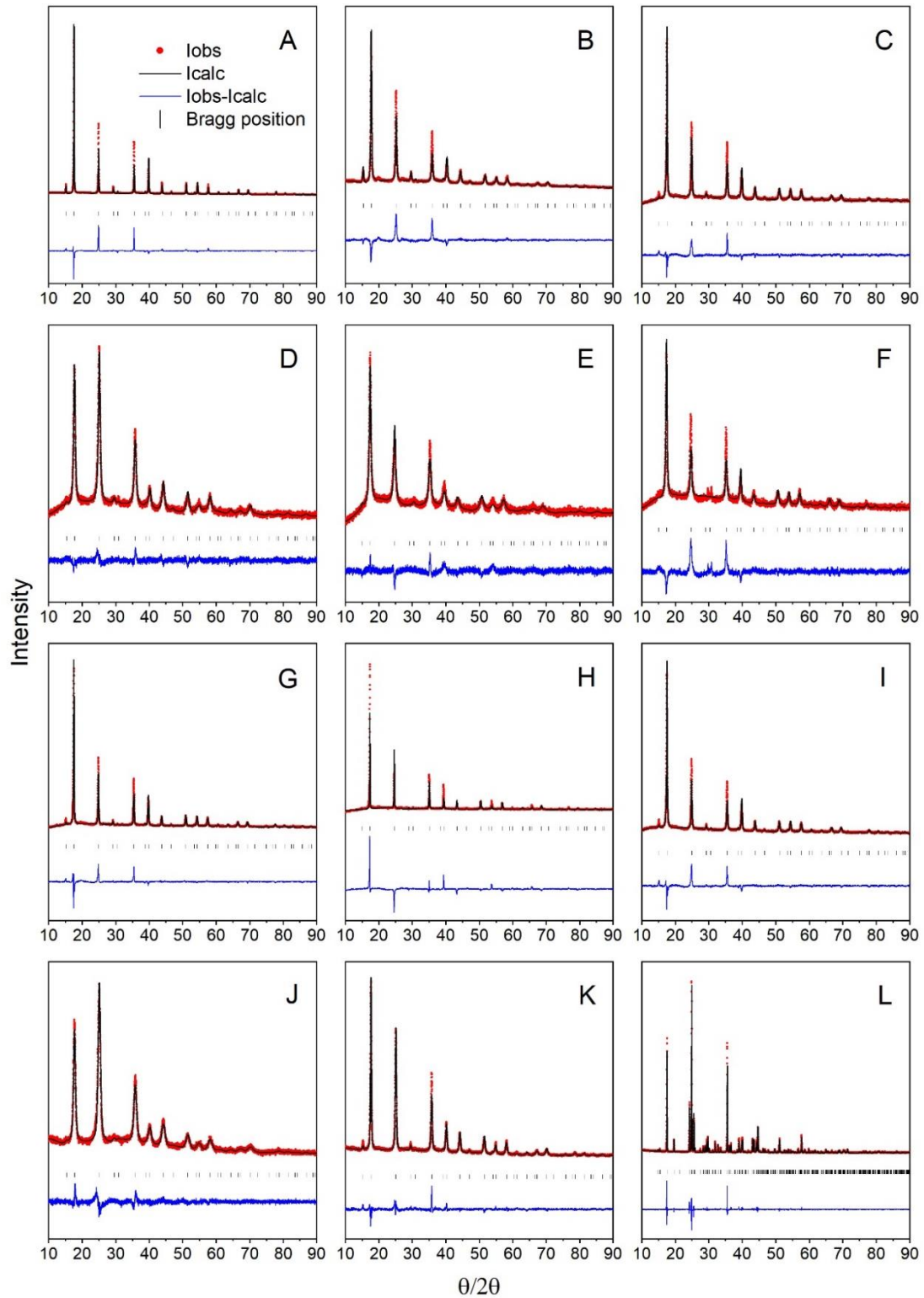
Powder X-ray diffraction



**Figure S1:** Rietveld refinement

**Table S1:** Crystallographic details

| A | Space group | *Fm-3m* |
|---|---|---|
| | Number of data points | 7995 |
| | Number of background points | 27 |
| | Number of fitted parameters | 38 |
| | RBragg | 18.5 |
| | Rf | 9.16 |
| B | Space group | *Fm-3m* |
| | Number of data points | 7995 |
| | Number of background points | 24 |
| | Number of fitted parameters | 34 |
| | RBragg | 17.9 |
| | Rf | 9.91 |
| C | Space group | *Fm-3m* |
| | Number of data points | 11243 |
| | Number of background points | 16 |
| | Number of fitted parameters | 27 |
| | RBragg | 11.7 |
| | Rf | 6.79 |
| D | Space group | *Fm-3m* |
| | Number of data points | 11243 |
| | Number of background points | 15 |
| | Number of fitted parameters | 27 |
| | RBragg | 4.02 |
| | Rf | 4.85 |
| E | Space group | *Fm-3m* |
| | Number of data points | 11243 |
| | Number of background points | 14 |
| | Number of fitted parameters | 21 |
| | RBragg | 8.65 |
| | Rf | 6.77 |
| F | Space group | *Fm-3m* |
| | Number of data points | 11243 |
| | Number of background points | 15 |
| | Number of fitted parameters | 22 |
| | RBragg | 16.6 |
| | Rf | 8.92 |
| G | Space group | *Fm-3m* |
| | Number of data points | 11243 |
| | Number of background points | 17 |
| | Number of fitted parameters | 28 |
| | RBragg | 9.99 |
| | Rf | 7.90 |

| H | Space group | *Fm-3m* |
|---|---|---|
| | Number of data points | 11243 |
| | Number of background points | 15 |
| | Number of fitted parameters | 22 |
| | RBragg | 40.5 |
| | Rf | 21.7 |
| I | Space group | *Fm-3m* |
| | Number of data points | 11243 |
| | Number of background points | 22 |
| | Number of fitted parameters | 33 |
| | RBragg | 14.7 |
| | Rf | 9.15 |
| J | Space group | *Fm-3m* |
| | Number of data points | 7995 |
| | Number of background points | 12 |
| | Number of fitted parameters | 24 |
| | RBragg | 3.04 |
| | Rf | 2.76 |
| K | Space group | *Fm-3m* |
| | Number of data points | 7995 |
| | Number of background points | 20 |
| | Number of fitted parameters | 31 |
| | RBragg | 5.53 |
| | Rf | 4.80 |
| L | Space group | *P2$_1$/c* |
| | Number of data points | 7995 |
| | Number of background points | 24 |
| | Number of fitted parameters | 43 |
| | RBragg | 6.28 |
| | Rf | 6.07 |

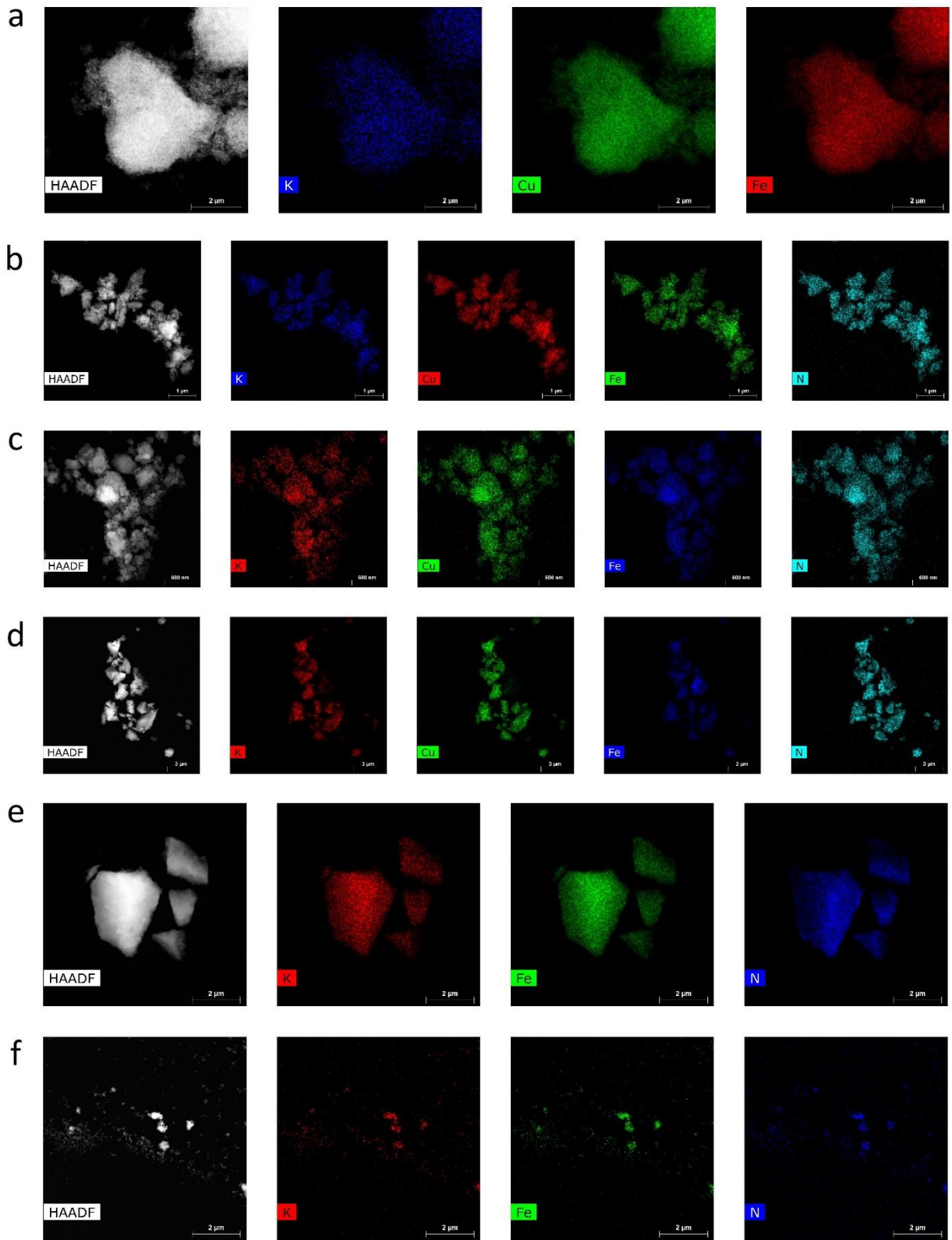Transmission electron microscopy
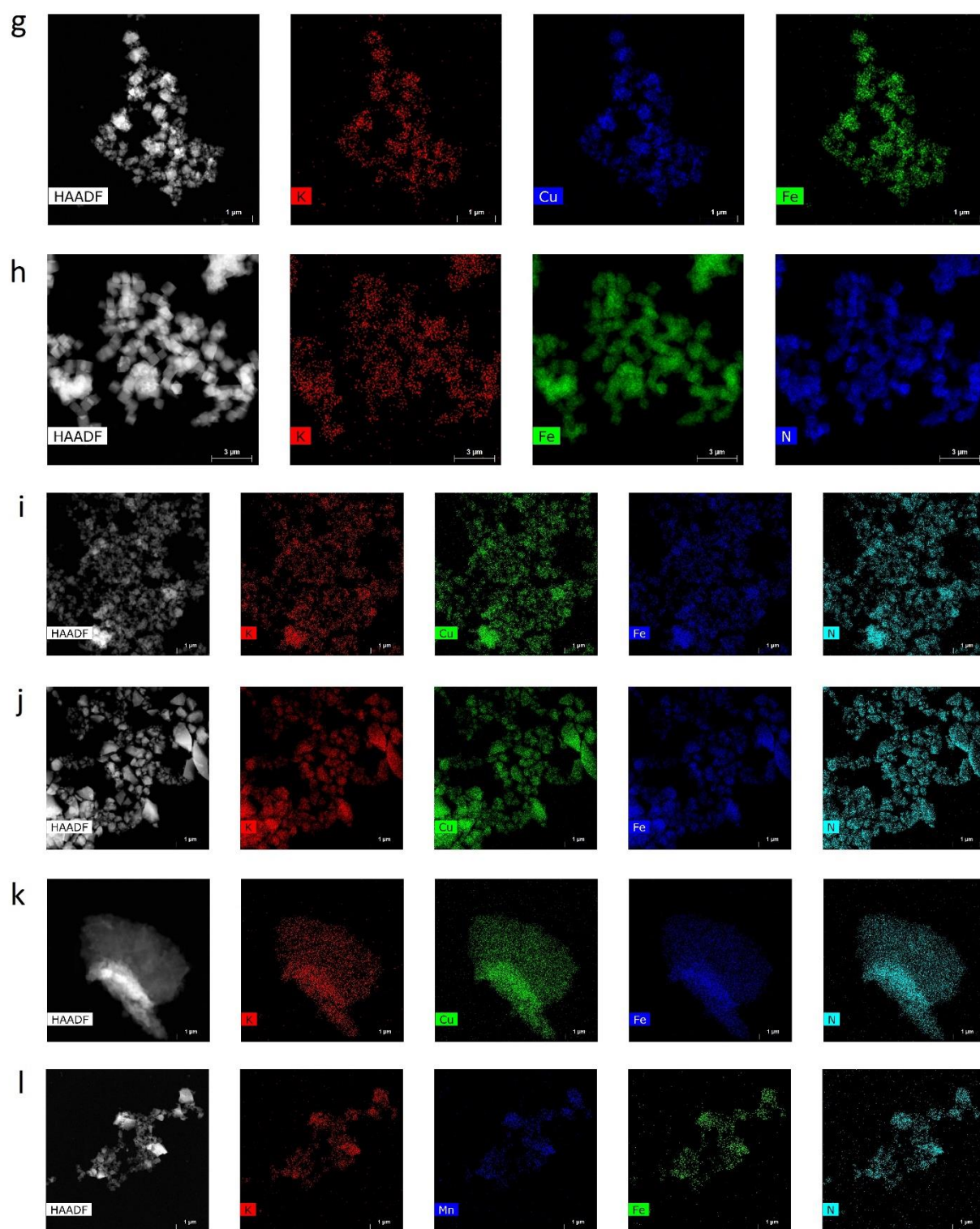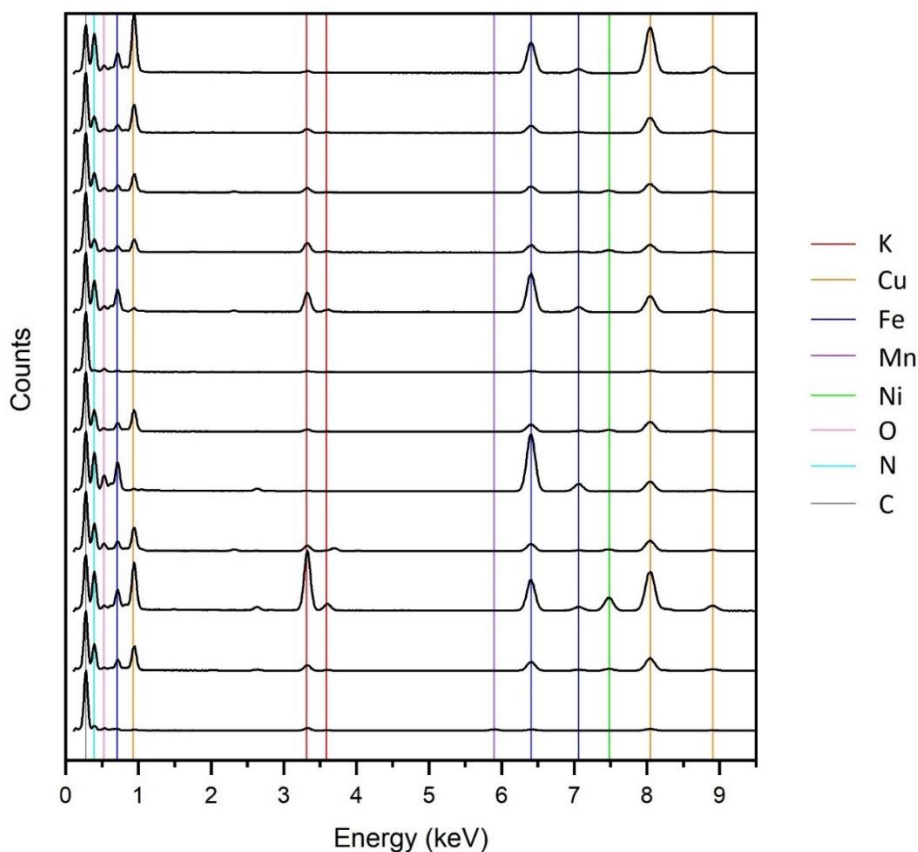


**Figure S2:** STEM-EDS

**Figure S3:** STEM-EDS

## Energy dispersive spectroscopy (STEM-EDS)

It has been suggested that PBAs grown in the presence of excess chloride may contain Cl in the framework.[1] EDS spectra of sample G, Cu[Fe] precipitated in the presence of excess KCl, shows no Cl signal, indicating that Cl is not included in the framework.
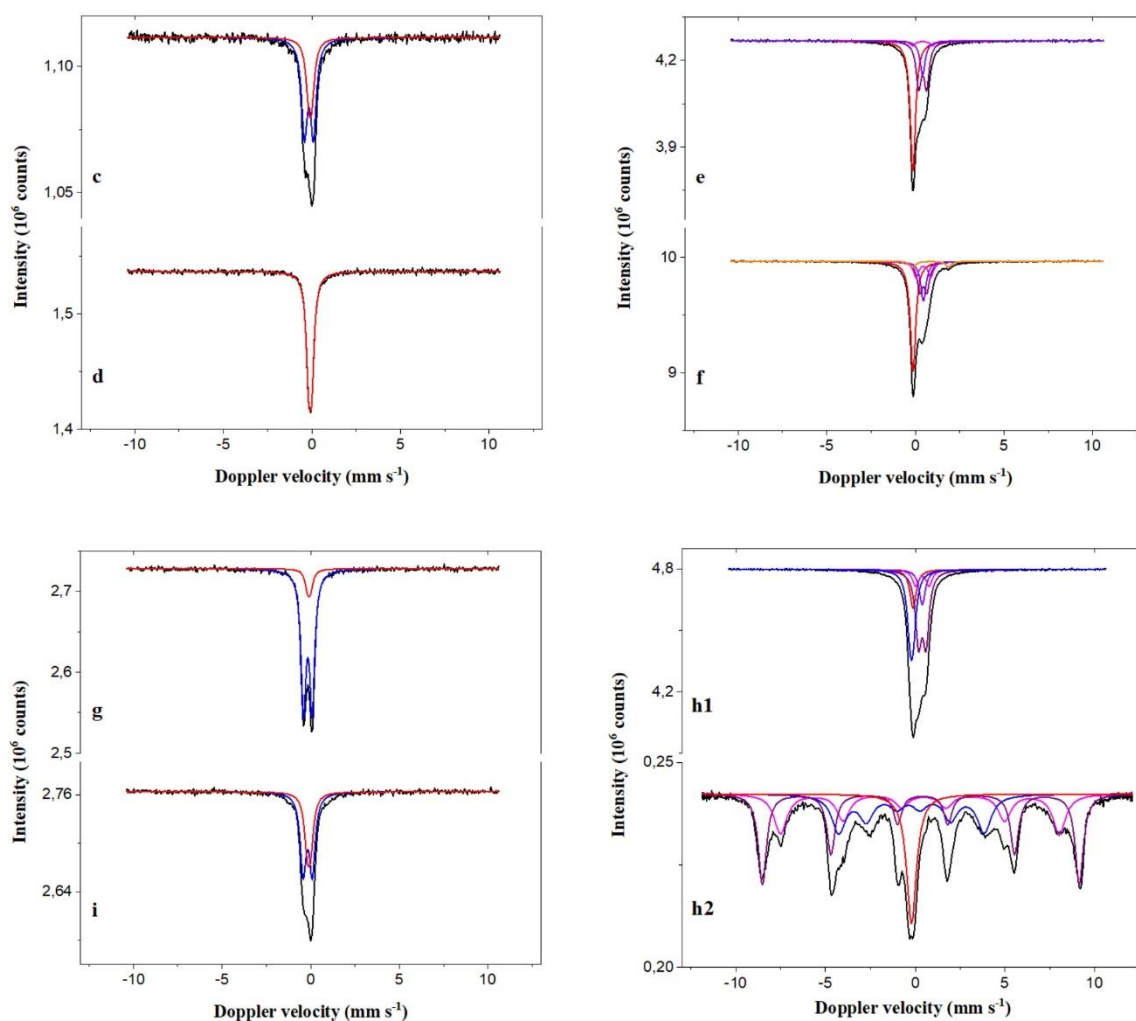


**Figure S4:** EDS spectra

**Table S2:** EDS table

| Element # | Element | Line | Energy (keV) |
|---|---|---|---|
| 6 | C | Kα1,2 | 0.277 |
| 8 | O | Kα1,2 | 0.5249 |
| 14 | N | Kα1,2 | 0.3924 |
| 19 | K | Kα2 | 3.3111 |
| 19 | K | Kα1 | 3.3138 |
| 19 | K | Kβ1,3 | 3.5896 |
| 25 | Mn | Kα1 | 5.8988 |
| 28 | Ni | Kα2 | 7.4609 |
| 28 | Ni | Kα1 | 7.4782 |
| 29 | Cu | Lα1,2 | 0.9297 |
| 29 | Cu | Kα2 | 8.0278 |
| 29 | Cu | Kα1 | 8.0478 |
| 29 | Cu | Kβ1,3 | 8.9053 |

# Mössbauer spectroscopy



**Figure S5:** Mössbauer spectra obtained at 300K except h2 at 4.2K.

Mössbauer spectra of samples C-I were measured at 300 K. The fits have been constrained to a single linewidth ($\Gamma$) for all doublets, as Grandjean *et al.*[2] Grandjean *et al.* suggest that the use of different linewidths for the single iron(II) doublet and single iron(III) doublet might conceal variations in the local iron(III) electronic environment

Prussian blues are mixed valence compounds. The single quadrupole doublet with an isomer shift varying from -0.09 to -0.14 mm/s results from LS Fe(II) ions coordinated to six carbon. The three doublets with an isomer shift of approximately 0.40 mm/s result from HS Fe(III) ions coordinated to six nitrogen.

Mössbauer spectral parameters vary somewhat with temperature. The temperature dependence of the fitted parameters were investigated by Grandjean *et al.*,[2] indicating that the temperature dependence agrees well with the Debye model.

H1 and H2 is the same compound, measured at 300 K (H1) and 4.3 K (H2). The quadrupole doublets become magnetic sextets at low temperature.


**Table S3:** Mössbauer fitted parameters

| Sample | T (K) | IS (mm/s) | QS (mm/s) | Hyperfine field (T) | Γ (mm/s) | Phase | Spectral contribution (%) |
|--------|-------|-----------|-----------|---------------------|----------|-------|---------------------------|
| C | 300 | -0.09 | 0.17 | - | 0.39 | LS Fe$^{II}$ | 34 |
|   |     | -0.17 | 0.50 | - | 0.39 | LS Fe$^{III}$ | 66 |
| D | 300 | -0.09 | 0.18 | - | 0.33 | LS Fe$^{II}$ | 100 |
| E | 300 | -0.14 | 0.00 | - | 0.35 | LS Fe$^{II}$ | 50 |
|   |     | 0.41 | 0.38* | - | 0.35 | HS Fe$^{III}$ | 50 |
| F | 300 | -0.13 | 0.00 | - | 0.36 | LS Fe$^{II}$ | 44 |
|   |     | 0.45 | 0.38* | - | 0.36 | HS Fe$^{III}$ | 51 |
|   |     | 0.87 | 2.00 | - | 0.36 | HS Fe$^{II}$ | 5 |
| G | 300 | -0.09 | 0.17 | - | 0.34 | LS Fe$^{II}$ | 11 |
|   |     | -0.16 | 0.49 | - | 0.34 | LS Fe$^{III}$ | 89 |
| H1 | 300 | -0.12 | 0.00 | - | 0.41 | LS Fe$^{II}$ | 11 |
|    |     | -0.20 | 0.16 | - | 0.41 | LS Fe$^{III}$ | 30 |
|    |     | 0.40 | 0.39* | - | 0.41 | HS Fe$^{III}$ | 59 |
| H2 | 4.2 | -0.20 | 0.00 | - | 0.67 | LS Fe$^{II}$ | 15 |
|    |     | -0.29 | 0.17 | 25.2 | 0.94 | LS Fe$^{III}$ | 25 |
|    |     | 0.37 | -0.22 | 48.3 | 0.86 | HS Fe$^{III}$ | 25 |
|    |     | 0.37 | -0.11 | 54.9 | 0.55 | HS Fe$^{III}$ | 35 |
| I | 300 | -0.09 | 0.19 | - | 0.39 | LS Fe$^{II}$ | 37 |
|   |     | -0.17 | 0.51 | - | 0.34 | LS Fe$^{III}$ | 63 |

Experimental uncertainties: Isomer shift (IS): ± 0.02 mm/s; quadrupole splitting (QS): ± 0.02 mm/s; line width (Γ): ± 0.03 mm/s; spectral contribution: ± 3 %.

*Average quadrupole splitting value (as in Grandjean *et al.*[2])


**Stoichiometry of Fe[Fe] samples**

The stoichiometry of Fe[Fe] samples is determined using Mössbauer spectroscopy data. The LS/HS ratio provides the number of vacancies, and potassium content is determined by charge balance.

Example calculation, sample H: $K_x Fe^{III}[Fe^{III/II}(CN)_6]_y$

From Mössbauer: 40% Fe is low spin: C-Fe, 60% Fe is high spin: N-Fe

Y : 40/60 *100 = 67 %

X : 3 + (0.67*15/40)*2 + (0.67*25/40)*3 − 0.67*6 = 0.74

The stoichiometry is therefore $K_{0.74}Fe^{III}[Fe^{III/II}(CN)_6]_{0.67}$

# References

1       D. E. Stilwell, K. H. Park and M. H. Miles, *J. Appl. Electrochem.*, 1992, **22**, 325–331.

2       F. Grandjean, L. Samain and G. J. Long, *Dalt. Trans.*, 2016, **45**, 18018–18044.