A cobalt(II)-terpyridine complex showing field-induced slow magnetic relaxation behavior via reverse spin-crossover

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EXPERIMENTAL SECTION

Physical measurements

Elemental analyses of C, H, and N were performed at an Elementar Vario MICRO analyzer. Infrared spectra were obtained in the range of 600–4000 cm^{-1} on a Bruker tensor II spectrometer. Powder X-ray diffraction data (PXRD) were recorded on a Bruker D8 Advance diffractometer with Cu Kα X-ray source (λ = 1.54056 Å) operated at 40 kV and 40 mA between 5 and 35° (2θ). Simulated PXRD patterns were obtained from the Mercury software. Thermal gravimetric analysis (TGA) was carried out on freshly filtered crystals using the Mettler Toledo TGA2 instrument in an insert Ar atmosphere over a temperature range of 30–600 °C with a heating rate of 10 °C/min. Differential scanning calorimetry thermal analysis was carried out on a Mettler Toledo DSC3.

Magnetic measurements

Direct current (dc) magnetic susceptibility from 2 to 300 K with applied 1000 Oe dc field were performed using a Quantum Design SQUID VSM magnetometer on the crushed single crystals sample of **1**. Alternative current (ac) magnetic susceptibility data were collected in a zero-dc field or an applied 1000 Oe dc fields in the temperature range of 2-8 K, under an ac field of 2 Oe, oscillating at frequencies in the range of 1-1000 Hz. All magnetic data were corrected for the diamagnetic contributions of the sample holder and of core diamagnetism of the sample using Pascal's constants.

X-ray Crystallography

Single crystal X-ray crystallographic data were collected on a Bruker D8 Venture diffractometer with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å) at different temperature controlled by Oxford Cryosystems low-temperature device. The APEX III program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT.[S1] Absorption corrections were applied with SADABS.[S2] The structures were solved by direct methods and refined by full-matrix least-squares method on *F*2 using the SHELXTL[S3] crystallographic software package integrated in Olex 2.[S4] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. CCDC 2284062 and 2284063 are the supplementary crystallographic data for this paper. They can be obtained freely from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

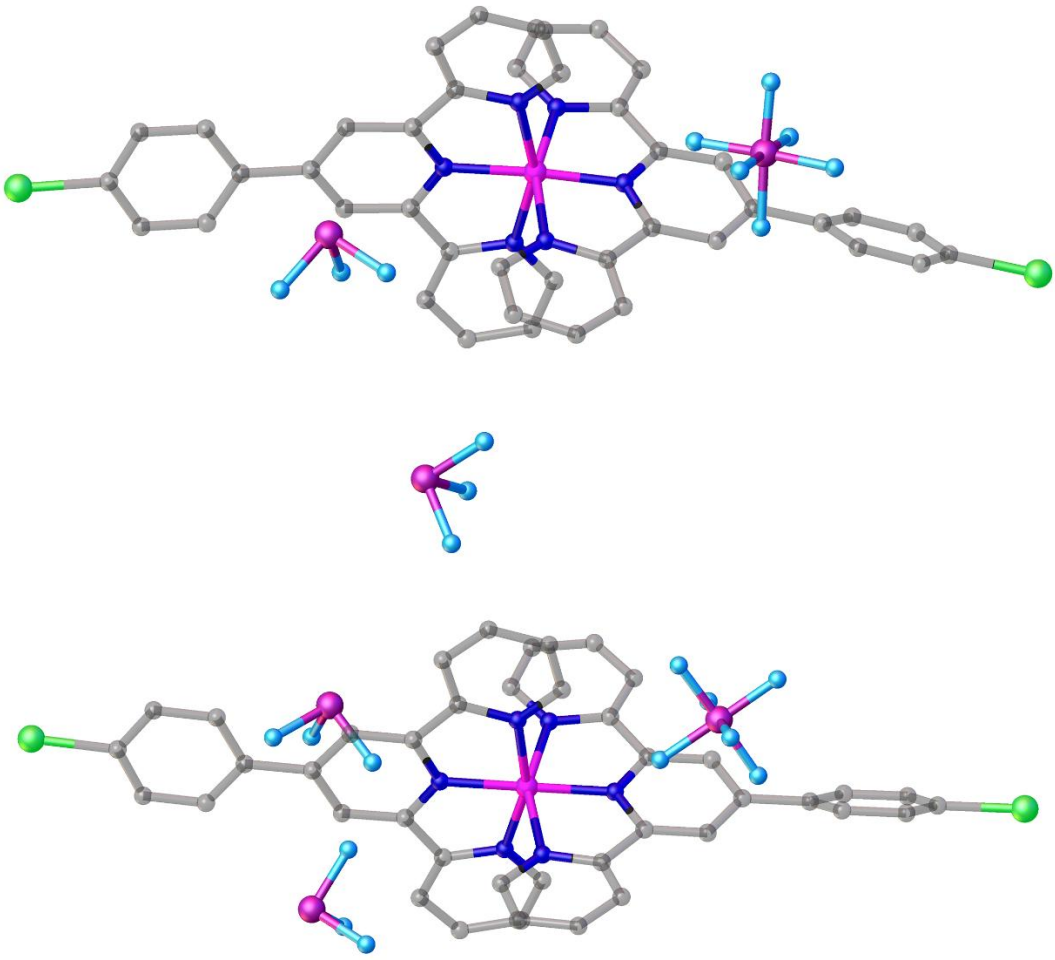

Figure S1. The asymmetric units of **1** at 100 K (up) and 290 K (down).

Table S1. Selected bond lengths (Å) in **1**.

T / K	100
Co1-N1	1.914(4)
Co1-N2	2.138(5)
Co1-N3	2.109(5)
Co1-N4	2.023(5)
Co1-N5	1.877(4)
Co1-N6	2.032(5)
$Co\text{-}N_{average}$	2.016

T / K	290
Co1-N1	1.916(4)
Co1-N2	2.120(5)
Co1-N3	2.121(5)
Co1-N4	2.036(4)
Co1-N5	1.898(4)
Co1-N6	2.036(4)
$Co\text{-}N_{average}$	2.0212

Table S2. Selected bond angles (Å) in **1**.

T / K	100
N1-Co1-N2	78.4(2)
N1-Co1-N3	80.3(2)
N1-Co1-N4	100.73(19)
N1-Co1-N6	98.1(2)
N3-Co1-N2	158.51(19)
N1-Co1-N5	175.6(2)

T / K	290
N1-Co1-N2	78.75(19)
N1-Co1-N3	78.94(19)
N1-Co1-N4	101.60(18)
N1-Co1-N6	178.40(19)
N3-Co1-N2	157.69(18)
N1-Co1-N5	98.13(18)

Table S3. Continuous Shape Measure (CSM) analysis for six-coordinated Co(II) in **1**.

Compound, Metal center	T / K	CSM parameters* six-coordinated coordination sphere					Determined coordination geometry
		HP-6	PPY-6	OC-6	TPR-6	JPPY-6	
Co	100	33.666	23.188	**2.394**	11.867	27.059	OC-6
	290	33.945	22.959	**2.504**	12.060	26.816	

*CSM parameters for six-coordinated complexes:

HP-6 - the parameter related to the hexagon (D_{6h});

PPY-6 - the parameter related to the pentagonal pyramid (C_{5v});

OC-6 - the parameter related to the octahedron (O_h);

TPR-6 - the parameter related to the trigonal prism (D_{3h});

JPPY-6 - the parameter related to the Johnson pentagonal pyramid (*C5v*)

Table S4. Computed octahedral distortion parameters for **1**.

	1	
	100 K	290 K
$\sum^{a}$	87.19	92.09
Θ^{b}	304.83	305.25

[a] θ for the sum of the deviations from 60° of the 24 trigonal angles of the projection of the [CoN_6] octahedron onto its trigonal faces. [b] Σ is the sum of the deviation from 90° of the 12 cis angles of the CoN_6 octahedron.

Table S5. The possible hydrogen bonds in **1** at 100 K calculated by PLATON.

D-H...A	d(D- H)	d(H...A)	d(D...A)	＜(DHA)
C(7)-H(7)...F(6)	0.95	2.55	3.4808	167
C(8)-H(8)...F(7)	0.95	2.43	3.3611	167
C(16)-H(16)...F(9)	0.95	2.55	3.3342	140
C(17)-H(17)...F(1)	0.95	2.94	3.3725	147
C(18)-H(18)...Br(1)	0.95	2.90	3.5365	125
C(25)-H(25)...F(6)	0.95	2.54	3.4811	171
C(29)-H(29)...F(6)	0.95	2.51	3.4550	174
C(32)-H(32)...F(1)	0.95	2.53	3.4408	160
C(32)-H(32)...F(2)	0.95	2.48	3.0629	119
C(34)-H(34)...F(7)	0.95	2.52	3.4355	162
C(35)-H(35)...F(5)	0.95	2.41	3.2051	141
C(48)-H(40)...F(8)	0.95	2.49	3.1822	129

Table S6. The possible hydrogen bonds in **1** at 290 K calculated by PLATON.

D-H...A	d(D- H)	d(H...A)	d(D...A)	＜(DHA)
C(19)-H(19)...F(2)	0.93	2.48	3.3357	153
C(36)-H(36)...F(10)	0.93	2.48	3.2876	145

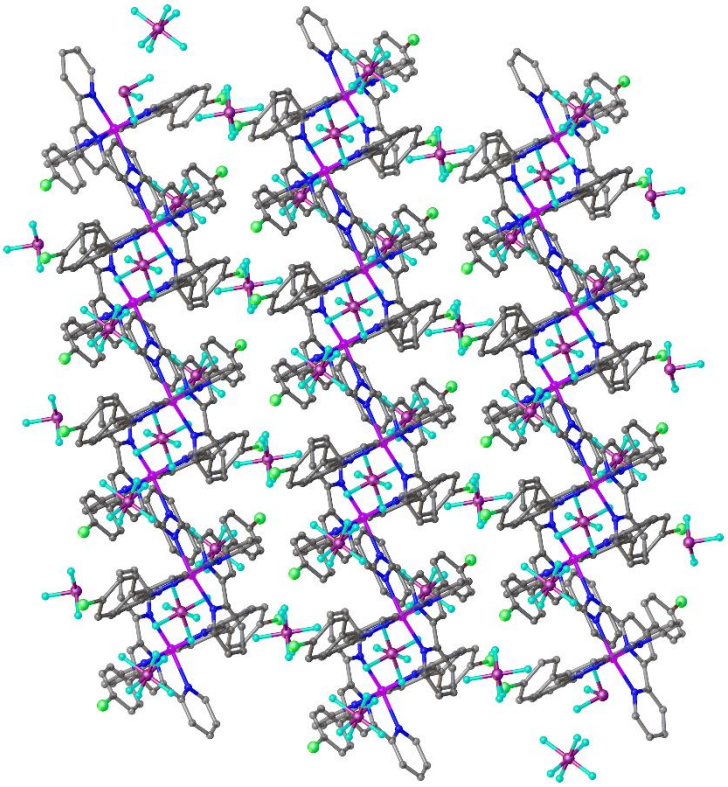

Figure S2. Portion of the packing structure of **1** along the [010] direction.

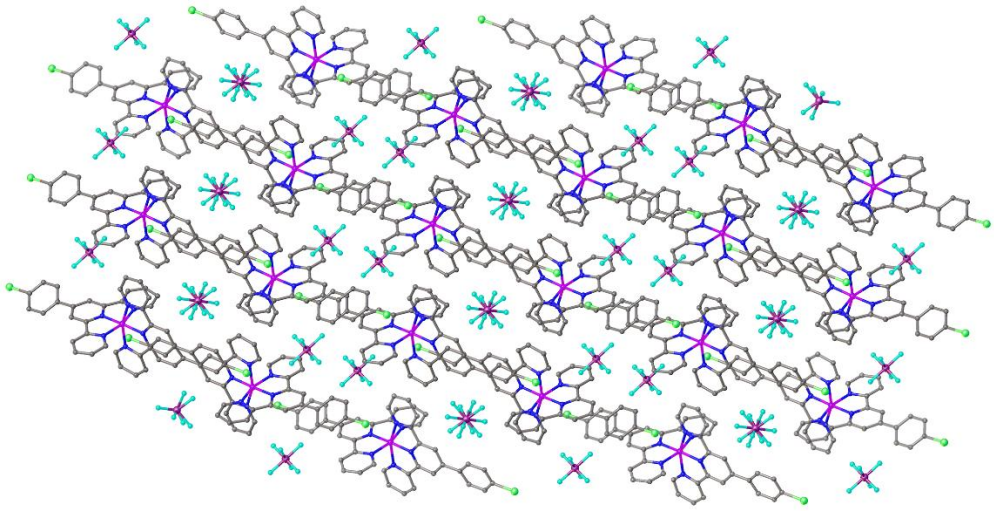

Figure S3. Portion of the packing structure of **1** along the [001] direction.

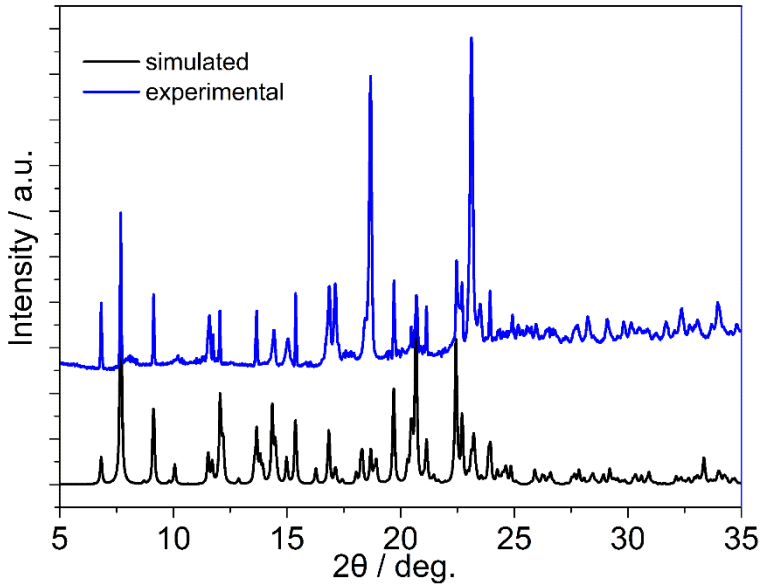

Figure S4. Powder X-ray diffraction pattern of **1**.

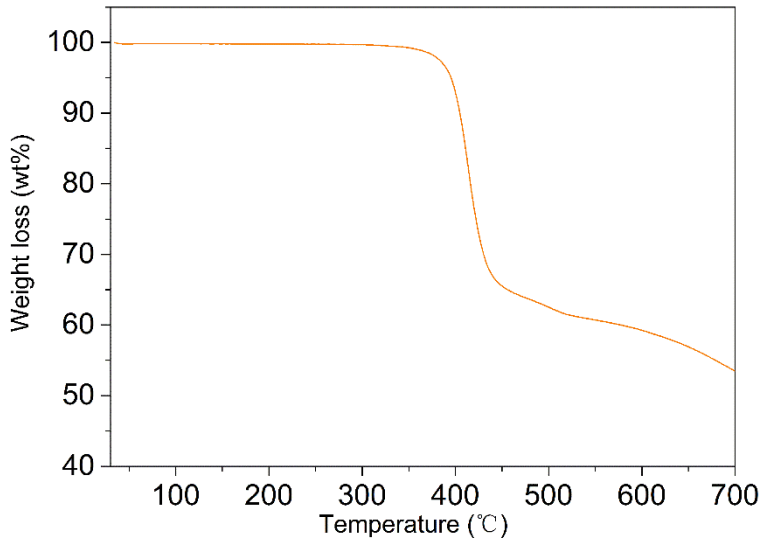

Figure S5. Thermal gravimetric analysis of **1**.

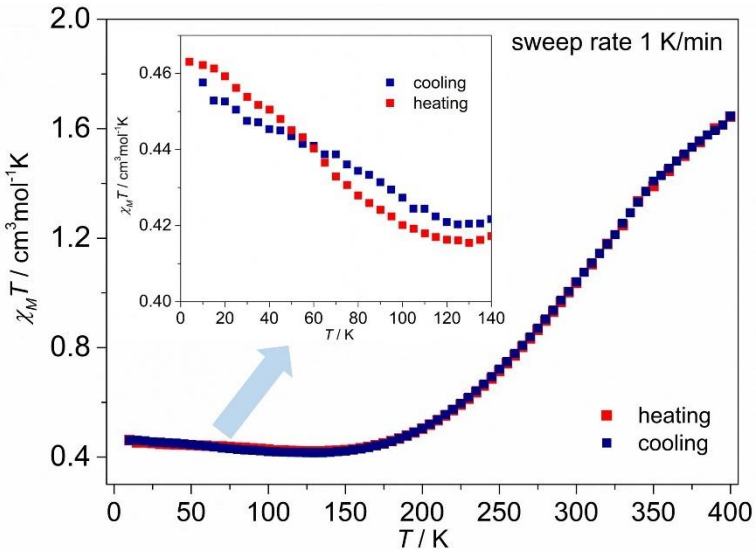

Figure S6. Temperature-dependent magnetic susceptibility of **1** measured using 1 K/min sweep rate. Insert: highlight of the $\chi_M T$ in the temperature range of 5-140 K.

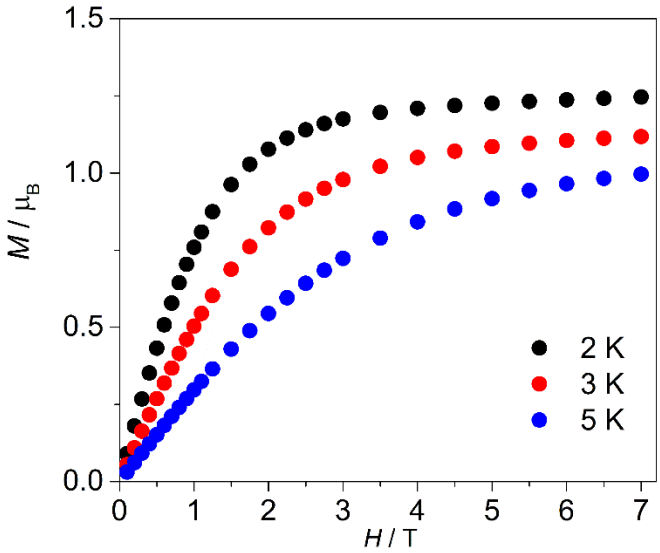

Figure S7. The magnetization curves for **1** measured at 2, 3, and 5 K.

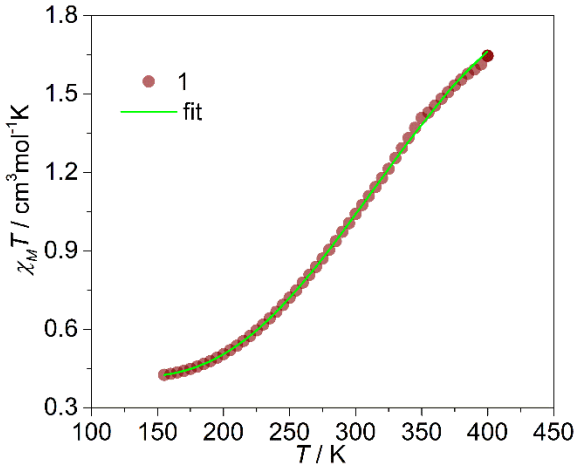

Figure S8. A fit to the thermodynamic magnetic behavior for **1**.

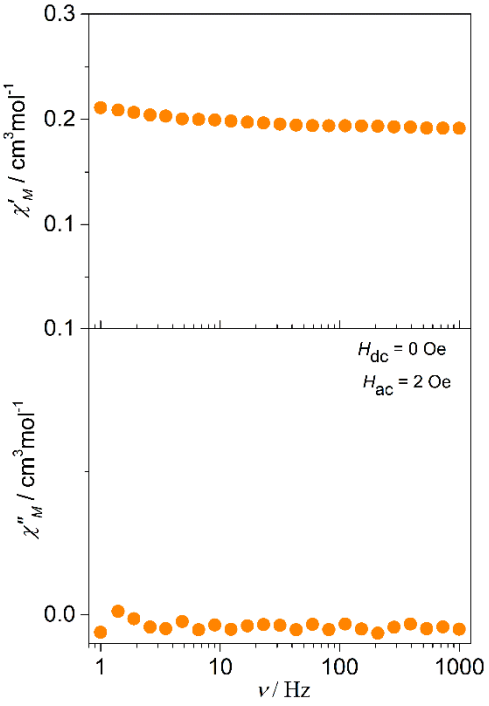

Figure S9. Frequency dependence of the ac susceptibility measured under zero dc field at 2.0 K for **1**.

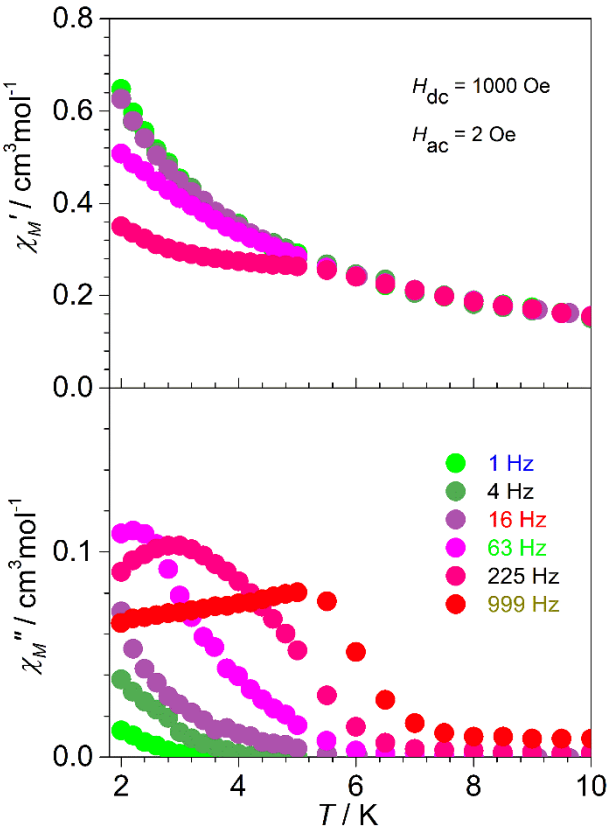

Figure S10. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibilities for **1**.

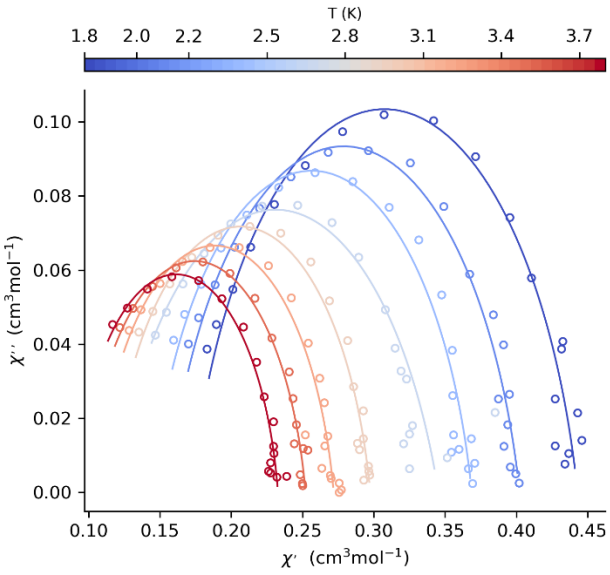

Figure S11. Cole-Cole plots for **1**.

Table S7. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **1** under 1000 Oe dc filed according to the generalized Debye model.

T / K	τ / s	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	α
1.8	0.00208	0.108	0.45207	0.08696
2	0.00192	0.09368	0.412	0.10933
2.2	0.0017	0.08068	0.38164	0.10723
2.5	0.00142	0.08677	0.3453	0.04257
2.8	0.00115	0.07536	0.32203	0.10643
3.1	9.004E-4	0.06169	0.30244	0.08445
3.4	6.00965E-4	0.07649	0.26498	0.0807
3.7	3.77534E-4	0.07805	0.2332	0.02782

References

S1) SAINT Software Users Guide, version 7.0; Bruker Analytical X-Ray Systems: Madison, WI, 1999.

S2) G. M. Sheldrick, SADABS, version 2.03; Bruker Analytical X-Ray Systems, Madison, WI, 2000.

S3) G. M. Sheldrick, SHELXTL, Version 6.14, Bruker AXS, Inc.; Madison, WI 2000-2003.

S4) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Crystallogr., 2009, 42, 339−341.