Supporting information for

Activation of SO_2 by $[Zn(Cp^*)_2]$ and $[(Cp^*)Zn^I–Zn^I(Cp^*)]$

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Experimental details

General Considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glovebox. Elemental analyses were carried out with an Elementar Vario Micro Cube. Hydrocarbon solvents were predried by using an MBraun solvent purification system (SPS-800) and then degassed, dried and stored in vacuo over $LiAlH_4$. Tetrahydrofuran was distilled under nitrogen from potassium before storage over $LiAlH_4$. NMR spectra were recorded on a Bruker Avance II 300 MHz and were referenced to the residual ^1H or ^{13}C signals of the deuterated solvents. IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit. $[Zn(Cp^*)_2]$[1] and $[(Cp^*)Zn–Zn(Cp^*)]$[2] were prepared by published procedures. High purity SO_2 from Air Liquide was used as received.

Syntheses

Synthesis of [Zn(O_2SCp)$_2$(tmeda)] (**1**)*

[Zn(Cp*)$_2$] (0.10 g, 0.30 mmol) was dissolved in tmeda (1.5 mL), and then thf (8 mL) was condensed onto the solution. SO_2 (0.30 mmol) was then condensed onto the stirring solution, and then the liq. N_2/*i*PrOH cooling bath was removed after five minutes. Stirring for approximately 1.5 h gave a small amount of white solid and a clear, colourless solution. Filtration and storage of the solution at −30 °C yielded colourless crystals. The solution was decanted and the solid was washed with pentane (5 mL) to afford a white solid (0.076 g, 87 %). Single crystals of **1** were grown from overnight storage of a concentrated solution in thf at −30 °C. ^{1}H NMR (300 MHz, C_4D_8O, 298 K): δ 1.32 (vbr, s, 6H, *sp*^{3}C–*CH*$_3$ of $O_2SC_5Me_5$), 1.82 (vbr s, 24H, *sp*^{2}C–*CH*$_3$ of O_2SC_5*Me*$_5$), 2.52 (s, 12H, *Me*$_2$N(CH$_2$)$_2$N*Me*$_2$), 2.64 (s, 4H, Me$_2$N(*CH*$_2$)$_2$NMe$_2$); ^{1}H NMR (300 MHz, C_4D_8O, 273 K): δ 1.31 (br, s, 6H, *sp*^{3}C–*CH*$_3$ of $O_2SC_5Me_5$), 1.82 (vbr s, 12H, *sp*^{2}C–*CH*$_3$ of O_2SC_5*Me*$_5$), 1.86 (s, 12H, *Me*$_2$N(CH$_2$)$_2$N*Me*$_2$), 2.54 (s, 12H, *Me*$_2$N(CH$_2$)$_2$N*Me*$_2$), 2.64 (s, 4H, Me$_2$N(*CH*$_2$)$_2$NMe$_2$); ^{1}H NMR (300 MHz, C_4D_8O, 253 K): δ 1.32 (s, 6H, *sp*^{3}C–*CH*$_3$ of $O_2SC_5Me_5$), 1.82 (vbr s, 12H, *sp*^{2}C–*CH*$_3$ of O_2SC_5*Me*$_5$), 1.85 (s, 12H, *Me*$_2$N(CH$_2$)$_2$N*Me*$_2$), 2.52 (s, 12H, *Me*$_2$N(CH$_2$)$_2$N*Me*$_2$), 2.64 (s, 4H, Me$_2$N(*CH*$_2$)$_2$NMe$_2$); ^{13}C{^{1}H} (300 MHz, C_4D_8O, 298 K): δ 47.3 (*Me*$_2$*N*(CH$_2$)$_2$*NMe*$_2$), 57.2 (s, Me$_2$N(C*H*$_2$)$_2$NMe$_2$) (Note: signals corresponding to the carbon atoms of the $O_2SC_5Me_5$ ligands were not observed due to fluxional behaviour); IR (ATR, cm^{-1}): υ 3017 vw, 2973 vw, 2913w, 2851wsh, 1474m, 1460m, 1438wsh, 1376vw, 1363vw, 1286w, 1124vw, 1023m, 1012m, 953s, 800m, 771w, 691w, 669w, 640w, 567m, 544m, 508vs, 462w, 442w, 421w; elemental anal. calcd. $C_{26}H_{46}N_2O_4S_2Zn$ (580.16): C 53.83, H 7.99, N 4.83, S 11.05; found: C 54.28, H 9.33, N 4.51, S 10.85.

Synthesis of [Zn_4(O_2SCp)$_6$O]·1.5(C_5H_{12}) (**2**)*

SO_2 (0.30 mmol) was condensed onto a stirring solution of [Cp*Zn^{I}–Zn^{I}Cp*] (0.060 g, 0.15 mmol) in thf (8 mL), and after five minutes the liq. N_2/*i*PrOH cooling bath was removed. The clear solution quickly turned into a cloudy, white suspension. Stirring was continued overnight but no further change was noted. After drying under vacuum, pentane (8 mL) was added to the white solid. The mixture was briefly stirred and then the clear, colourless solution was filtered from a small amount of white solid into another Schlenk flask. Concentration under vacuum afforded colourless crystals after overnight storage at room temperature. The solvent was decanted and then

the crystals were dried under vacuum to give a white solid (0.037 g, 33 %). Single crystals of **2**·1.5(C_5H_{12}) were grown from storage of a concentrated solution at −30 °C. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.87 (t, 9H, *CH*$_3$, pentane), 1.23 (overlapping signals, 9H, *CH*$_2$, pentane), 1.63–2.15 (broad overlapping signals, 90H, O_2SC_5*Me*$_5$); Note: the ^{13}C{^{1}H} NMR spectrum only showed free pentane since the carbon atoms of the $O_2SC_5Me_5$ ligands were not observed due to fluxional behaviour; IR (ATR, cm^{-1}): υ 2969 w, 2915 m, 2857w, 1439w, 1378w, 1065w, 1019msh, 941vs, 803vw, 702vw, 668vw, 604vw, 547vwsh, 519wsh, 479m, 445wsh; elemental anal. calcd. $C_{65}H_{102}O_{13}S_6Zn_4$ (1473.25) (loss of 0.5 pentane of crystallisation): C 50.52, H 6.65, S 12.45; found: C 50.70, H 6.08, S 13.33.

Thermal decomposition of [Zn(O$_2$SCp)$_2$(tmeda)] to afford [Zn$_2$(S$_2$O$_4$)(SO$_4$)(tmeda)$_2$] (**3**)*

Complex **1** was generated in situ as above. The resulting colourless solution was then heated at 70 °C. The colour of the solution quickly changed to yellow, and heating was stopped after four hours. After cooling, the solution was stored at −30 °C. Overnight, colourless crystals deposited. The bulk solid was washed once with pentane (5 mL) and then dried under vacuum to afford a white solid (0.025 g, 29 % based on [Zn(Cp*)$_2$]). Single crystals of **3**·thf were grown from overnight storage of a concentrated solution in thf at −30 °C. Due to its low solubility, no NMR data could be acquired. IR (ATR, cm^{-1}): υ 2979vw, 2889vw, 2847w, 2803w, 1473m, 1465m, 1457m, 1291w, 1251vw, 1191vw, 1167vw, 1182vw, 1102vw, 1052vs, 1011vs, 1000sh, 954m, 880vs, 799s, 767w, 698w, 668w, 641w, 590w, 547w, 513w, 488m, 438w, 419s, 411w; elemental anal. calcd. $C_{12}H_{32}N_4O_7S_3Zn_2$ (571.35) (loss of solvent of crystallisation): C 25.23, H 5.65, N 9.81; found: C 25.20, H 5.66, N 8.98. $(C_5Me_5)_2$ was detected in the reaction mixture and was identified by ^{1}H NMR spectroscopy: ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.15 (s, 3H, *sp*^{3}C–*CH*$_3$ of $(C_5Me_5)_2$), 1.67 (s, 6H, *sp*^{2}C–CH$_3$ of $(C_5Me_5)_2$), 1.76 (s, 6H, *sp*^{2}C–CH$_3$ of $(C_5Me_5)_2$).

NMR spectra

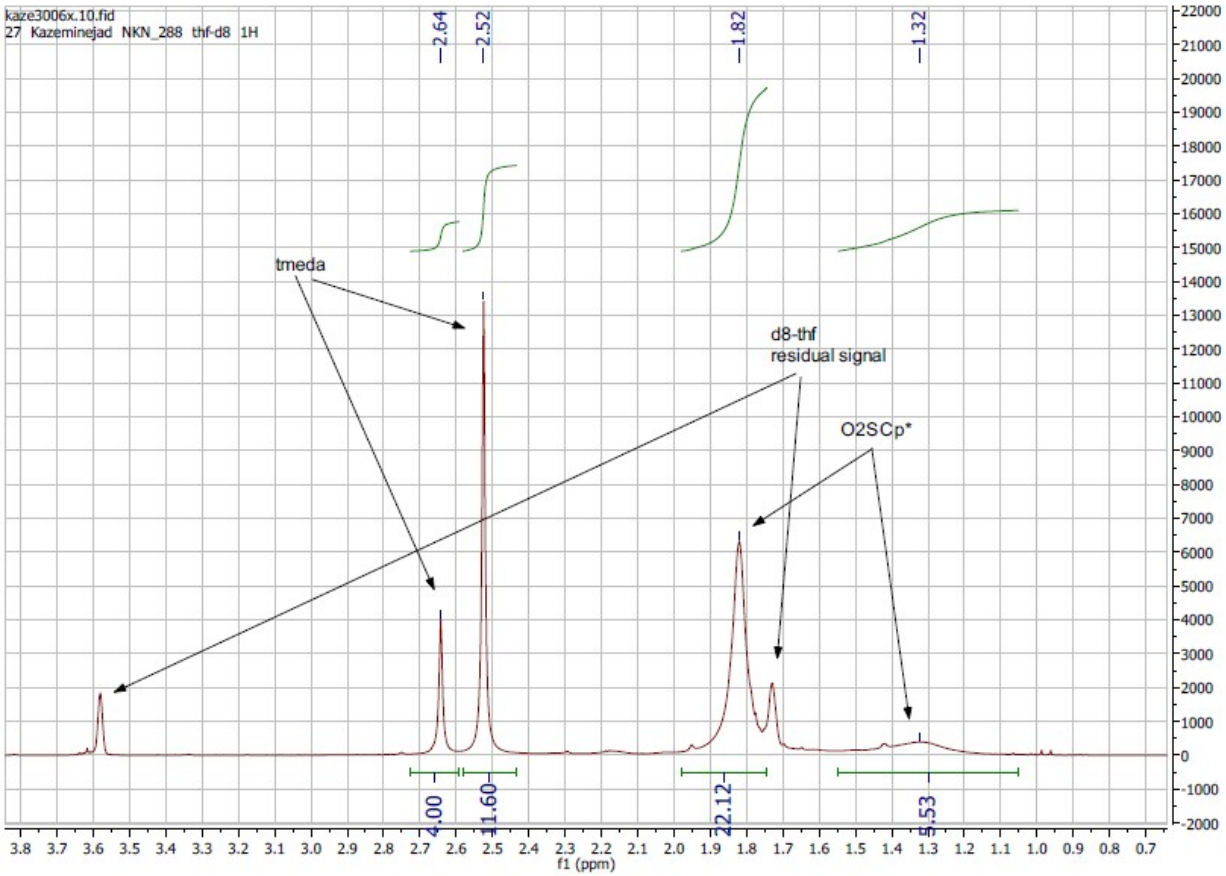


Fig. S1 ^{1}H NMR spectrum (300 MHz, C_4D_8O, 298 K) of **1**.

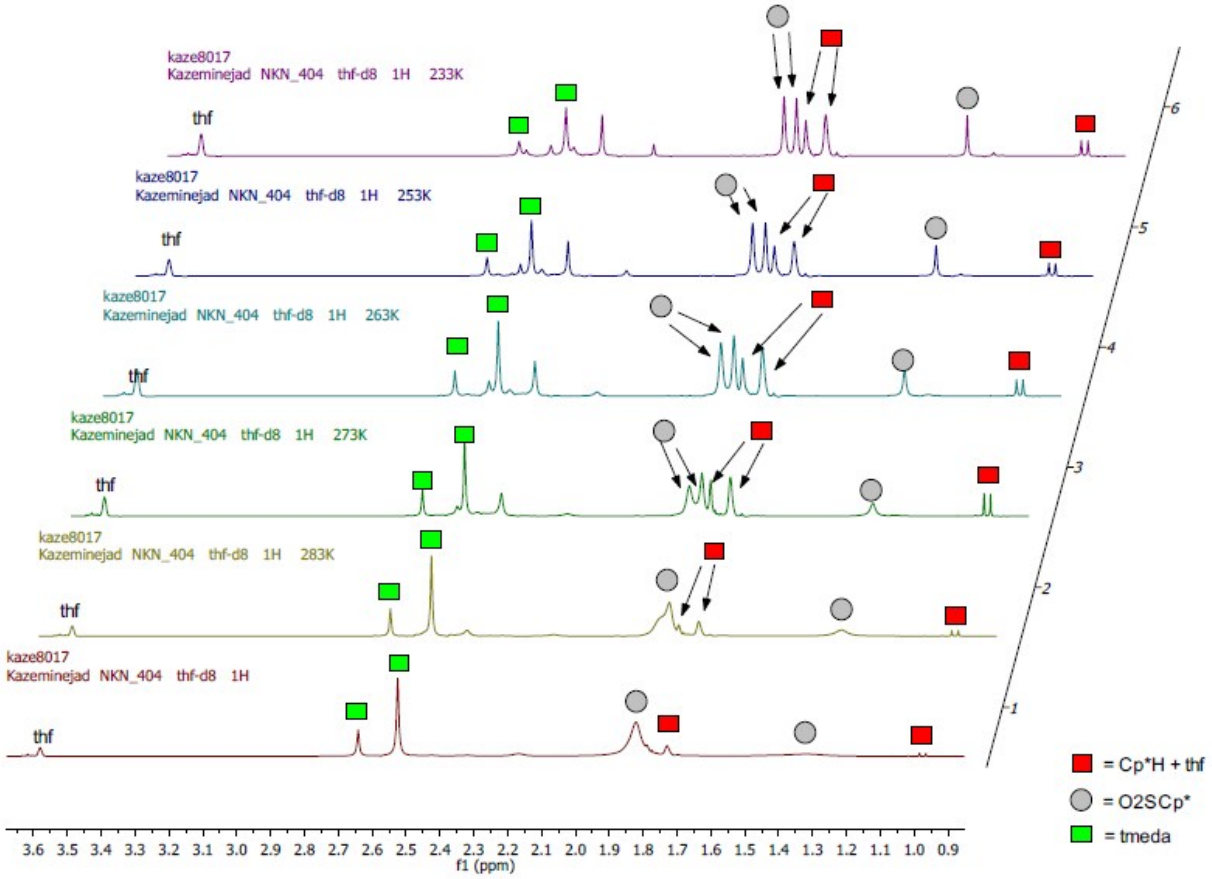


Fig. S2 Variable temperature 1H NMR spectra of **1** in d_8-thf. Note: the amount of Cp*H in the room temperature (1) spectrum is negligible but the amount of it appears to increase at lower temperatures because the solubility of **1** decreases markedly as the temperature decreases.

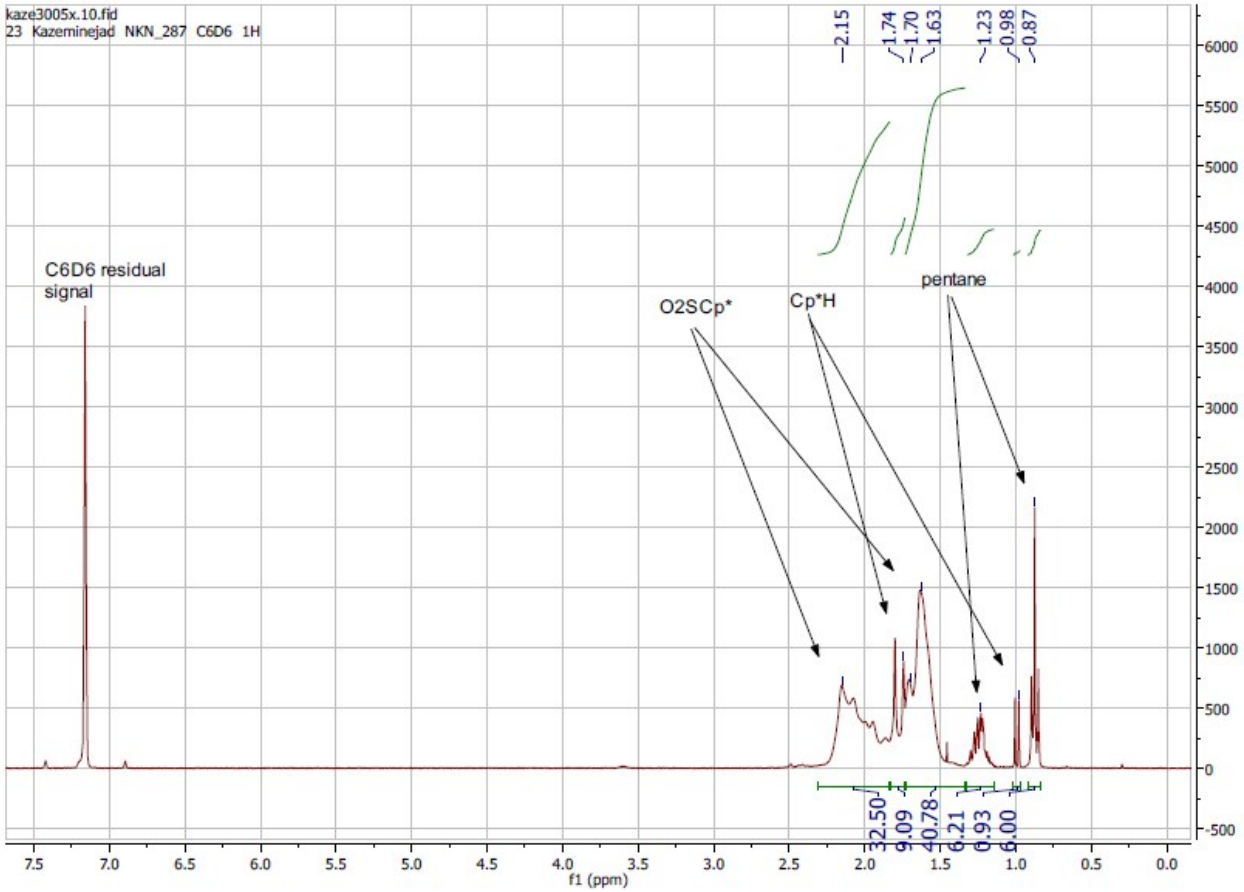
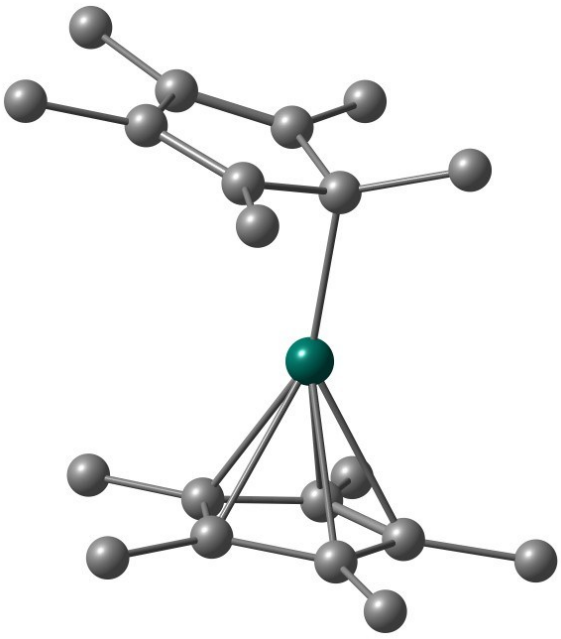


Fig. S3 ^{1}H NMR spectrum (300 MHz, C_6D_6, 298 K) of **2**.

Computational details and data

Electronic structure calculations of the reaction mechanism proposed were carried out using Density Functional Theory (DFT). The calculations were carried out with the Gaussian09 software[3] at the DFT level using the hybrid functional B3PW91.[4] The zinc atom was treated with the small core pseudopotential from Stuttgart's Institute for Theoretical Chemistry,[5] while the sulfur, oxygen, nitrogen, carbon and hydrogen atoms were treated with the all electron 6-31G** Pople basis set.[6] The geometry optimizations (both from the minima and the transition states) were performed without any symmetry constraints. Analytical calculations of the vibrational frequencies of the optimized geometry were done to confirm the minima and transition states obtained. Intrinsic reaction coordinate calculations were carried out to confirm that the transition states correspond to the ones that connect the intermediates obtained.



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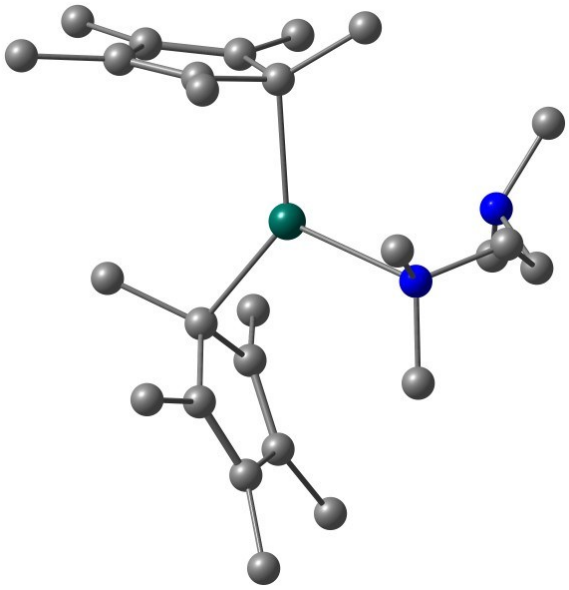
7502 – $Zn(cp^*)_2$ with tmeda



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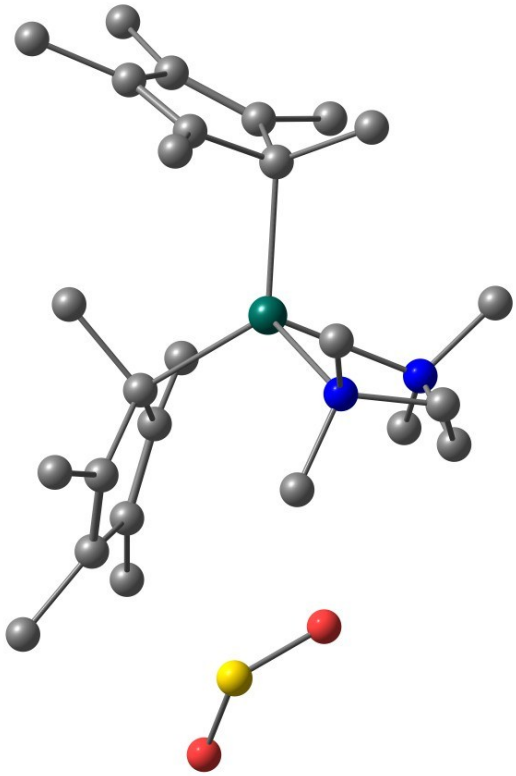
8103 - $Zn(cp^*)_2$ with tmeda and SO_2 adduct



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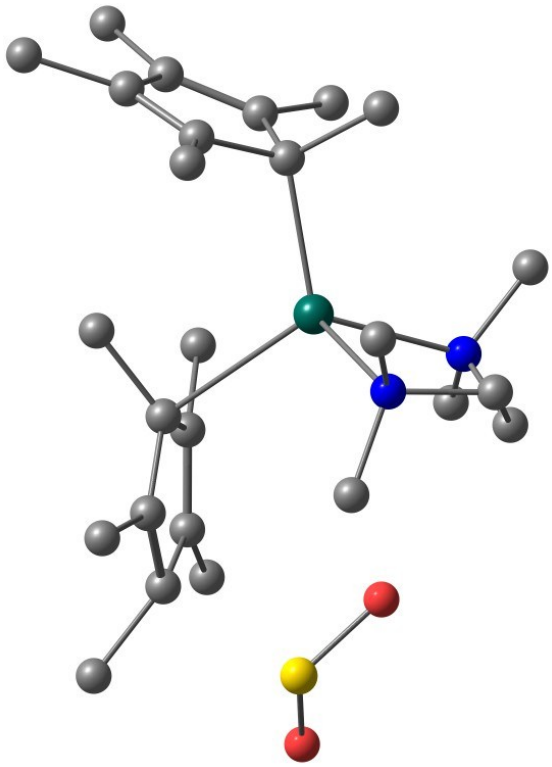
7804 – Transition state of the SO_2 insertion



Zn -1.200247 1.734159 1.537936

S -3.045900 6.291835 1.580617

O -3.644122 4.918016 1.710053

O -3.813778 7.192051 0.677478

N -3.467005 1.481488 1.328519

N -1.800535 2.168443 3.725074

C -0.987957 1.502881 4.754047

C -1.800099 3.615333 4.011885

C -3.895051 0.078230 1.205379

C -2.560373 5.775811 -1.873047

C -0.853201 7.422759 0.247145

C 0.537989 5.529307 2.203601

C 1.099941 3.115029 0.335883

C -1.135145 2.934307 -1.901594

C -0.331477 5.068682 1.080237

C -1.213278 5.951804 0.358472

C -1.647143 5.207470 -0.835051

C -1.074776 3.963427 -0.811460

C -0.236104 3.835751 0.398639

C -1.178590 -0.808820 -1.039868

C 1.847372 -0.598544 -1.992089

C 3.638570 0.062276 0.421827

C 1.849274 0.400865 3.018027

C -0.723551 -1.189441 2.053372

C -4.009120 2.228057 0.173372

C -4.011253 2.042499 2.586626

C -3.176848 1.634713 3.787336

C 1.297194 -0.351252 -0.620750

C 2.148603 -0.048309 0.526042

C 1.363967 0.130590 1.628468

C -0.073217 -0.048248 1.249064

C -0.007757 -0.372903 -0.213095

H 4.112823 0.203068 1.396521

H 3.935938 0.910730 -0.208812

H 4.078061 -0.834012 -0.032947

H 1.321462 -0.207213 3.762506

H 1.722225 1.451539 3.315536

H 2.914465 0.174793 3.119797

H -0.785699 -0.980864 3.126159

H -0.123011 -2.103116 1.941012

H -1.731954 -1.427928 1.708927

H -1.930073 -0.020865 -1.178098

H -1.692973 -1.669645 -0.590582

H -0.866405 -1.118057 -2.040808

H 1.063557 -0.810319 -2.723575

H 2.542076 -1.447972 -1.998440

H 2.410745 0.268421 -2.360346

H -2.074496 6.583653 -2.436900

H -3.453064 6.212305 -1.408685

H -2.871589 5.017602 -2.597594

H -0.929064 1.927047 -1.528220

H -0.383733 3.133051 -2.678418

H -2.108308 2.919930 -2.402988

H 1.031039 2.145586 -0.157956

H 1.548031 2.947807 1.319051

H 1.810733 3.724756 -0.241218

H 1.323047 6.210206 1.843434

H 1.040894 4.698629 2.706852

H -0.033931 6.091613 2.952949

H 0.063150 7.548195 -0.342475

H -0.682345 7.875662 1.230317

H -1.658293 7.981421 -0.236536

H -2.378418 4.156565 3.261576

H -0.772516 3.979038 3.996229

H -2.224336 3.804046 5.010736

H 0.027653 1.900097 4.737755

H -0.944681 0.428194 4.572512

H -1.412415 1.674515 5.755378

H -3.729779 3.279172 0.250694

H -5.106324 2.147372 0.149823

H -3.610112 1.800242 -0.749002

H -4.990819 0.024047 1.117271

H -3.591701 -0.499423 2.079189

H -3.452012 -0.375862 0.319445

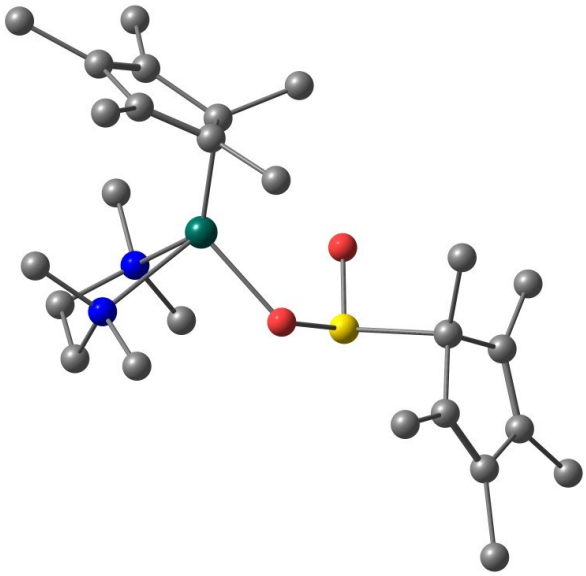
H -4.038399 3.129247 2.485435

H -5.046492 1.696300 2.733215

H -3.104527 0.543846 3.859220

H -3.673034 1.982614 4.707735

7805 - $Zn(cp^*)_2$ with SO2 inserted and tmeda



Zn -0.572406 -1.382753 1.620442

S -3.558849 -0.882215 1.912403

O -2.812608 -0.000194 2.897542

O -2.453814 -1.463661 0.931077

N -0.701477 -2.676825 3.524651

N -0.112037 -3.407858 0.710798

C -3.653910 1.440888 0.297351

C -4.539537 -1.079083 -1.417845

C -7.530111 -1.678100 -0.403187

C -8.095999 0.003824 2.121975

C -5.479595 1.735307 2.840389

C -0.044377 0.294615 -1.263994

C 2.375664 0.251522 3.298994

C 4.335608 -0.959756 1.101398

C 2.926227 -0.860837 -1.660461

C 0.039626 1.492896 1.656406

C -0.843152 -3.564461 -0.556508

C -0.629692 -4.356165 1.709232

C -0.170984 -3.989202 3.111994

C 0.123171 -2.110482 4.600955

C -2.078422 -2.824999 4.026311

C -5.226189 -0.564018 -0.195996

C -6.499225 -0.793915 0.225400

C -6.769659 0.008336 1.429618

C -5.663144 0.731522 1.749433

C -4.562730 0.341220 0.800001

C 1.321321 -3.629871 0.470857

C 2.247008 -0.487719 -0.375478

C 2.909797 -0.535098 0.914599

C 2.032165 -0.104985 1.881538

C 0.727211 0.189740 1.249099

C 0.959297 -0.032714 -0.198496

H -3.177407 1.948977 1.139976

H -4.231221 2.176045 -0.273539

H -2.870290 1.038937 -0.349714

H -3.573956 -1.526066 -1.161424

H -4.338950 -0.268821 -2.132178

H -5.143656 -1.828374 -1.937110

H -5.360511 2.748441 2.432339

H -4.577498 1.516725 3.421634

H -6.336302 1.755914 3.519718

H -8.899095 0.337049 1.452394

H -8.102651 0.658419 2.996690

H -8.367251 -1.004249 2.459667

H -7.882329 -2.444046 0.299221

H -7.145299 -2.192369 -1.287155

H -8.414424 -1.106130 -0.711810

H -0.210097 1.378533 -1.339074

H -1.022364 -0.160040 -1.067304

H 0.285191 -0.045473 -2.250661

H 3.321741 -1.886660 -1.644188

H 3.785488 -0.207959 -1.862651

H 2.254565 -0.784413 -2.520366

H 4.623886 -0.964301 2.156729

H 5.031171 -0.288670 0.579814

H 4.525619 -1.966774 0.704331

H 1.488803 0.305082 3.935694

H 2.855058 1.239339 3.352513

H 3.074596 -0.457605 3.759026

H -0.196907 1.526116 2.723534

H -0.903370 1.635924 1.126013

H 0.687276 2.351446 1.426116

H 1.904297 -3.422834 1.369361

H 1.659657 -2.933634 -0.295362

H 1.509710 -4.665117 0.143590

H -0.447553 -2.854722 -1.286201

H -1.897978 -3.341251 -0.392136

H -0.729086 -4.584068 -0.957320

H 1.149390 -1.982700 4.253969

H 0.121553 -2.761027 5.489755

H -0.277515 -1.134308 4.882169

H -2.095870 -3.480709 4.911076

H -2.720384 -3.255981 3.256089

H -2.473500 -1.840585 4.280747

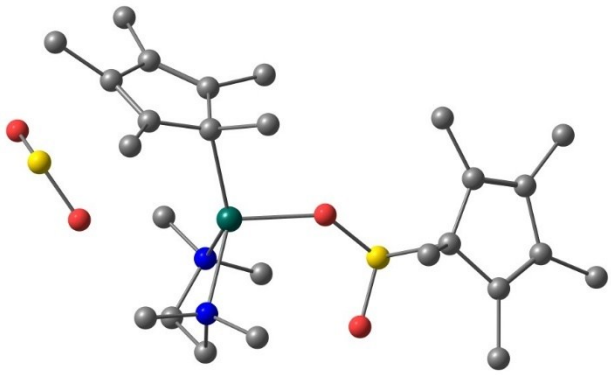
H 0.921564 -3.944654 3.147917

H -0.479604 -4.772307 3.822327

H -1.722325 -4.331232 1.654818

H -0.312207 -5.385169 1.471889

8106 - Zn(cp*)SO_2cp* with a SO_2 adduct



Zn -2.321819 2.593576 4.619781

S -3.804780 4.575857 7.978156

S -0.810461 1.722706 1.787813

O -4.120589 4.359972 6.537940

O -3.194474 5.888436 8.278259

O -1.028548 1.684452 3.356712

O -2.178508 1.711449 1.127256

N -2.594996 4.559741 3.663877

N -4.317942 2.118300 3.870987

C -2.188927 3.232856 9.958631

C -0.058974 4.923353 8.401140

C 0.712709 3.230927 5.794098

C -0.989085 0.546011 6.135601

C -3.379165 1.039522 8.064247

C -0.477878 3.038930 6.686657

C -0.763030 3.732112 7.833641

C -1.915281 3.104746 8.481288

C -2.327379 2.026090 7.677392

C -1.484244 1.952090 6.504871

C -4.345024 0.810337 3.182734

C -4.532962 3.208616 2.887327

C -4.057272 4.559256 3.414727

C -1.865597 4.704431 2.388377

C -2.211014 5.700286 4.521530

C -5.377522 2.118027 4.896758

C -1.159874 -0.310759 -0.941680

C 1.896594 0.234356 -1.760794

C 3.613361 0.414147 0.790363

C 1.749830 0.004711 3.358121

C -0.984089 -1.075309 2.110392

C 1.310505 0.134613 -0.387719

C 2.131273 0.213503 0.832220

C 1.337842 0.055812 1.924184

C -0.089947 -0.040505 1.457143

C 0.011113 -0.071405 -0.046691

H 1.382704 -0.905748 3.849039

H -1.992994 -1.030689 1.690082

H -1.052608 -0.905280 3.188164

H -0.584252 -2.080164 1.937366

H -1.976630 0.376460 -0.699742

H -1.547138 -1.332186 -0.823209

H -0.894096 -0.184260 -1.994687

H 1.133596 0.155932 -2.538637

H 2.636024 -0.556599 -1.939881

H 2.418058 1.189081 -1.903393

H 3.871612 1.365001 0.307354

H 4.108781 -0.375622 0.211837

H 4.057060 0.422851 1.788667

H 1.348194 0.851564 3.923591

H 2.838124 0.014041 3.461325

H 0.365131 4.707770 9.390466

H -0.753433 5.763289 8.524684

H 0.763616 5.253637 7.761392

H 0.476559 3.046677 4.741387

H 1.514424 2.527596 6.059379

H 1.130734 4.237915 5.882970

H -0.401128 0.554987 5.219249

H -1.816156 -0.154344 5.980192

H -0.367395 0.144990 6.947485

H -3.077239 0.452464 8.942216

H -3.594467 0.333684 7.258438

H -4.320069 1.538000 8.333379

H -1.419792 2.698908 10.530340

H -3.159223 2.809259 10.234908

H -2.172934 4.278058 10.283277

H -5.385621 3.054686 5.449754

H -5.189116 1.309277 5.606312

H -6.356677 1.945901 4.424979

H -4.131484 0.020820 3.908151

H -3.593016 0.801114 2.391444

H -5.341352 0.628185 2.752597

H -2.721456 5.640815 5.479528

H -2.463223 6.650192 4.027250

H -1.131525 5.670968 4.685509

H -2.059865 5.698617 1.959068

H -2.168621 3.940581 1.671957

H -0.793309 4.605376 2.568939

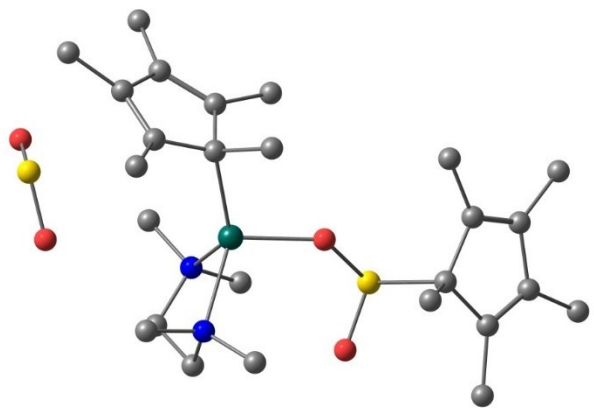
H -4.548922 4.804135 4.358173

H -4.315320 5.343086 2.686099

H -3.979443 2.932670 1.984862

H -5.599712 3.273627 2.624252

8107 – Transition state of the 2nd SO_2 insertion



Zn -1.191209 1.646527 1.969179

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S -4.473932 1.565816 1.882051

O 3.076306 2.961682 -0.365802

O 2.306499 3.442138 1.955558

O -4.461532 2.699576 2.894345

O -3.044430 0.882718 1.900792

N -1.100670 2.828351 3.803300

N -1.302883 3.586404 0.936167

C -2.659089 3.890988 0.441123

C -0.371096 3.682906 -0.203155

C 0.254999 2.903701 4.375636

C -9.077347 0.716977 1.401214

C -7.507137 -1.478046 -0.084422

C -4.634143 -1.841083 1.288236

C -4.918866 -0.222215 4.013193

C -7.280566 1.859564 3.805326

C -5.699981 -0.853141 1.629054

C -6.925963 -0.709861 1.060507

C -7.675329 0.343179 1.766491

C -6.911146 0.847772 2.770876

C -5.555330 0.192898 2.701569

C -1.288124 -0.199880 -0.804144

C 1.674975 0.107095 -1.961073

C 3.645757 -0.279380 0.416735

C 2.055594 -0.172506 3.133906

C -0.706672 -1.143953 2.183260

C -2.022521 2.325439 4.842042

C -1.552312 4.160516 3.337157

C -0.914736 4.536817 2.004947

C 1.247902 0.060860 -0.526092

C 2.188723 0.047663 0.582974

C 1.468807 0.043656 1.774323

C 0.027962 0.011420 1.471991

C -0.024060 -0.012658 -0.019162

H -4.337987 -2.428109 2.167322

H -4.852262 0.631251 4.694060

H -3.911109 -0.612859 3.847765

H -5.522806 -0.999097 4.494014

H -6.539827 2.664693 3.840981

H -7.317502 1.407587 4.806146

H -8.264031 2.295513 3.609467

H -9.462018 1.525041 2.027602

H -9.759807 -0.136352 1.504061

H -9.142675 1.046867 0.356919

H -7.747993 -0.815679 -0.925501

H -8.442608 -1.975519 0.200474

H -6.823303 -2.244646 -0.456357

H -3.729844 -1.344372 0.923035

H -4.970112 -2.545744 0.522917

H 2.257365 -0.781333 -2.238538

H 2.307924 0.980282 -2.158200

H 0.818677 0.154528 -2.639008

H -2.144913 0.291814 -0.333091

H -1.546405 -1.265843 -0.877487

H -1.194379 0.173265 -1.828766

H -1.770722 -1.149627 1.943226

H -0.624037 -1.074277 3.273282

H -0.277820 -2.110088 1.882140

H 2.391294 -1.211178 3.261865

H 1.329238 0.028177 3.924711

H 2.928475 0.465161 3.316473

H 3.757651 -1.325056 0.102003

H 4.207753 -0.159305 1.347280

H 4.124522 0.336215 -0.353126

H 0.988299 3.200990 3.626977

H 0.536508 1.920668 4.757894

H 0.275275 3.617447 5.213325

H -1.717698 1.317026 5.133810

H -3.037182 2.302340 4.439868

H -1.985727 2.973376 5.730866

H 0.650935 3.498339 0.117683

H -0.421231 4.683003 -0.658625

H -0.642924 2.940502 -0.956083

H -2.666217 4.872167 -0.056912

H -3.381165 3.895341 1.258466

H -2.959811 3.129343 -0.281757

H 0.176326 4.523850 2.077628

H -1.215085 5.559876 1.731459

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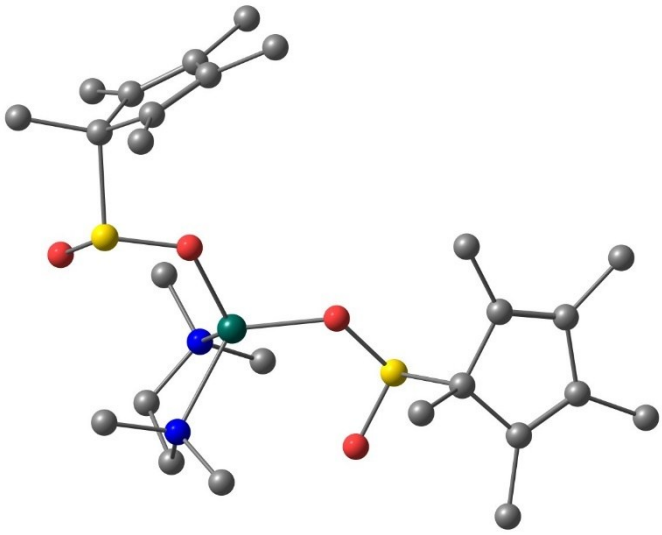
H -1.310861 4.926968 4.089647

8108 - Zn(cp*)$_2$ with 2 SO_2 inserted



Zn -2.507694 2.735253 3.924307

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S -0.891000 1.854525 1.439311

O -2.249313 2.368217 5.792988

O -3.769709 4.169057 6.732229

O -1.092598 1.797869 3.013964

O -2.257250 2.111599 0.821273

N -2.630207 4.802120 3.344967

N -4.561405 2.557238 3.294511

C -2.988803 3.219076 9.617954

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C 1.574310 3.532050 7.754476

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C 0.191626 3.040787 8.045664

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C -2.078931 2.835844 8.454552

C -1.438745 1.475374 8.531723

C -0.118425 1.613145 8.257871

C -4.807829 1.355273 2.472660

C -4.711115 3.774977 2.464843

C -4.085011 4.989046 3.141759

C -1.883824 5.070077 2.100508

C -2.142329 5.699701 4.410689

C -5.506563 2.565858 4.428033

C -1.372013 0.067137 -1.411506

C 1.801792 0.078428 -1.928973

C 3.268871 -0.193879 0.769170

C 1.105190 -0.400934 3.134363

C -1.629584 -0.853766 1.605332

C 1.077574 0.012723 -0.621410

C 1.777962 -0.117024 0.667781

C 0.868031 -0.180242 1.676165

C -0.500358 0.007577 1.077949

C -0.265127 0.027273 -0.409416

H 0.680487 -1.359375 3.462630

H -2.570518 -0.601612 1.108394

H -1.753655 -0.708552 2.682327

H -1.413061 -1.910593 1.417322

H -2.078331 0.870736 -1.178811

H -1.941238 -0.872738 -1.413078

H -0.993047 0.219333 -2.425802

H 1.115150 0.171570 -2.773549

H 2.411682 -0.818797 -2.093887

H 2.487486 0.934173 -1.962541

H 3.743630 0.697952 0.341391

H 3.664806 -1.055659 0.217002

H 3.604935 -0.281408 1.804884

H 0.629008 0.379958 3.735055

H 2.172960 -0.421115 3.368550

H -1.277019 5.665708 9.162709

H -1.983845 5.533689 7.557692

H -0.227516 5.760090 7.746850

H 1.975504 3.074216 6.841830

H 2.270330 3.280756 8.565149

H 1.602978 4.616483 7.621851

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H 0.516367 -0.444360 8.412208

H 1.762546 0.734943 8.838171

H -2.736356 0.278274 9.773784

H -1.566804 -0.650113 8.830221

H -2.983651 0.051231 8.045087

H -2.411403 3.238118 10.547739

H -3.806840 2.500460 9.741518

H -3.429980 4.206741 9.457360

H -5.315885 3.407251 5.096764

H -5.375354 1.648417 5.006034

H -6.542293 2.605492 4.059705

H -4.668733 0.466058 3.092793

H -4.091757 1.335870 1.648226

H -5.838418 1.356515 2.087636

H -2.667531 5.470996 5.340678

H -2.296215 6.752272 4.130397

H -1.073512 5.527715 4.558071

H -2.025928 6.115220 1.788430

H -2.203113 4.393973 1.305336

H -0.819962 4.898589 2.280186

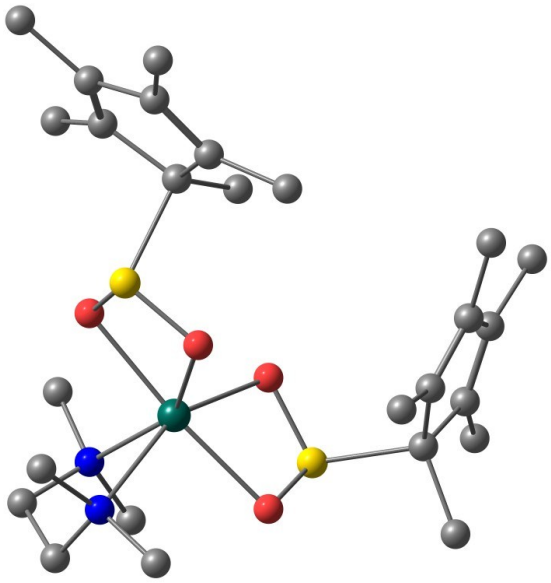
H -4.533305 5.152231 4.126088

H -4.274998 5.889014 2.538000

H -4.214070 3.573445 1.511416

H -5.774964 3.970453 2.260912

09 – Final product



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O -4.620804 0.034750 3.568274

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O -1.870993 -1.102196 1.717806

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C -2.763342 3.332421 -0.663538

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C -1.171468 -0.150483 6.421017

C -2.509503 -2.157348 6.224889

C -3.601385 -2.836695 5.406718

C -2.342567 -3.730563 3.542642

C -4.571948 -2.936927 3.189487

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C 2.022789 -0.363030 1.877850

C 0.645820 -0.009603 1.384441

C 0.652300 -0.407408 -0.067020

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H -2.772416 2.425600 -1.272230

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H -4.566634 -2.361469 5.604961

H -3.692399 -3.890433 5.717933

Crystallographic details and data

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the cold stream of a STOE StadiVari diffractometer. Using Olex2,[7] all structures were solved using either SHELXS or SHELXT.[8] The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full matrix least-squares techniques on F, minimizing the function $(F_o\text{-}F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, using the program SHELXL-2014.[9] Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and the relevant codes are: 1490512–1490514. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Crystal data for **1**: $C_{26}H_{46}N_2O_4S_2Zn$ (M = 580.14 g/mol): monoclinic, space group P2/c (no. 13), a = 9.6180(7) Å, b = 10.1691(5) Å, c = 15.0935(11) Å, β = 103.265(6)°, V = 1436.85(17) Å^3, Z = 2, T = 100.0 K, μ(MoKα) = 1.033 mm^{-1}, *Dcalc* = 1.341 g/cm^3, 6786 reflections measured (4.872° ≤ **1**2Θ ≤ 52.148°), 2838 unique (R_{int} = 0.0339, R_{sigma} = 0.0337) which were used in all calculations. The final R_1 was 0.0275 (I > 2σ(I)) and wR_2 was 0.0700 (all data).

Crystal data for **2**·1.5(C_5H_{12}): $C_{67.5}H_{108}O_{13}S_6Zn_4$ (M = 1581.37 g/mol): triclinic, space group P-1 (no. 2), a = 13.8362(7) Å, b = 15.0709(8) Å, c = 20.3113(10) Å, α = 89.161(4)°, β = 79.646(4)°, γ = 73.544(4)°, V = 3992.8(4) Å^3, Z = 2, T = 100.0 K, μ(MoKα) = 1.397 mm^{-1}, *Dcalc* = 1.315 g/cm^3, 35842 reflections measured (3.402° ≤ 2Θ ≤ 52.286°), 15667 unique (R_{int} = 0.1492, R_{sigma} = 0.1321) which were used in all calculations. The final R_1 was 0.0903 (I > 2σ(I)) and wR_2 was 0.2452 (all data).

Crystal data for **3**·thf: $C_{16}H_{40}N_4O_8S_3Zn_2$ (M = 643.44 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.9030(8) Å, b = 15.8305(8) Å, c = 13.4913(9) Å, β = 103.699(5)°, V = 2677.4(3) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 2.071 mm^{-1}, *Dcalc* = 1.596 g/cm^3, 12736 reflections measured

(4.034° ≤ 2Θ ≤ 52.152°), 5244 unique (R_{int} = 0.0402, R_{sigma} = 0.0725) which were used in all calculations. The final R_1 was 0.0323 (I > 2σ(I)) and wR_2 was 0.0582 (all data).

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