Supporting Information for

A Ladder type Iron(II) Coordination Polymer with Cooperative Spin Transition

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The intensity data of **5** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated MoKα radiation. The data were corrected for Lorentz and polarisation effects. The structures were solved by Direct Methods (SIR97)[1] and refined by full-matrix least-square techniques against $Fo^2 - Fc^2$ (SHELXL-97).[2] All hydrogen atoms were calculated in idealised positions except for the solvent bonded hydrogens that were not considered. ORTEP-III[3] was used for the structure representation, SCHAKAL-99[4] to illustrate molecule packing. The crystallographic data are summarised in Supporting Information Table S1. The quality of the data is inferior. The remaining residue densities cannot be assigned to any solvent molecules. We will therefore only be publishing the conformation of the molecule and the crystal data.

Special refinement details:

There is a twin axis: [-1-1-1], the volume fraction of the twin component from refinement is 0.43408.

Disorder was observed for one of the pyridine rings and the ethylene group of the bispyridylethane axial ligand. This (approx. 50:50) disorder was refined by setting a free variable. The disordered atoms were not set anisotrop.

The solvent atoms were left isotrop, free variables were set to determine the occupancies, H-atoms were not considered.

During the structure refinement difficulties were encountered for the terminal carbon C18 of the ethyl ester group of the Schiff base like ligand (large U compared to neighbours) thus a free variable was set to allow for partial occupancies. A chemical explanation might be, that a partial replacement of the ethyl ester group by a methyl group did occur during the complex synthesis with methanol as solvent. Such behaviour was already frequently observed for iron complexes of this ligand type.

Magnetic susceptibility data were collected using a Quantum Design MPMSR-2 SQUID magnetometer under an applied field of 0.5 T over the temperature range 2–400 K in the settle mode. The samples were placed in gelatine capsules held within a plastic straw. The data were corrected for the diamagnetism of the ligands, using tabulated Pascal's constants and of the sample holder.

The powder diffractograms A and B were recorded on a STOE StadiP diffractometer (transmission geometry) using Ge monochromated CuKα1 radiation and a Mythen1K detector. For cooling the diffractometer is equipped with an Oxford Cryostream LT system (liquid nitrogen). The powder patterns of the HS state (A) and the LS state (B) of **6** are both similar. A shift of the signals due to the bond length changes upon spin transition is clearly visible. The simulated powder pattern of 5 (C) is similar to both, the HS and the LS species. It is difficult to tell which pattern (A or B) is closer to the simulated one, as the spin transition is incomplete in the low temperature region and an overly of both patterns is observed for the diffractrogram B.

All syntheses of the iron(II) complexes were carried out under argon using Schlenk tube techniques. All solvents were purified as described in literature and distilled under argon.[5] The syntheses of anhydrous iron(II) acetate[6] and the ligand H_4L2^*[7] were published before, bipy, bpee, bpea and bppa were used as received (Aldrich).

$[Fe_2L2^*(MeOH)_4]$: A solution of iron(II) acetate (2.60 g, 14.8 mmol) and H_4L2^* (4.00 g, 6.30 mmol) in methanol (200 mL) was heated to reflux for 4 h. After 24 h at 4°C the product precipitated as light brown solid, which was filtered off, washed with methanol (2 × 5 mL) and dried *in vacuo* (yield 4.52 g, 76%). Elemental analysis calcd (%) for $C_{38}H_{54}Fe_2N_4O_{16}$ (934.54): C 48.9 H 5.8, N 6.0; found: C 49.3, H 5.2, N 6.4.

$[Fe_2L2^*(bpea)_2]\cdot x\,MeOH$ (**5**): For the diffusion setup 0.44 g (2.39 mmol) bpea and 0.1 g (0.12 mmol) $[Fe_2L2^*(MeOH)_4]$ were converted in methanol (30mL). Brown crystals were obtained after four weeks.

$[Fe_2L2^*(bpea)_3]\cdot MeOH$: A suspension of $[Fe_2L2^*(MeOH)_4]$ (0.20 g, 0.24 mmol) and bpea (0.88 g, 4.77 mmol) in methanol (30 mL) was heated to reflux for 1 h. The formation of a precipitate was observed in the boiling heat. After cooling and filtration $[Fe_2L2^*(bpea)_3]\cdot MeOH$ was washed with methanol (2 × 5 mL) and dried *in vacuo* (yield

0.10 g, 30%). Elemental analysis calcd (%) for $C_{71}H_{78}Fe_2N_{10}O_{13}$ (1911.12): C 61.30, H 5.65, N 10.07; found: C 60.76, H 5.53, N 9.99.

$[Fe_2L2^*(bppa)_2]\cdot2.5$ Tol: A suspension of $[Fe_2L2^*(MeOH)_4]$ (0.22 g, 0.24 mmol) and bppa (0.70 g, 3.53 mmol) in toluene (30 mL) was heated to reflux for 2 h. The formation of a precipitate was observed in the boiling heat. After cooling and filtration $[Fe_2L2^*(bppa)_2]\cdot2.5$ Tol was obtained as brown solid that was washed with toluene (2 × 5 mL) and dried *in vacuo* (yield 0.10 g, 29%). IR (KBr): $\tilde{\nu}$ = 1689(s) (COO), 1571(s) cm^{-1} (CO); MS (FAB-(+), 70 eV): *m/z* (%): 806 (14) $[FeL2a^+]$, 199 (100) $[bpea + H^+]$. Elemental analysis calcd (%) for $C_{77.5}H_{86}Fe_2N_8O_{12}$ (1433.25): C 65.0, H 6.1, N 7.8; found: C 65.2, H 6.1, N 7.8.

$[Fe_2L2^*(bpea)_2]\cdot2$ Tol: A suspension of $[Fe_2L2^*(MeOH)_4]$ (0.27 g, 0.29 mmol) and bpea (1.06 g, 5.78 mmol) in toluene (25 mL) was heated to reflux for 2 h. The formation of a precipitate was observed in the boiling heat. After cooling and filtration $[Fe_2L2^*(bpea)_2]\cdot2$ Tol was obtained as yellow ochre solid that was washed with toluene (2 × 5 mL) and dried *in vacuo* (yield 0.36 g, 91%). IR (KBr): $\tilde{\nu}$ = 1690(s) (COO), 1574(s) cm^{-1} (CO); MS (FAB-(+), 70 eV): *m/z* (%): 806 (14) $[FeL2a^+]$, 185 (9) $[bpea + H^+]$; 154 (100), 136 (70). Elemental analysis calcd (%) for $C_{72}H_{78}Fe_2N_8O_{12}$ (1359.13): C 63.6, H 5.8, N 8.2; found: C 62.9, H 5.7, N 8.1.

$[Fe_2L2^*(bpee)_2]\cdot1.5$ Tol (**5’**): A suspension of $[Fe_2L2^*(MeOH)_4]$ (0.27 g, 0.29 mmol) and bpee (0.79 g, 4.33 mmol) in toluene (30 mL) was heated to reflux for 5 h. The formation of a precipitate was observed in the boiling heat. After cooling and filtration **5’** was obtained as greenish solid that was washed with toluene (2 × 5 mL) and dried *in vacuo* (yield 0.27 g, 80%). IR (KBr): $\tilde{\nu}$ = 1688(s) (COO), 1572(s) cm^{-1} (CO); MS (FAB-(+), 70 eV): *m/z* (%): 806 (13) $[FeL2a^+]$, 183 (50) $[bpee + H^+]$; 154 (100), 136 (71). Elemental analysis calcd (%) for $C_{68.5}H_{70}Fe_2N_8O_{12}$ (1309.03): C 62.8, H 5.4, N 8.6; found: C 62.6, H 5.5, N 8.1.

$[Fe_2L2^*(bipy)_2]\cdot$Tol: A suspension of $[Fe_2L2^*(MeOH)_4]$ (0.22 g, 0.24 mmol) and bipy (0.55 g, 3.53 mmol) in toluene (30 mL) was heated to reflux for 2 h. The formation of a precipitate was observed in the boiling heat. After cooling and filtration $[Fe_2L2^*(bipy)_2]\cdot$Tol was obtained as brown solid that was washed with toluene (2 × 5 mL) and dried *in vacuo* (yield 0.19 g, 71%). IR (KBr): $\tilde{\nu}$ = 1690(s) (COO), 1573(s) cm^{-1} (CO); MS (FAB-(+), 70 eV): *m/z* (%): 806 (2) $[FeL2a^+]$, 157 (9) $[bipy + H^+]$; 154 (100), 136 (68). Elemental analysis calcd (%) for $C_{61}H_{62}Fe_2N_8O_{12}$ (1210.88): C 60.5, H 5.2, N 9.3; found: C 60.7, H 5.2, N 9.4.

Figure S1. Plot of the $\chi_M T$ product versus T for the compound $[Fe_2L2^*(bpea)_3]\cdot MeOH$, $[Fe_2L2^*(bpea)_2]\cdot 2$ Tol and $[Fe_2L2^*(bppa)_2]\cdot 2.5$ Tol.

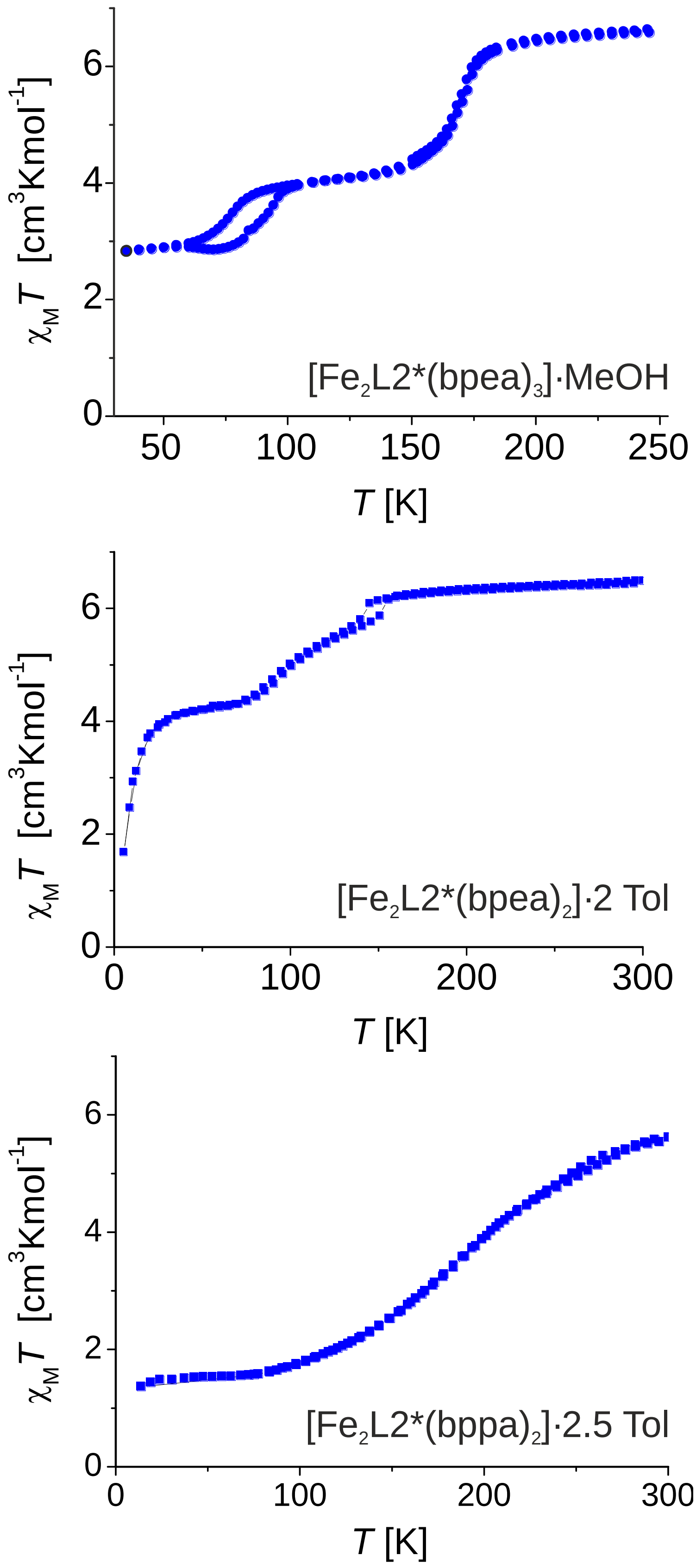

Figure S2. Packing of the molecules of **5** in the crystal projected along [1 0 0], top, and [0 1 0], bottom. Solvent molecules, disordered parts and hydrogen atoms are omitted for clarity.

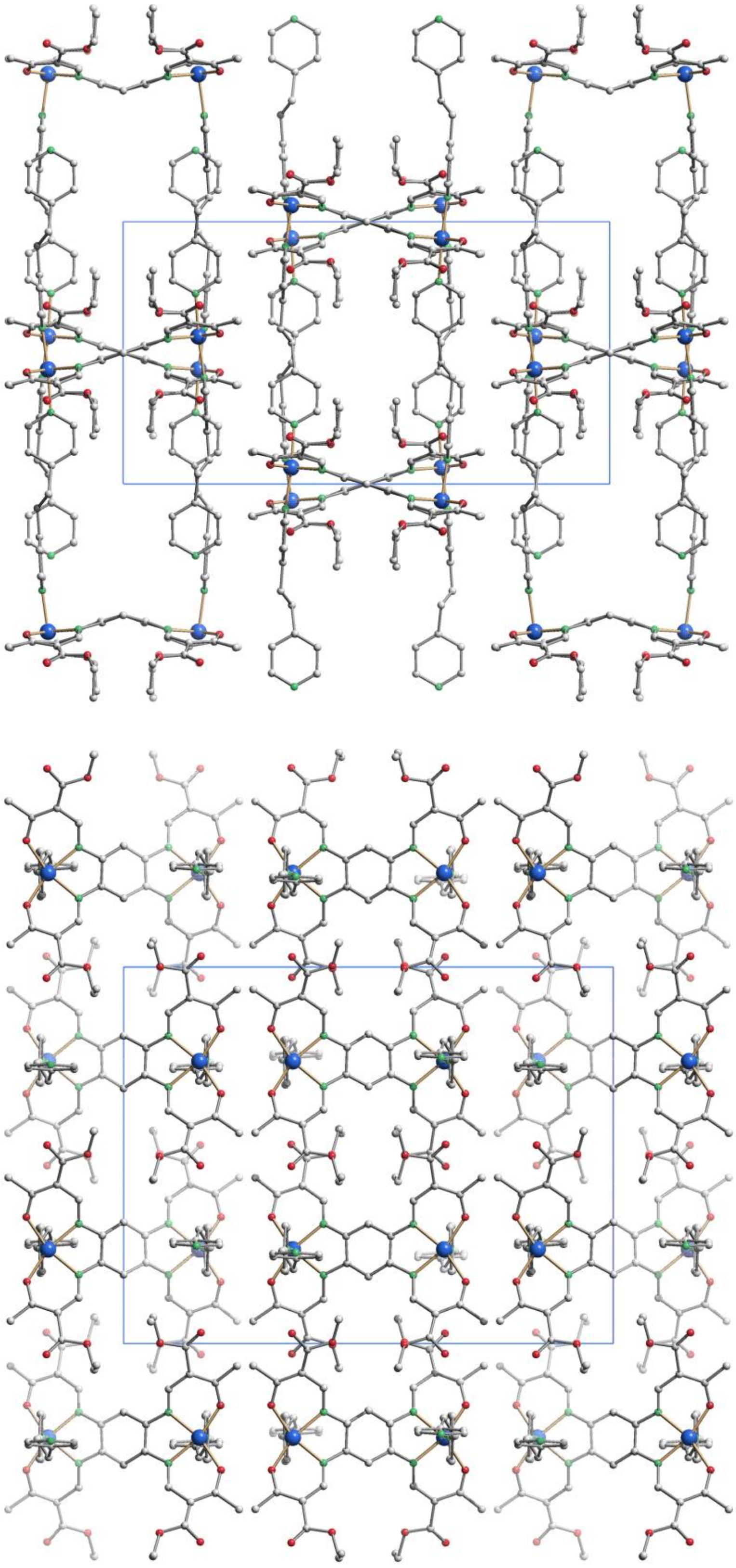

Figure S3. X-ray powder pattern of **6** at RT (A, HS) and 173 K (B, LS). C: calculated pattern from the single crystal X-ray structure analysis of **5** at 200 K (HS).

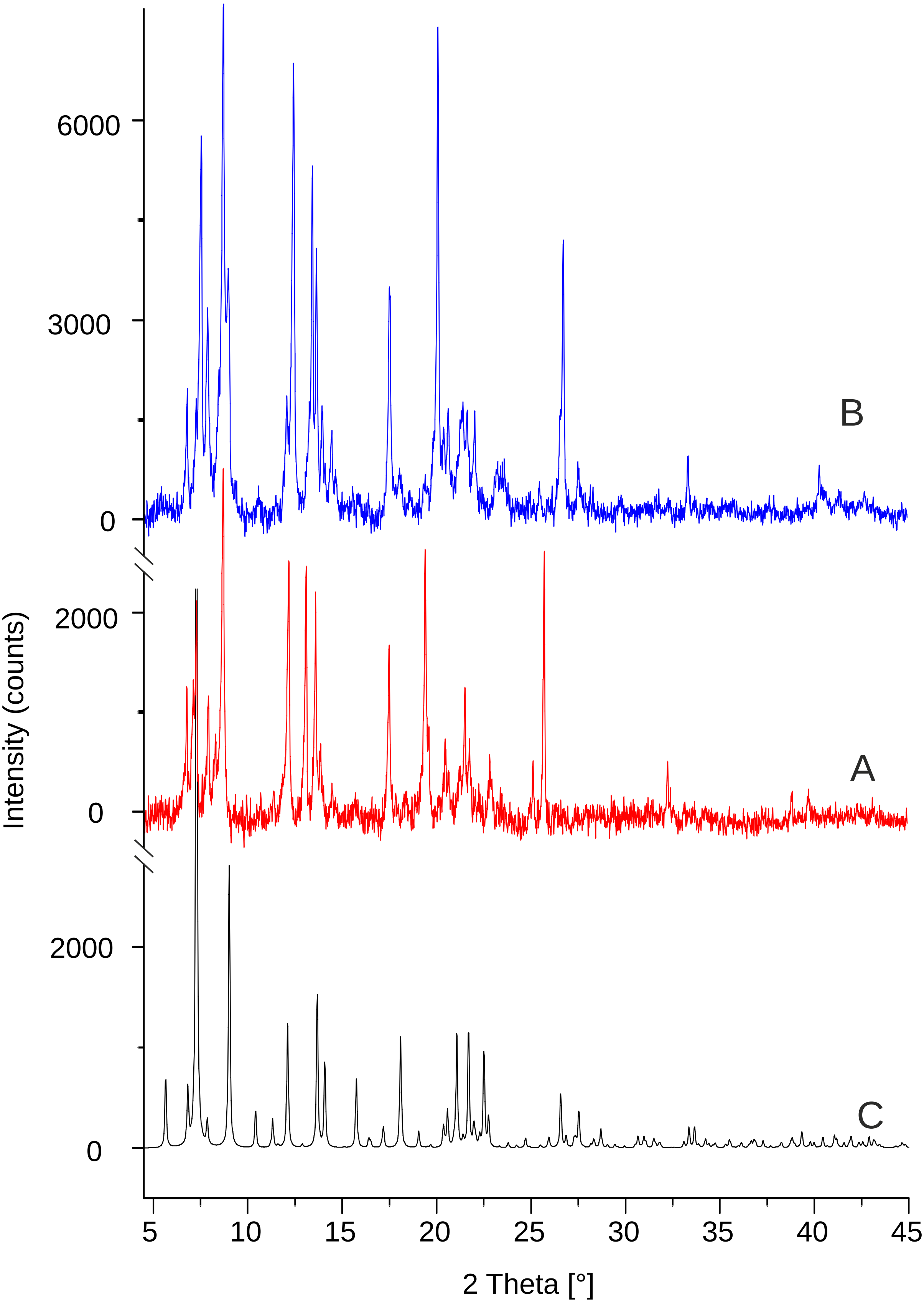

Table S1. Crystallographic data of **5**.

formula	$C_{30}H_{42.5}N_4O_{8.25}Fe$
M_r / g mol^{-1}	647.02
crystal system	orthorhombic
space group	I 2 2 2
a / Å	13.7280(9)
b / Å	19.5970(13)
c / Å	25.8760(13)
α / °	90
β / °	90
γ / °	90
V / Å^3	6961.4(7)
Z	8
ρ / g cm^{-3}	1.218
μ / mm^{-1}	0.483
crystal size	0.14 × 0.07 × 0.05
T / K	200(2)
diffractometer	KappaCCD
λ (MoK_α) / Å	0.71073
Θ-range / °	3.15 – 27.52
reflns. collected	37138
indep. reflns. (R_{int})	7968 (0.1965)
mean I / σ (I)	4.34
reflns. with $I \geq 2\sigma$ (I)	2946
x, y (weighting scheme)	0.13710
parameters	348
restraints	1
R (F) (all data)	0.0857 (0.2688)
wR (F^2) (all data)	0.2040 (0.2841)
S	0.980
shift/error$_{max}$	0.000
Flack parameter	0.43(6)
max., min. resd. dens. / e Å^{-3}	0.619, –0.554

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