Supplementary Material (ESI) for Chemical Communications

Inorganic Chemistry Crystallography Service

Single-crystal X-ray diffraction report for $[Zn(C_8H_{14}N_6S_2)(DMSO)]\cdot DMSO$ (ARC428)

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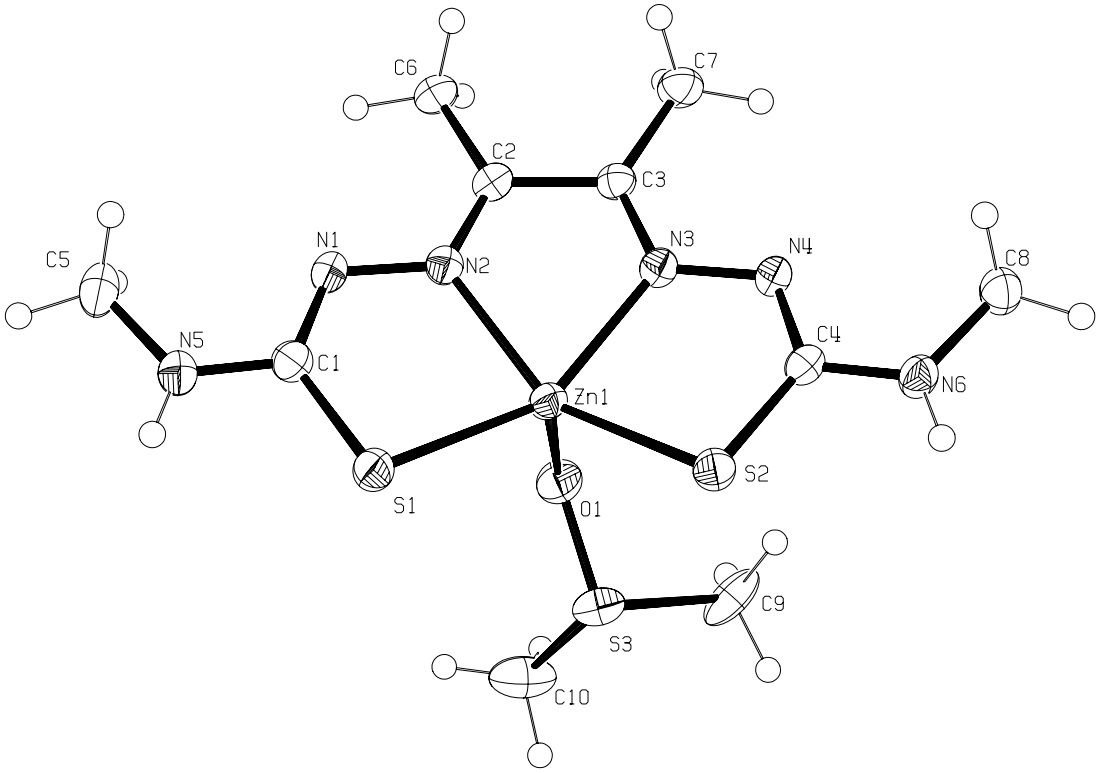


Non-coordinated solvent not shown. One of the two orientations of the disordered ligand (S(3), C(9), C(10)) is shown.

Crystals of **ARC428** were grown by evaporation of a DMSO solution. A single crystal having dimensions approximately 0.08 x 0.20 x 0.20 mm was mounted on a glass fibre using perfluoropolyether oil and cooled to 230 K at a rate of 120 K/hr in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package[1]. The crystal was found to be monoclinic, with unit cell parameters *a* = 17.0917(3), *b* = 8.0671(2), *c* = 17.6030(3) Å, β = 117.8697(9)°.

On further cooling a considerable change in unit-cell parameters occurred, indicative of a phase change (see Comment below). This was accompanied by considerable physical damage to the crystal, which acquired a 'frosted' appearance. The crystal was cooled to 150K and a complete diffraction data set measured. Examination of the systematic absences of the intensity data showed the space group to be $P\,2_1/c$. The structure was solved using the direct-methods program SIR92,[2] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[3] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The thermal parameters of the coordinated DMSO refined to excessively large values and examination of its geometry showed it to be almost planar. This was interpreted as being due to disorder. Additional atomic positions were identified in a difference Fourier map and a model constructed in which two orientations of the DMSO were related by a mirror plane passing through the O atom. Coordinates, anisotropic thermal parameters and site occupancies of the disordered non-hydrogen atoms were refined, with the total occupancy of the two DMSO sites constrained to be unity. The two O-S bond lengths were restrained to their common mean (esd

0.02 Å) as were the four S-C bond lengths. Similarity restraints were also applied to the O-S-C and C-S-C angles (esd 2°). The NH hydrogen atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0348, wR = 0.0407.

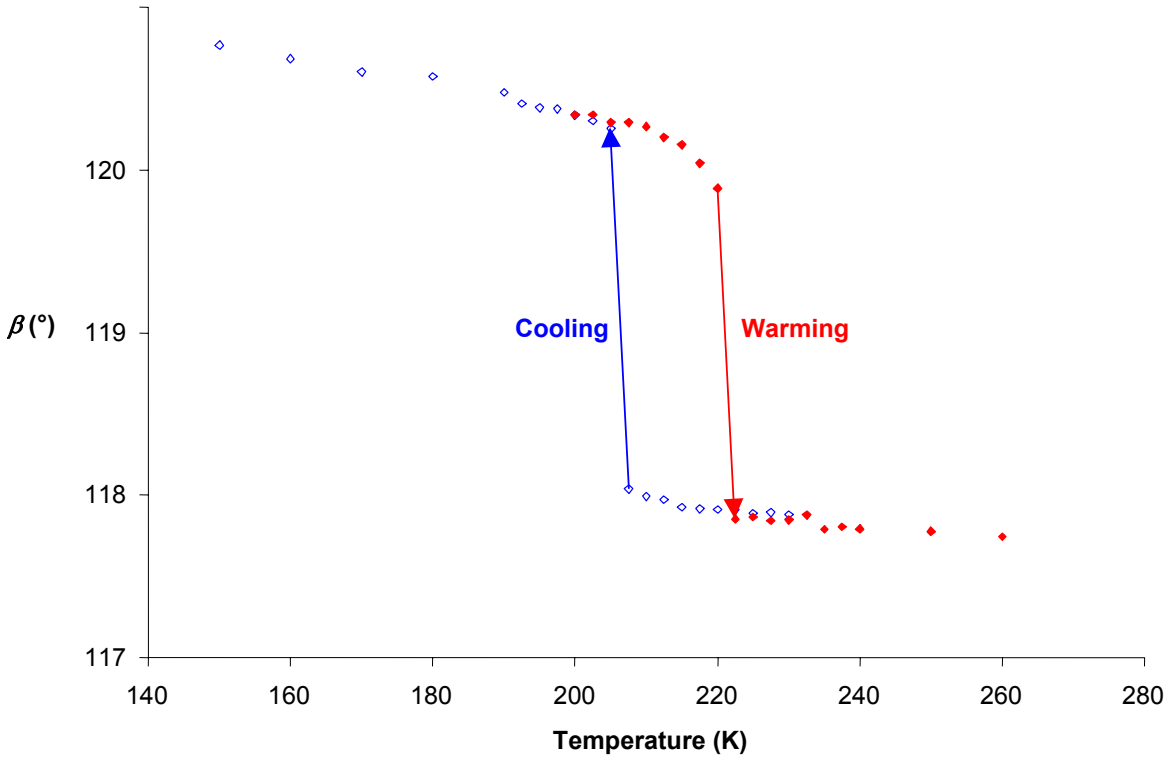
Attached is a thermal ellipsoid plot (ORTEP-3[4]) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning geometrically-positioned H atoms.

Comments:

The asymmetric unit of the crystal contains one Zn complex (with a coordinated DMSO fragment) and a 'free' DMSO molecule which interacts with the complex through hydrogen-bonding (see below). At 150K, the free solvent is not exhibits no evidence of disorder whereas the coordinated DMSO is disordered, apparently over 2 sites.

Measurements of the unit-cell parameters at a range of temperatures were made by the following procedure. An initial cell determination was performed at a temperature well above the transition point of the phase change using a scan consisting of 10 consecutive 2° exposures. The diffraction pattern was indexed using the DENZO-SMN package.[1] The temperature was then decreased by a small increment at a rate of 120 K/hr and a similar 10x2° scan measured. In order to ensure that a common choice of axes was used, this second pattern was not indexed *ab initio* but instead used to perform least-squares refinement of the orientation matrix obtained previously. This process was repeated iteratively over a range of temperatures above and below the phase change, then repeated while the crystal was warmed up to high temperature. The complete results are listed below (Table 7).

The presence of the phase change is most clearly shown by the value of β, which varies by over 2°. This is plotted graphically below:



It can be seen that this is a first order phase change which exhibits extensive hysteresis. The phase change is fully reversible, and appears to be completely reproducible.

A full data collection has been performed on the high-temperature phase at 230 K. It is essentially isostructural with the low-temperature form but exhibits more extensive disorder. The coordinated DMSO fragment appears to be disordered over at least 3 positions but as the C atom locations are not clearly resolved this cannot be meaningfully modelled. In addition, the 'free' DMSO also is disordered over at least 2 sites.

Most of the atoms of the thiosemicarbazone ligand are approximately coplanar, with the rms deviation of the atoms S(1) to S(2) from their best plane being 0.04 Å. The Zn atom is displaced from this plane by 0.47 Å towards the coordinated DMSO. The two NHMe substituents are displaced from the plane away from the DMSO (displacements: N(5) 0.18, C(5) 0.37, N(6) 0.18, C(8) 0.37 Å). There is a small twisting of the Me-C-C-Me linkage, as shown by the C(7)-C(2)-C(3)-C(7) torsion angle of 5.8°.

One of the NH groups of the ligand forms a hydrogen bond to the O atom of the non-coordinated DMSO (N(5)···O(2) 2.871(4) Å). The second group forms a hydrogen bond to one of the imine N atoms of a neighbouring complex (N(6)···N(4)' 3.048(3) Å, symmetry operator generating acceptor -*x*, *y* - 1/2, -*z* + 1/2). This second type of hydrogen bond links the molecules to form chains running along the crystallographic screw axis parallel to the *b* axis.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.
2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.
3 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.
4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.

Table 1: Crystal data and refinement details

Crystal identification	ARC428
Chemical formula	$C_{12}H_{26}N_6O_2S_4Zn$
Formula weight	480.00
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P\,2_1/c$
a (Å)	17.1632(5)
b (Å)	8.1574(3)
c (Å)	17.4311(6)
α (°)	90
β (°)	120.6784(13)
γ (°)	90
Cell volume (Å^3)	2098.9
Z	4
Calculated density (Mg/m^3)	1.519
Absorption coefficient (mm^{-1})	1.586
F_{000}	1002.696
Crystal size (mm)	0.08 x 0.20 x 0.20
Description of crystal	Yellow block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.73, 0.88
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-22 \leq h \leq 19$, $0 \leq k \leq 10$, $0 \leq l \leq 22$
Reflections measured	19382
Unique reflections	5095
R_{int}	0.057
Observed reflections ($I > 3\sigma(I)$)	3307
Refinement method	Full-matrix least-squares on *F*
Parameters refined	262
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0822
R	0.0348
wR	0.0407
Residual electron density (min, max) (eÅ^{-3})	-0.64, 0.74

Table 2: Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
Zn(1)	0.19574(2)	0.38580(4)	0.17669(2)	0.0227
S(1)	0.30791(5)	0.30631(9)	0.14563(5)	0.0288
C(1)	0.30343(18)	0.4872(4)	0.08893(18)	0.0263
N(1)	0.24586(16)	0.6111(3)	0.06690(15)	0.0266
N(2)	0.18187(15)	0.5814(3)	0.09051(15)	0.0239
C(2)	0.11656(18)	0.6844(3)	0.06899(17)	0.0235
C(3)	0.04859(17)	0.6304(3)	0.09345(17)	0.0220
N(3)	0.06815(15)	0.4926(3)	0.13645(15)	0.0225
N(4)	0.00988(15)	0.4270(3)	0.16064(15)	0.0226
C(4)	0.03415(18)	0.2768(3)	0.19360(17)	0.0225
S(2)	0.12904(5)	0.16501(9)	0.20981(5)	0.0276
N(5)	0.36565(18)	0.4987(3)	0.06396(18)	0.0325
C(5)	0.3686(2)	0.6333(5)	0.0111(2)	0.0432
C(6)	0.1058(2)	0.8445(4)	0.02369(19)	0.0280
C(7)	-0.0352(2)	0.7278(4)	0.0655(2)	0.0300
N(6)	-0.02208(17)	0.1982(3)	0.21338(17)	0.0259
C(8)	-0.1087(2)	0.2664(4)	0.1936(2)	0.0306
O(1)	0.26944(14)	0.5027(3)	0.29980(13)	0.0347
S(3)*	0.31599(11)	0.3598(2)	0.3752(1)	0.0322
C(9)*	0.2496(9)	0.3778(16)	0.4256(7)	0.0419
C(10)*	0.4237(5)	0.4448(9)	0.4506(5)	0.0477
S(103)†	0.32695(11)	0.4727(2)	0.3967(1)	0.0343
C(109)†	0.2651(9)	0.4097(18)	0.4447(8)	0.0454
C(110)†	0.3803(5)	0.2836(9)	0.4003(4)	0.0458
O(2)	0.52308(15)	0.2969(3)	0.12219(16)	0.0458
S(4)	0.58928(6)	0.2730(1)	0.21997(6)	0.0381
C(11)	0.5571(3)	0.4145(6)	0.2771(3)	0.0539
C(12)	0.6907(2)	0.3769(5)	0.2421(3)	0.0467

*disordered atom, refined site occupancy 0.495(4)
†disordered atom, refined site occupancy 0.505(4)

Table 3: Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(1)	0.407(2)	0.433(4)	0.085(2)	0.04(1)
H(2)	-0.004(2)	0.114(4)	0.242(2)	0.027(8)
H(51)	0.4201	0.6166	0.0006	0.0582
H(52)	0.3773	0.7388	0.0438	0.0582
H(53)	0.3104	0.6375	-0.0474	0.0582
H(61)	0.1569	0.8604	0.0125	0.0334
H(62)	0.1062	0.9351	0.0625	0.0334
H(63)	0.0470	0.8456	-0.0344	0.0334
H(71)	-0.0722	0.6734	0.0877	0.0364
H(72)	-0.0183	0.8408	0.0911	0.0364
H(73)	-0.0713	0.7347	-0.0011	0.0364
H(81)	-0.1395	0.1882	0.2138	0.0389
H(82)	-0.0984	0.3731	0.2256	0.0389
H(83)	-0.1476	0.2847	0.1279	0.0389
H(91)*	0.2705	0.2957	0.4749	0.0521
H(92)*	0.2563	0.4908	0.4505	0.0521
H(93)*	0.1846	0.3571	0.3801	0.0521
H(101)*	0.4589	0.3662	0.5006	0.0472
H(102)*	0.4156	0.5502	0.4750	0.0472
H(103)*	0.4572	0.4659	0.4185	0.0472
H(1091)†	0.3070	0.3912	0.5100	0.0567
H(1092)†	0.2199	0.4963	0.4358	0.0567
H(1093)†	0.2327	0.3054	0.4161	0.0567
H(1101)†	0.4216	0.2507	0.4638	0.0512
H(1102)†	0.4162	0.2967	0.3700	0.0512
H(1103)†	0.3331	0.1972	0.3691	0.0512
H(111)	0.5993	0.4036	0.3429	0.0647
H(112)	0.5602	0.5288	0.2581	0.0647
H(113)	0.4938	0.3903	0.2624	0.0647
H(121)	0.7376	0.3651	0.3067	0.0533
H(122)	0.7138	0.3277	0.2050	0.0533
H(123)	0.6773	0.4957	0.2271	0.0533

Table 4: Anisotropic thermal parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	0.02464(16)	0.02172(16)	0.02345(16)	0.00392(13)	0.01359(12)	0.00324(12)
S(1)	0.0320(4)	0.0275(4)	0.0337(4)	0.0064(3)	0.0217(3)	0.0073(3)
C(1)	0.0263(13)	0.0299(14)	0.0233(13)	0.0004(11)	0.0130(11)	0.0015(11)
N(1)	0.0282(11)	0.0296(12)	0.0276(11)	0.006(1)	0.018(1)	0.002(1)
N(2)	0.0246(11)	0.0250(12)	0.0244(11)	0.0026(9)	0.0142(9)	0.0022(9)
C(2)	0.0274(13)	0.0218(13)	0.0212(12)	0.001(1)	0.0123(11)	0.0001(11)
C(3)	0.0240(12)	0.0217(13)	0.0194(11)	0.000(1)	0.011(1)	0.002(1)
N(3)	0.025(1)	0.0220(11)	0.0229(11)	0.0003(9)	0.0136(9)	-0.0000(9)
N(4)	0.0252(11)	0.0226(11)	0.0228(11)	0.0013(9)	0.0143(9)	-0.0007(9)
C(4)	0.0267(13)	0.0217(12)	0.0198(12)	-0.000(1)	0.012(1)	-0.002(1)
S(2)	0.0290(3)	0.0208(3)	0.0365(4)	0.0058(3)	0.0192(3)	0.0040(3)
N(5)	0.0316(13)	0.0376(14)	0.0360(14)	0.0092(12)	0.0228(11)	0.0071(11)
C(5)	0.0456(18)	0.051(2)	0.0487(19)	0.0126(17)	0.0356(17)	0.0058(16)
C(6)	0.0321(14)	0.0242(14)	0.0272(13)	0.0049(11)	0.0147(12)	0.0020(11)
C(7)	0.0334(15)	0.0255(14)	0.0320(15)	0.0055(12)	0.0173(13)	0.0075(12)
N(6)	0.0294(12)	0.0206(11)	0.0322(12)	0.004(1)	0.019(1)	0.0010(9)
C(8)	0.0309(15)	0.0303(15)	0.0359(16)	0.0025(12)	0.0209(13)	0.0018(12)
O(1)	0.034(1)	0.0455(13)	0.023(1)	0.0017(9)	0.0133(8)	0.000(1)
S(3)	0.0379(9)	0.0281(11)	0.0239(7)	0.0039(6)	0.0109(6)	0.0045(6)
C(9)	0.077(6)	0.035(5)	0.019(4)	-0.004(4)	0.028(4)	-0.013(4)
C(10)	0.045(4)	0.036(3)	0.037(3)	0.002(3)	0.003(3)	0.003(3)
S(103)	0.0454(9)	0.0298(11)	0.0209(7)	-0.0042(6)	0.0120(6)	0.0017(7)
C(109)	0.065(5)	0.044(6)	0.033(5)	-0.018(4)	0.029(4)	-0.011(4)
C(110)	0.048(4)	0.047(4)	0.033(3)	0.007(3)	0.014(3)	0.014(3)
O(2)	0.0320(12)	0.0641(17)	0.0364(12)	-0.0117(12)	0.014(1)	0.0059(11)
S(4)	0.0350(4)	0.0343(4)	0.0417(4)	0.0003(3)	0.0171(3)	-0.0008(3)
C(11)	0.046(2)	0.074(3)	0.0422(19)	-0.0220(19)	0.0225(17)	-0.0113(19)
C(12)	0.0318(16)	0.049(2)	0.053(2)	0.0037(17)	0.0168(15)	-0.0006(15)

Table 5: Bond lengths (Å)

Zn(1) - S(1)	2.3418(7)
Zn(1) - N(2)	2.120(2)
Zn(1) - N(3)	2.116(2)
Zn(1) - S(2)	2.3585(8)
Zn(1) - O(1)	2.084(2)
S(1) - C(1)	1.756(3)
C(1) - N(1)	1.326(4)
C(1) - N(5)	1.346(4)
N(1) - N(2)	1.377(3)
N(2) - C(2)	1.294(4)
C(2) - C(3)	1.498(4)
C(2) - C(6)	1.488(4)
C(3) - N(3)	1.297(3)
C(3) - C(7)	1.491(4)
N(3) - N(4)	1.376(3)
N(4) - C(4)	1.327(3)
C(4) - S(2)	1.759(3)
C(4) - N(6)	1.342(4)
N(5) - C(5)	1.450(4)
N(5) - H(1)	0.82(3)
N(6) - C(8)	1.454(4)
N(6) - H(2)	0.82(3)
O(1) - S(3)*	1.629(3)
O(1) - S(103)*	1.478(2)
S(3) - C(9)*	1.764(12)
S(3) - C(10)*	1.774(7)
S(103) - C(109)*	1.732(13)
S(103) - C(110)*	1.779(7)
O(2) - S(4)	1.503(2)
S(4) - C(11)	1.786(4)
S(4) - C(12)	1.792(4)

*bond length included in geometric restraint

Note – geometrically-positioned H atoms have been excluded

Table 6: Bond angles (°)

S(1) - Zn(1) - N(2)	81.54(6)
S(1) - Zn(1) - N(3)	150.59(6)
N(2) - Zn(1) - N(3)	74.47(9)
S(1) - Zn(1) - S(2)	113.84(3)
N(2) - Zn(1) - S(2)	148.78(7)
N(3) - Zn(1) - S(2)	81.14(6)
S(1) - Zn(1) - O(1)	103.06(6)
N(2) - Zn(1) - O(1)	100.08(9)
N(3) - Zn(1) - O(1)	97.75(9)
S(2) - Zn(1) - O(1)	102.28(6)
Zn(1) - S(1) - C(1)	95.30(9)
S(1) - C(1) - N(1)	128.0(2)
S(1) - C(1) - N(5)	115.2(2)
N(1) - C(1) - N(5)	116.7(3)
C(1) - N(1) - N(2)	111.7(2)
Zn(1) - N(2) - N(1)	121.75(17)
Zn(1) - N(2) - C(2)	117.49(18)
N(1) - N(2) - C(2)	120.3(2)
N(2) - C(2) - C(3)	114.3(2)
N(2) - C(2) - C(6)	125.3(2)
C(3) - C(2) - C(6)	120.3(2)
C(2) - C(3) - N(3)	114.2(2)
C(2) - C(3) - C(7)	120.8(2)
N(3) - C(3) - C(7)	125.0(2)
Zn(1) - N(3) - C(3)	117.86(18)
Zn(1) - N(3) - N(4)	121.95(16)
C(3) - N(3) - N(4)	120.0(2)
N(3) - N(4) - C(4)	112.0(2)
N(4) - C(4) - S(2)	127.5(2)
N(4) - C(4) - N(6)	116.4(2)
S(2) - C(4) - N(6)	116.1(2)
Zn(1) - S(2) - C(4)	95.16(9)
C(1) - N(5) - C(5)	123.2(3)
C(1) - N(5) - H(1)	118.2(27)
C(5) - N(5) - H(1)	118.1(27)
C(4) - N(6) - C(8)	122.6(2)
C(4) - N(6) - H(2)	117.7(25)
C(8) - N(6) - H(2)	119.4(25)
Zn(1) - O(1) - S(3)	107.08(14)
Zn(1) - O(1) - S(103)	143.25(17)
O(1) - S(3) - C(9)*	99.6(5)
O(1) - S(3) - C(10)*	102.4(3)
C(9) - S(3) - C(10)*	107.0(5)
O(1) - S(103) - C(109)*	112.6(5)
O(1) - S(103) - C(110)*	102.4(3)
C(109) - S(103) - C(110)*	99.0(6)
O(2) - S(4) - C(11)	106.22(17)
O(2) - S(4) - C(12)	105.83(17)
C(11) - S(4) - C(12)	96.72(19)

*bond angle included in geometric restraint

Note – geometrically-positioned H atoms have been excluded

Table 7: Unit-cell parameters

Results obtained by cooling crystal from 230K							
Temp (K)	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ(°)	Vol. (Å^3)
230.0	17.1078	8.0699	17.6100	90.	117.8803	90.	2149.0
227.5	17.0982	8.0669	17.6037	90.	117.8934	90.	2146.0
225.0	17.0847	8.0642	17.5955	90.	117.8877	90.	2142.7
222.5	17.0928	8.0659	17.5956	90.	117.9099	90.	2143.7
220.0	17.0798	8.0634	17.5875	90.	117.9116	90.	2140.4
217.5	17.0738	8.0628	17.5819	90.	117.9154	90.	2138.7
215.0	17.0662	8.0617	17.5743	90.	117.9269	90.	2136.3
212.5	17.0851	8.0639	17.5813	90.	117.9712	90.	2139.3
210.0	17.0899	8.0650	17.5802	90.	117.9927	90.	2139.6
207.5	17.1000	8.0681	17.5818	90.	118.0369	90.	2141.0
205.0	17.2482	8.1793	17.5231	90.	120.2569	90.	2135.4
202.5	17.2475	8.1797	17.5247	90.	120.3040	90.	2134.6
200.0	17.2398	8.1789	17.5175	90.	120.3400	90.	2131.7
197.5	17.2480	8.1811	17.5211	90.	120.3784	90.	2132.9
195.0	17.2425	8.1816	17.5130	90.	120.3839	90.	2131.3
192.5	17.2423	8.1812	17.5107	90.	120.4115	90.	2130.2
190.0	17.2414	8.1780	17.5091	90.	120.4783	90.	2127.7
180.0	17.2534	8.1789	17.5042	90.	120.5773	90.	2126.6
170.0	17.2410	8.1748	17.4920	90.	120.6061	90.	2121.9
160.0	17.1906	8.1625	17.4570	90.	120.6852	90.	2106.6
150.0	17.1617	8.1536	17.4355	90.	120.7702	90.	2096.3
Results obtained by warming crystal from 200K							
Temp (K)	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ(°)	Vol. (Å^3)
200.0	17.2411	8.1801	17.5176	90.	120.3414	90.	2132.2
202.5	17.2521	8.1789	17.5259	90.	120.3419	90.	2134.2
2005	17.2346	8.1756	17.5223	90.	120.2939	90.	2131.8
207.5	17.2246	8.1699	17.5200	90.	120.2943	90.	2128.8
210.0	17.2059	8.1667	17.5133	90.	120.2677	90.	2125.4
212.5	17.2185	8.1675	17.5265	90.	120.2021	90.	2130.2
215.0	17.2434	8.1721	17.5440	90.	120.1569	90.	2137.6
217.5	17.2695	8.1736	17.5631	90.	120.0422	90.	2146.0
220.0	17.2264	8.1676	17.5438	90.	119.8892	90.	2140.1
222.5	17.2254	8.0997	17.6698	90.	117.8526	90.	2179.7
225.0	17.1435	8.0831	17.6352	90.	117.8660	90.	2160.4
227.5	17.1339	8.0840	17.6314	90.	117.8422	90.	2159.4
230.0	17.1322	8.0858	17.6316	90.	117.8469	90.	2159.6
232.5	17.1326	8.0847	17.6314	90.	117.8775	90.	2158.7
235.0	17.1674	8.0916	17.6473	90.	117.7903	90.	2168.7
237.5	17.1006	8.0756	17.6166	90.	117.8050	90.	2151.9
240.0	17.1361	8.0821	17.6354	90.	117.7909	90.	2160.7
250.0	17.1588	8.0900	17.6500	90.	117.7776	90.	2167.7
260.0	17.1379	8.0871	17.6523	90.	117.7436	90.	2165.3

Note: the esds provided by the diffractometer software have not been shown. These are typically 0.003 Å for cell edge lengths, 0.01° for angles, but may be substantially underestimated as a consequence of neglect of systematic errors arising from crystal and instrument misalignment.