

Electronic Supplementary Information

Metallotectons: Using enantiopure tris(dipyrinato)cobalt(III) complexes to build chiral molecular materials

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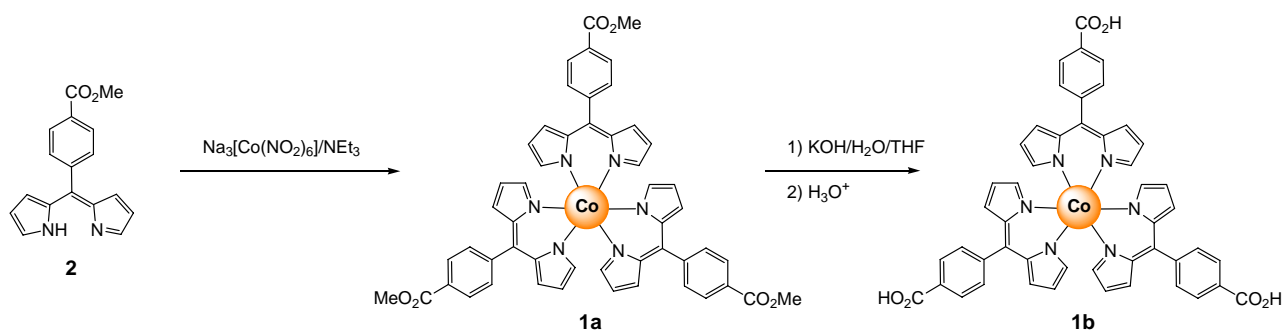
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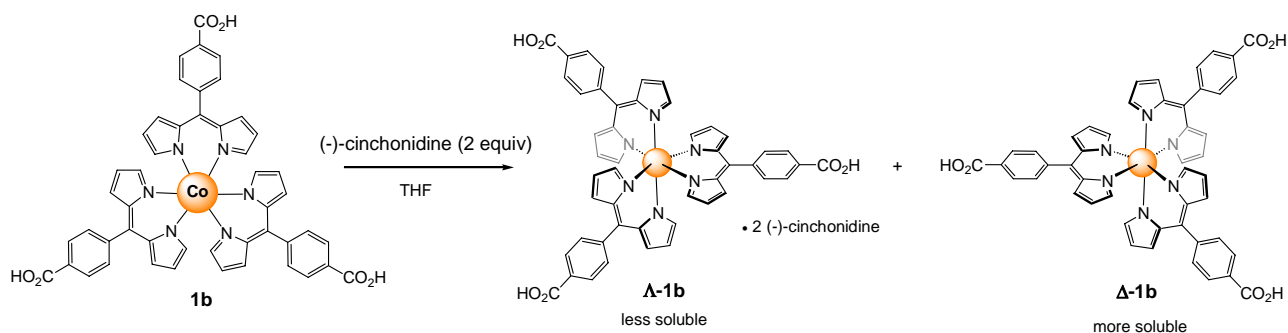
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I. Synthesis of Racemic Complex **1b**



Dipyrrin **2** (3.16 g, 11.4 mmol)¹ was dissolved in a mixture of MeOH (70 mL) and triethylamine (10 mL), and a solution of Na₃[Co(NO₂)₆] (1.35 g, 3.34 mmol) in H₂O (2.5 mL) was added. The mixture was heated at 60 °C under N₂ for 16 h. The resulting orange-red suspension was cooled to 25 °C, and H₂O (100 mL) was added to complete the precipitation of complex **1a** as a red-brown solid. The product was separated by filtration, washed with H₂O, and dried under vacuum. Chromatography (SiO₂, CH₂Cl₂) furnished a purified sample of compound **1a** as a dark red solid (1.12 g, 1.26 mmol, 37%). Spectroscopic data matched those reported in the literature.¹ Complex **1a** was then converted into compound **1b** by hydrolysis with aqueous KOH according to the published procedure.¹

II. Resolution of Complex **1b**



A solution of racemic complex **1b** (805 mg, 0.948 mmol) in hot THF (20 mL) was mixed with a solution of (-)-cinchonidine (558 mg, 1.90 mmol) in hot THF (20 mL). The orange solution was cooled to 25 °C and allowed to stand overnight. The resulting orange precipitate was separated by filtration, and the filtrate was set aside (see below). The filtered solid was washed copiously with hot THF and dried in air. A ¹H NMR spectrum showed that this material had the stoichiometry **1b** • 2 (-)-cinchonidine (720 mg, 0.500 mmol, corresponding to 53% of the total amount of complex **1b** initially present). The material was then dissolved in ethyl acetate with a small amount of added CF₃COOH for chromatographic purification (SiO₂, ethyl acetate (99.7%)/CF₃COOH (0.3%)). An intense orange band was collected, solvent was removed by evaporation under reduced pressure, and the residue was further dried under vacuum at 50 °C overnight to give a purified sample of complex Δ -**1b** (405 mg, 0.477 mmol, 50% of the total amount of complex **1b** initially present). The ee of this material was determined by HPLC to be approximately 80%. The solid was dissolved in THF (10 mL), and a solution of (-)-cinchonidine (202 mg, 0.686 mmol) in hot THF (10 mL) was added. The orange mixture was cooled to 25 °C and allowed to stand overnight. The resulting

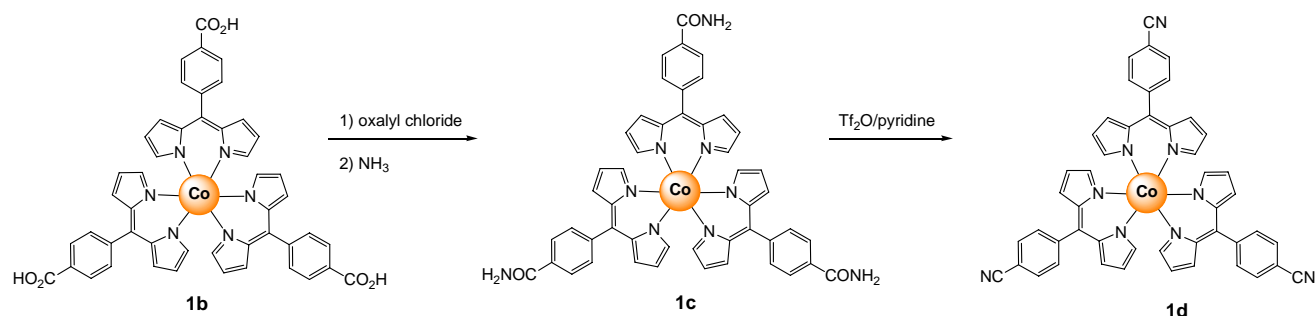
crystalline orange precipitate was separated by filtration, washed with hot THF, CH₂Cl₂, and acetone, and dried in air. The solid was shown by ¹H NMR spectroscopy to have the composition **1b** • 2 (-)-cinchonidine (451 mg, 0.314 mmol). This material was then dissolved in ethyl acetate with a small amount of added CF₃COOH and purified chromatographically (SiO₂, ethyl acetate (99.7%)/CF₃COOH (0.3%)). An intense orange band was collected, solvent was removed by evaporation under reduced pressure, and the residue was further dried under vacuum at 50 °C overnight to give a purified sample of complex Δ-**1b** (242 mg, 0.285 mmol, 30% of the total amount of complex **1b** initially present). The ee of this material ranged from 95 to 100%. Recrystallization could be achieved by allowing vapors of pentane to diffuse into a solution of the solid in THF. This provided an analytically pure sample of complex Δ-**1b** with an ee of 100% as a dark orange-red solid: ¹H NMR (400 MHz, acetone-d₆, 25 °C) δ 6.44 (m, 6H), 6.51 (s, 6H), 6.71 (m, 6H), 7.62 (d, ³J = 8.3 Hz, 6H), 8.18 (d, ³J = 8.3 Hz, 6H); ¹³C NMR (100 MHz, acetone-d₆, 25 °C) δ 120.22, 129.72, 131.33, 131.83, 134.01, 136.26, 143.36, 164.24, 153.41, 165.93; HRMS (ESI) calcd for C₄₈H₃₃CoN₆O₆ + H *m/e* 849.1866, found 849.1862; UV-VIS (THF, 10⁻⁵ M) 507 nm (48500 M⁻¹ cm⁻¹), 468 nm (57000 M⁻¹ cm⁻¹), 400 nm (20300 M⁻¹ cm⁻¹), 309 nm (30700 M⁻¹ cm⁻¹); CD (THF, 5 × 10⁻⁵ M) 514 nm (631 M⁻¹ cm⁻¹), 468 nm (-437 M⁻¹ cm⁻¹); HPLC (ChiralPak 1A, 150 × 4.6 mm, hexane/THF/CF₃COOH 85/15/0.05, flow rate = 3 mL/min) *t* = 37.4 min. Anal. Calcd for C₄₈H₃₃CoN₆O₆ • H₂O • 0.5 THF: C, 66.52; H, 4.35; N, 9.31. Found: C, 67.17; H, 3.98; N, 9.42.

Enantiomerically pure complex Δ-**1b** could be isolated from the initial filtrate by chromatography (SiO₂, ethyl acetate (99.7%)/CF₃COOH (0.3%)). An orange band was collected, solvent was removed by evaporation under reduced pressure, and the residue was dried under vacuum at 50 °C overnight. This yielded a purified sample of complex Δ-**1b** (343 mg, 0.404 mmol, 43% of total amount of complex **1b** initially present). HPLC showed the ee of the material to be 100%. An analytically pure sample of orange crystals was obtained by allowing vapors of pentane to diffuse into a solution of the solid in THF: ¹H NMR (400 MHz, acetone-d₆, 25 °C) δ 6.44 (m, 6H), 6.51 (s, 6H), 6.71 (m, 6H), 7.62 (d, ³J = 8.3 Hz, 6H), 8.18 (d, ³J = 8.3 Hz, 6H); ¹³C NMR (100 MHz, acetone-d₆, 25 °C) δ 120.22, 129.72, 131.33, 131.83, 134.01, 136.26, 143.36, 164.24, 153.41, 165.93; HRMS (ESI) calcd for C₄₈H₃₃CoN₆O₆ + H *m/e* 849.1866, found 849.1875; UV-VIS (THF, 10⁻⁵ M) 507 nm (46800 M⁻¹ cm⁻¹), 470 nm (54800 M⁻¹ cm⁻¹), 401 nm (19800 M⁻¹ cm⁻¹), 309 nm (28300 M⁻¹ cm⁻¹); CD (THF, 5 × 10⁻⁵ M) 515 nm (-658 M⁻¹ cm⁻¹), 467 nm (448 M⁻¹ cm⁻¹); HPLC (ChiralPak 1A, 150 × 4.6 mm, hexane/THF/CF₃COOH 85/15/0.05, flow rate = 3 mL/min) *t* = 32.1

min. Anal. Calcd for $C_{48}H_{33}CoN_6O_6 \cdot H_2O \cdot 0.5 THF$: C, 66.52; H, 4.35; N, 9.31. Found: C, 66.26; H, 4.12; N, 9.16.

III. Synthesis of Complexes **1d** and **1e**

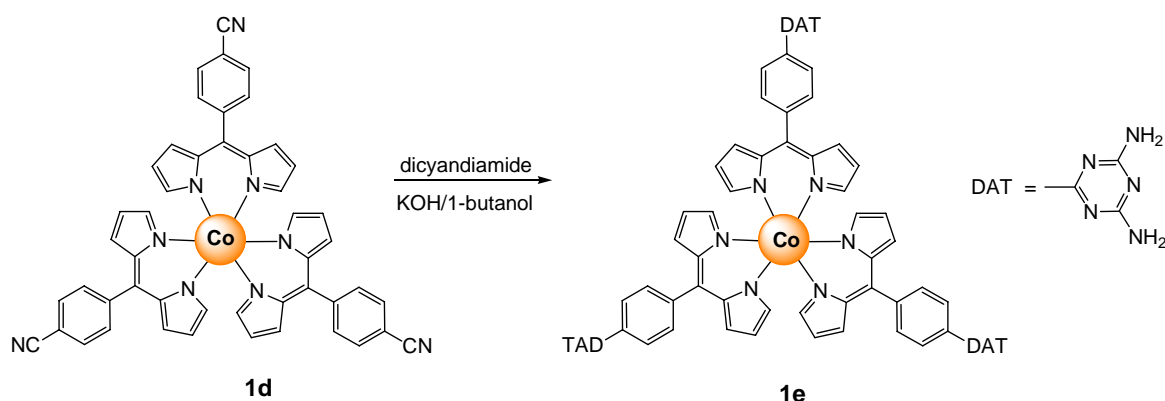
Synthesis of Complex **1d**²



Enantiomerically pure complex **1b** (205 mg, 0.242 mmol) was dissolved in dry THF (3 mL, with a trace of DMF added). The solution was cooled in an ice bath, and oxalyl chloride (109 μ L, 159 mg, 1.25 mmol) was added dropwise under dry N_2 with stirring. The mixture was kept at 0 °C for 40 min and then at 25 °C for a further 2 h. Volatiles were then removed under reduced pressure to leave a dark red-orange film. A solution of NH_3 (0.5 M in dioxane, 5 mL) was then added to give a red suspension. The suspension was sonicated briefly and then stirred at 25 °C for 60 min. Volatiles were then removed by evaporation under reduced pressure, toluene was added to the residue, and insoluble complex **1c** was separated by filtration as a red-orange solid, which was washed with toluene and ether. This material was judged to be of sufficiently high purity (as determined by 1H NMR spectroscopy) to be carried forward to the next step without further purification. The crude complex **1c** was dissolved in a mixture of dry dioxane (5 mL) and dry pyridine (3 mL), and the solution was cooled in an ice bath under dry N_2 . Triflic anhydride (600 μ L, 1.01 g, 3.58 mmol) was added with stirring, and the mixture was kept at 0 °C for 20 min and then at 25 °C for 5 h. MeOH (2 mL) was added, volatiles were removed by evaporation under reduced pressure, and the dark red residue was purified by chromatography (SiO_2 , CH_2Cl_2 , R_f 0.45). Purified complex **1d** was isolated from the fastest-moving orange band (75 mg, 94.7 μ mol, 39% overall from complex **1b**). HPLC indicated that the reaction proceeded without racemization. Crystallization of complex **1d** as large, analytically pure prisms could be achieved by allowing vapors of pentane to diffuse into a solution in $CHCl_3$: 1H NMR (400 MHz, acetone- d_6 , 25 °C) δ 6.45 (dd, $^3J = 4.4$ Hz, $^4J = 1.7$ Hz, 6H), 6.53 (m, 6H), 6.70 (dd, $^3J = 4.4$ Hz, $^4J = 1.4$ Hz, 6H), 7.71 (d, $^3J = 8.2$ Hz, 6H), 7.98 (d, $^3J = 8.2$ Hz,

6H); HRMS (ESI) calcd for $C_{48}H_{30}CoN_9 + H$ m/e 792.2028, found 792.2028; UV-VIS (THF, 10^{-5} M) 508 nm ($46700 M^{-1} cm^{-1}$), 470 nm ($54800 M^{-1} cm^{-1}$), 402 nm ($19800 M^{-1} cm^{-1}$), 306 nm ($27200 M^{-1} cm^{-1}$); CD (Δ enantiomer, THF, 5×10^{-5} M) 515 nm ($-613 M^{-1} cm^{-1}$), 470 nm ($412 M^{-1} cm^{-1}$); HPLC (ChiralPak 1A, 150×4.6 mm, hexane/ CH_2Cl_2 80/20, flow rate = 3 mL/min) $t = 20.0$ min (Δ -**1d**) and 30.6 min (Λ -**1d**). Anal. Calcd for $C_{48}H_{30}CoN_9 \cdot 0.5 CHCl_3$: C, 68.45; H, 3.61; N, 14.81. Found: C, 68.12; H, 3.27; N, 14.51.

Synthesis of Complex **1e**



Enantiomerically pure complex **1d** (45 mg, 56.8 μ mol) was combined with dicyandiamide (96 mg, 1.14 mmol) and KOH (56 mg, 1.0 mmol) in 1-butanol (3 mL), and the mixture was stirred and heated at 80 °C for 70 h. Volatiles were removed from the resulting orange suspension by evaporation under reduced pressure. The orange residue was suspended in H_2O , and the mixture was briefly sonicated and then heated at 70 °C for 1 h. The product was separated by filtration as an orange solid and was washed with hot H_2O and CH_2Cl_2 to provide purified complex **1e** (36 mg, 34.5 μ mol, 61%). Crystals of analytically pure product were obtained by allowing vapors of pentane to diffuse into a solution of the complex in THF: 1H NMR (400 MHz, DMSO- d_6) δ 6.32 (m, 6H), 6.45 (dd, $^3J = 4.4$ Hz, $^4J = 1.3$ Hz, 6H), 6.69 (dd, $^3J = 4.4$ Hz, $^4J = 1.6$ Hz, 6H), 6.83 (br s, 12H), 7.53 (d, $^3J = 8.4$ Hz, 6H), 8.37 (d, $^3J = 8.4$ Hz, 6H); ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ 119.48, 126.88, 129.98, 132.87, 134.82, 137.57, 139.60, 145.73, 151.18, 167.42, 169.66; HRMS (ESI) calcd for $C_{54}H_{42}CoN_{21} + H$ m/e 1044.3336, found 1044.3372; UV/VIS (THF, 4×10^{-5} M) 506 nm ($49200 M^{-1} cm^{-1}$), 468 nm ($58700 M^{-1} cm^{-1}$), 400 nm ($20500 M^{-1} cm^{-1}$), 323 nm ($41300 M^{-1} cm^{-1}$); CD (Δ enantiomer, THF, 5×10^{-5} M) 516 nm ($639 M^{-1} cm^{-1}$), 468 nm ($-439 M^{-1} cm^{-1}$). Anal. Calcd for $C_{48}H_{30}CoN_9 \cdot H_2O \cdot THF$: C, 61.42; H, 4.62; N, 25.94. Found: C, 60.91; H, 4.12; N, 26.31.

IV. X-Ray Crystallographic Details

X-ray diffraction data were collected at 150 K with $\text{Cu}_{K\alpha}$ radiation using a Bruker SMART 6000 CCD diffractometer equipped with a rotating anode X-ray generator. Structures were solved by direct methods (SHELXS-97) and refined by a full-matrix least-squares method on $|F|^2$ using anisotropic displacement parameters for all non-hydrogen atoms (SHELXL-97). Hydrogen atoms (except the carboxylic acid protons of complex **1b**) were placed in ideal positions and refined with a riding model.

The percentage of volume accessible to guests was estimated by the PLATON program.³ PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the van der Waals surface of the network. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water. The van der Waals radii used to define surfaces for these calculations are as follows: C, 1.70 Å; H, 1.20 Å; N, 1.55 Å; O, 1.80 Å; and Co, 2.03 Å. If V is the volume of the unit cell and V_g is the guest-accessible volume as calculated by PLATON, then the porosity P in % is given by $100V_g/V$.

Crystal data: CCDC depositions 643751 (Δ -**1b**) and 643752 (Λ -**1e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Crystallographic Data for Complex Δ -**1b**

$2(\Delta$ -**1b**) \cdot 3 C_7H_8 \cdot H_2O ($\text{C}_{117}\text{H}_{92}\text{Co}_2\text{N}_{12}\text{O}_{13}$, $M_r = 1991.88$), $2.0 \times 0.50 \times 0.10$ mm, triclinic, P1, $a = 9.5089(6)$, $b = 13.8437(9)$, $c = 20.397(1)$ Å, $\alpha = 86.879(3)$, $\beta = 84.876(4)$, $\gamma = 81.320(4)^\circ$, $V = 2641.4(3)$ Å³, $\rho_{\text{calcd}} = 1.252$ Mg m⁻³, $T = 150$ K, reflections collected/unique: 35726/16321, $R_{\text{int}} = 0.083$. Final R factor for 13490 observed reflections ($I > 2\sigma(I)$) with 1311 parameters (3 restraints) was 0.048 ($R_w = 0.12$). GOF = 0.968, max./min. residual electron density = 0.346/−0.334 eÅ⁻³, Flack parameter = 0.006(2). The hydrogen atoms of the water molecule could not be located. A fourth toluene molecule was found in the unit cell; however, due to severe disorder, it could not be satisfactorily modelled. The SQUEEZE routine in Platon was used to account for this electron density.³

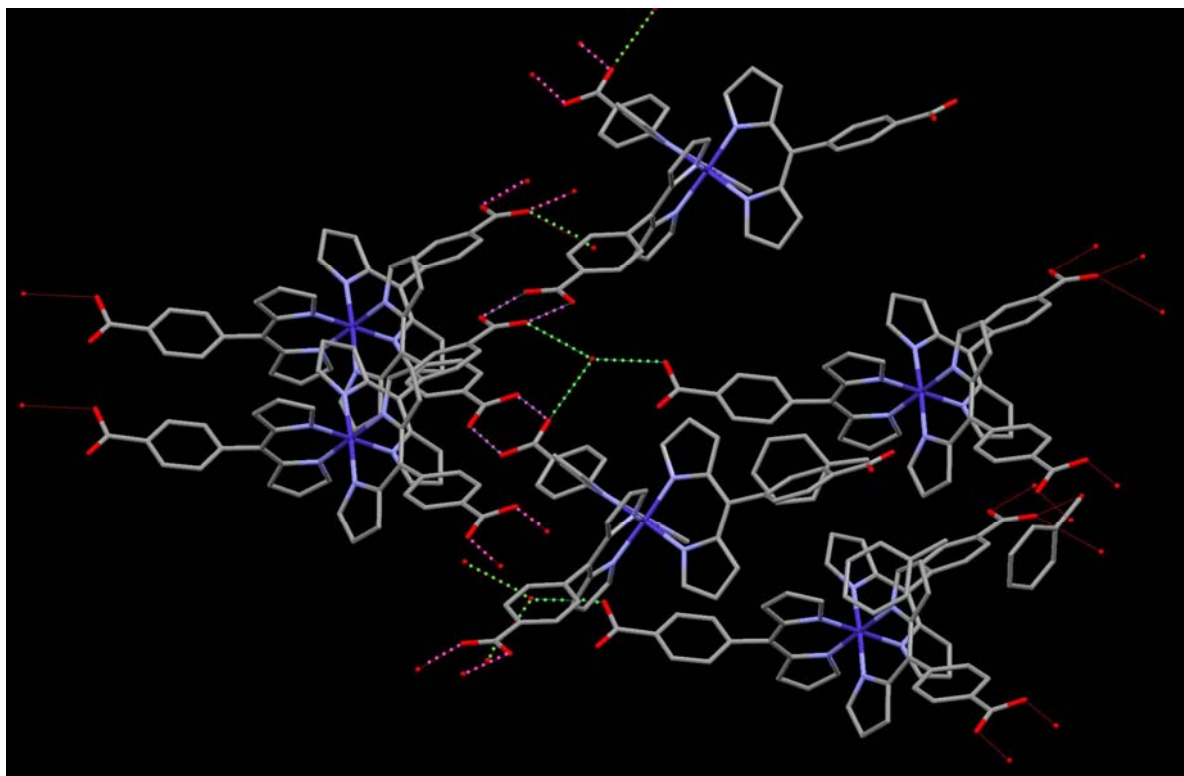


Figure S1. View showing the 1D zig-zag chains in the crystal structure of complex **Δ-1b** that are defined by cyclic hydrogen-bonded pairs of carboxyl groups. These hydrogen bonds are shown in pink. The chains are linked into a complex open 3D network by additional hydrogen bonds (green) involving included molecules of H₂O. Other guest molecules and all hydrogen atoms have been omitted for clarity.

Crystallographic Data for Complex **Δ-1e**

2(**Δ-1e**) • 3.5 DMSO • 3.5 H₂O (C₁₁₅H₁₁₂Co₂N₄₂O₇S_{3.5}, M_r = 2424.49), 0.20 × 0.10 × 0.03 mm, triclinic, P1, a = 9.6927(4), b = 14.9297(7), c = 22.8858(10) Å, α = 91.044(2), β = 101.393(2), γ = 101.736(2)°, V = 3172.8(2) Å³, ρ_{calcd} = 1.28 Mg m⁻³, T = 150 K, reflections collected/unique: 43028/16591, R_{int} = 0.057. Final R factor for 11285 observed reflections (I > 2σ(I)) with 1553 parameters (28 restraints) was 0.074 (R_w = 0.19). GOF = 1.00, max./min. residual electron density = 1.014/−0.638 eÅ⁻³, Flack parameter = −0.022(4). The sulfur atom of one of the DMSO molecules was disordered over two positions (S800 and S801). One of the DMSO molecules was refined with isotropic thermal parameters. The hydrogen atoms of the included water molecules could not be located on the electron density difference map.

References

- 1) C. Brückner, Y. Zhang, S. J. Rettig and D. Dolphin, *Inorg. Chim. Acta*, 1997, **263**, 279-286.
- 2) The synthesis of racemic complex **1d** has been reported by D. L. Murphy, M. R. Malachowski, C. F. Campana and S. M. Cohen, *Chem. Commun.*, 2005, 5506-5508.
- 3) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2001.