ChemComm
www.rsc.org/chemcomm

ESI – Complete Crystallographic Information

The crystals of **1** were synthesised as discussed previously in the literature.[4]
A typical red crystal was chosen 0.20 x 0.10 x 0.07 mm, mounted in fluoropolyether oil on a hair and quench cooled to 200 K using an Oxford Cryosystems Cryostream 600 series open flow N_2 cooling device.[7] Using a Bruker SMART-CCD 1000 area detector diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), several sets of ω-scans (0.3°/frames) at different ϕ settings were collected. On completion, the crystal was cooled to 120 K at 240 K/hr, where the data collection was repeated. The crystal was then warmed to 200 K at 180 K/hr then to 290 K at 360 K/hr where the crystal was removed. The Cryostream was then replaced with an Oxford Cryosystems HeliX open flow helium cryostat,[8] and the crystal was cooled to 30 K in stages. At 30 K a hemisphere of data was collected (ω-scans, 0.9°/frames), after which the crystal was irradiated for approximately 30 mins with a 25 mW red laser (λ = 633 nm) after which data were collected as at 200 K and 120 K. Cell parameters were determined and refined using the SMART software[9] and raw frame data were integrated using the SAINT program.[10] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL software[11] (crystal data are listed below). Reflection intensities were corrected for absorption effects by numerical integration based on measurements and indexing of the crystal faces (using SHELXTL software). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located in the difference map and refined with isotropic displacement parameters.

Single Crystal Data: $C_{22}H_{24}B_2FeN_{10}$, M_r = 505.98, monoclinic, **C**2/*c*, *Z* = 4.
200 K – *a* = 16.2215(15) Å, *b* = 15.0254(15) Å, *c* = 11.0397(11) Å, *b* = 114.858(4)°, *V* = 2441.5(4) Å, Data/restraints/parameters – 3510/0/207, R_{int} = 0.0514, Final R_1 = 0.0521, wR_2 = 0.0777 (I>2s (I)).
120 K – *a* = 16.1373(8) Å, *b* = 14.6208(8) Å, *c* = 10.8120(6) Å, *b* = 113.775(2)°, *V* = 23334.5(2) Å, Data/restraints/parameters – 3351/0/207, R_{int} = 0.0567, Final R_1 = 0.0501, wR_2 = 0.0856 (I>2s (I)).
30 K – *a* = 16.1106(11) Å, *b* = 14.5909(10) Å, *c* = 10.8281(8) Å, *b* = 113.895(3)°, *V* = 2327.2(3) Å, Data/restraints/parameters – 2662/0/207, R_{int} = 0.0606, Final R_1 = 0.0491, wR_2 = 0.0823 (I>2s (I)).
30 K-Irr – *a* = 16.0350(9) Å, *b* = 14.9377(9) Å, *c* = 11.0470(7) Å, *b* = 114.986(2)°, *V* = 2398.4(2) Å, Data/restraints/parameters – 2700/0/207, R_{int} = 0.0629, Final R_1 = 0.0630, wR_2 = 0.0969 (I>2s (I)).
$\Delta\rho_{min,max}$<±1 e.Å^3 in all cases.

The crystals of **2** were synthesised as discussed previously in the literature.[4]
A typical red crystal was chosen (0.28 x0.10x0.02 mm), mounted in epoxy resin (Araldite®) on a hair and quench cooled to 200 K using an Oxford Cryosystems Cryostream 600 series open flow N_2 cooling device.[8] Using a Bruker SMART-CCD 6000 area detector diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), data were collected as for **1**. On completion, the crystal was cooled to 100 K at 360 K/hr, where the data collection was repeated. A second red crystal (0.28 x 0.10 x 0.02 mm) was selected, mounted (as before), and quenched to 200 K using an Oxford Cryosystems HeliX.[7] Cell parameters recorded using a Bruker ProteumM diffractometer with Bede Microsource® (Mo-Kα radiation, λ = 0.71073 Å), agreed with those seen previously at 200 K, so the crystal was cooled to 30 K at 360 K/hr, where a hemisphere was collected (as before). On completion, the crystal was irradiated for approximately 2 mins with a 25 mW red laser (λ = 633 nm) after which another hemisphere was collected. The data treatment was carried out as for **1**, except that hydrogen atoms were positioned geometrically and refined using a riding model.

Single Crystal Data: $C_{22}H_{24}B_2FeN_{10}$, M_r = 505.98.
200 K – monoclinic, **C**2/*c*, *Z* = 4, *a* = 17.3607(16) Å, *b* = 16.0397(14) Å, *c* = 10.5614(9) Å, *b* = 121.617(4)°, *V* = 2504.4(4) Å, Data/restraints/parameters – 3370/0/216, R_{int} = 0.0485, Final R_1 = 0.0461, wR_2 = 0.0888 (I>2s (I)).
100 K – triclinic, **P**$\bar{1}$, *Z* = 2, *a* = 11.6730(13) Å, *b* = 11.0458(13) Å, *c* = 10.5651(12) Å, *a* = 69.520(3)°, *b* = 109.777(3)°, *g* = 93.368(3)°, *V* = 1198.1(2) Å, (the related larger cell: *a* = 16.5354(14) Å, *b* = 15.5923(13) Å, *c* = 10.5651(12) Å, *a* = 89.688(4)°, *b* = 118.202(3)°, *g* = 93.168(3)°, *V* = 2396.2(3) Å) Data/restraints/parameters – 6409/0/403, R_{int} = 0.0539, Final R_1 = 0.0628, wR_2 = 0.1296 (I>2s (I)).
30 K – triclinic, **P**$\bar{1}$, *Z* = 2, *a* = 16.655(2) Å, *b* = 11.0156(19) Å, *c* = 10.5664(8) Å, *a* = 69.492(3)°, *b* = 109.755(3)°, *g* = 93.280(3)°, *V* = 1192.9(4) Å, Data/restraints/parameters – 5832/0/407, R_{int} = 0.0546, Final R_1 = 0.0545, wR_2 = 0.0894 (I>2s (I)).
30 K-Irr – triclinic, **P**$\bar{1}$, *Z* = 2, *a* = 10.727(7) Å, *b* = 12.415(8) Å, *c* = 10.712(6) Å, *a* = 67.473(15)°, *b* = 110.377(15)°, *g* = 93.505(11)°, *V* = 1231.0(13) Å, Data/restraints/parameters – 5369/0/350, R_{int} = 0.0302, Final R_1 = 0.0798, wR_2 = 0.1620 (I>2s (I)).
$\Delta\rho_{min,max}$<±1.2 e.Å^3 in all cases.

All structures have been deposited with the CCDC (Nos 233281- 233288). The data is also available in CIF format.