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Bis(4′-chloro-2,2′:6′,2″-terpyridine-κ^3N,N',N'')-zinc(II) bis(trifluoromethanesulfonate)

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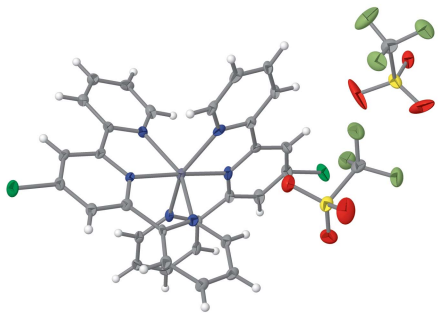
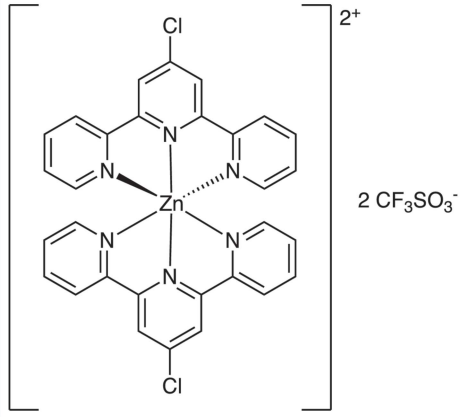
Structural data: full structural data are available from iucrdata.iucr.org

In the title complex, $[Zn(C_{15}H_{10}ClN_3)_2](CF_3SO_3)_2$, the Zn^{II} metal center is sixfold coordinated by three nitrogen atoms of each 4-chloroterpyridine ligand in a distorted octahedral geometry with triflouromethanesulfonate ions completing the outer coordination sphere of the complex. π–π stacking interactions between the pyridyl rings in adjacent molecules contribute to the alignment of the complexes in layers along the *c* axis.

3D view



Chemical scheme



Structure description

Terpyridine and its substituted derivatives continue to be versatile chelating ligands with several applications in areas as diverse as catalysis (Rupp *et al.*, 2019; Kobayashi & Nakazawa, 2021), supramolecular design (Kuai *et al.*, 2019; Ma *et al.*, 2021), and drug design (Qin *et al.*, 2019; Savic *et al.*, 2020). Recently, zinc(II) terpyridine complexes with phenyl-based substituents in the 4′-position of the terpyridine ring have shown excellent anticancer activity against several human carcinoma cell lines (Li *et al.*, 2019). Our research group interest currently lies in synthesizing metal complexes with applications in biological systems; as part of our research in this area, herein, we describe the synthesis and structure of the title zinc(II) complex.

The asymmetric unit of the title complex shows the 4-chloroterpyridine ligands surrounding the zinc metal center, with two trifluorosulfonate ions in the outer coordination sphere. The zinc(II) atom lies in an octahedral geometry defined by six pyridine nitrogen atoms from the two 4-chloroterpyridine ligands (Fig. 1). All the Zn—N bond distances are in good agreement with comparable bis(4-chloroterpyridine)zinc(II) complexes currently available in the Cambridge Structural Database (CSD, Groom *et al.*, 2016; version 5.43 with update June 2022; refcodes MOZHAL and MOZHEP; You *et al.*, 2009), but differ, by more than 0.1 Å in most cases, from those observed in complexes

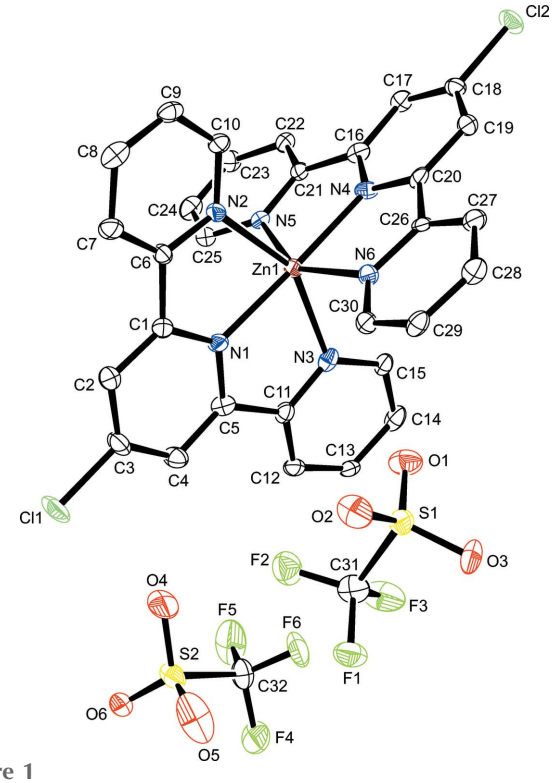


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level; H atoms are omitted for clarity.

where only one 4-chloroterpyridine is coordinated to the zinc(II) metal center (Adrian & Arman, 2020; refcode JABDID; Adrian *et al.*, 2020; refcode PADBUV; Huang & Qian, 2008; refcode HIVPOS; Dutta *et al.*, 2019; refcode DOHJES). The N—Zn—N angles also concur with the values reported in the previously referenced bis(4-chloroterpyridine)zinc(II) complexes. All relevant bonds and angles are presented in Table 1.

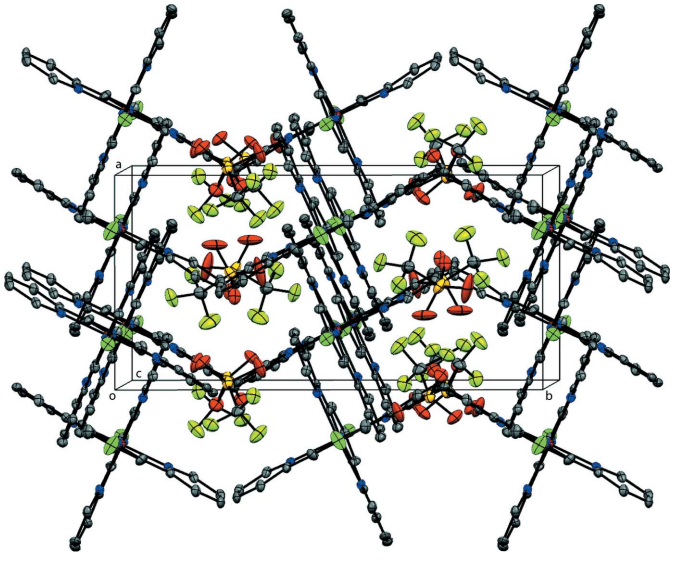


Figure 2
Packing for the title complex; H atoms are omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Zn1—N4	2.109 (5)	Zn1—N5	2.181 (6)
Zn1—N1	2.079 (5)	Zn1—N6	2.163 (6)
Zn1—N3	2.196 (6)	Zn1—N2	2.194 (6)
N4—Zn1—N3	106.9 (2)	N1—Zn1—N2	75.1 (2)
N4—Zn1—N5	74.8 (2)	N5—Zn1—N3	93.6 (2)
N4—Zn1—N6	75.1 (2)	N5—Zn1—N2	94.0 (2)
N4—Zn1—N2	102.3 (2)	N6—Zn1—N3	95.9 (2)
N1—Zn1—N4	177.4 (2)	N6—Zn1—N5	149.97 (18)
N1—Zn1—N3	75.7 (2)	N6—Zn1—N2	91.3 (2)
N1—Zn1—N5	105.4 (2)	N2—Zn1—N3	150.86 (18)
N1—Zn1—N6	104.5 (2)		

The packing diagram reveals the stacking of the asymmetric unit in alternating layers along the *c* axis (Fig. 2). π–π stacking interactions occur between the N5 and N6 pyridyl rings of adjacent molecules, with a centroid-to-centroid ($Cg\cdots Cg$) distance of 3.826 (4) Å and an offset distance of 1.379 (10) Å (Fig. 3). No other directional supramolecular interactions are present in the crystal packing of the title compound.

Synthesis and crystallization

Silver trifluoromethanesulfonate (0.377 g, 14.7 mmol) was added to an acetonitrile solution of zinc chloride (0.100 g, 7.34 mmol). The resulting solution was filtrated using a 0.45 mm PTFE syringe filter to remove silver chloride, and 4′-chloro-2,2′:6′,2″-terpyridine (0.393 g, 14.7 mmol) was added to yield the title compound. Crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether over the resulting acetonitrile solution at 277 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as a two-component twin with a final BASF parameter of 0.4619 (17).

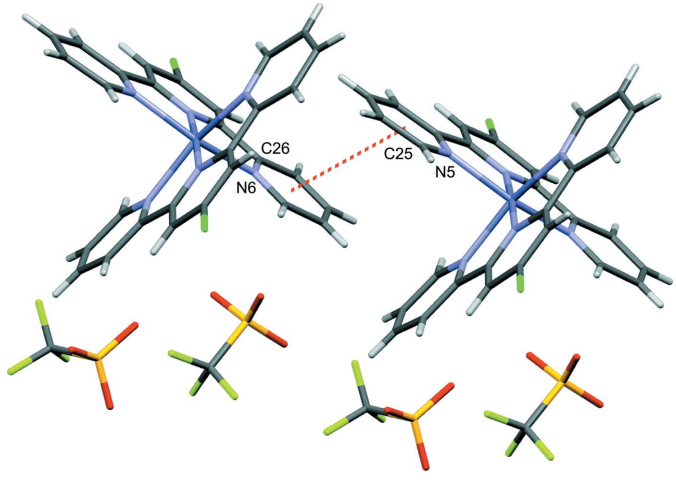


Figure 3
Capped stick representation of the title molecule showing the π–π stacking interactions (red).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Zn(C_{15}H_{10}ClN_3)_2](CF_3O_3S)_2$
M_r	898.93
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.9259 (2), 17.0711 (4), 22.0466 (5)
β (°)	90.287 (2)
V (Å^3)	3359.31 (13)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.46
Crystal size (mm)	0.22 × 0.07 × 0.04
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2019)
T_{min}, T_{max}	0.995, 0.999
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8675, 8675, 8049
R_{int}	0.065
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.600
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.069, 0.145, 1.15
No. of reflections	8675
No. of parameters	497
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, −0.71

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), SHELXT (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

IUCrData (2022). **7**, x221096 [https://doi.org/10.1107/S2414314622010963]

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Crystal data

$[Zn(C_{15}H_{10}ClN_3)_2](CF_3O_3S)_2$
M_r = 898.93
Monoclinic, $P2_1/c$
a = 8.9259 (2) Å
b = 17.0711 (4) Å
c = 22.0466 (5) Å
β = 90.287 (2)°
V = 3359.31 (13) Å^3
Z = 4
$F(000)$ = 1808
D_x = 1.777 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 10902 reflections
θ = 5.0–67.4°
μ = 4.46 mm^{-1}
T = 100 K
Needle, clear colourless
0.22 × 0.07 × 0.04 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2019)
T_{min} = 0.995, T_{max} = 0.999
8675 measured reflections
8675 independent reflections
8049 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 67.8°, θ_{min} = 3.3°
h = −10→10
k = −20→20
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.145
S = 1.15
8675 reflections
497 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 25.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.73770 (11)	0.49335 (5)	0.28538 (3)	0.01471 (19)
S1	1.0279 (2)	0.23997 (10)	0.39877 (7)	0.0239 (4)
Cl2	0.7635 (3)	0.50475 (11)	−0.01113 (6)	0.0255 (4)
S2	0.5232 (3)	0.25502 (11)	0.60978 (8)	0.0295 (4)
Cl1	0.7454 (3)	0.50507 (12)	0.58105 (6)	0.0373 (5)
N4	0.7432 (7)	0.4932 (3)	0.1897 (2)	0.0153 (10)
N1	0.7376 (8)	0.4982 (3)	0.3796 (2)	0.0180 (12)
F1	0.9720 (6)	0.1766 (3)	0.50582 (18)	0.0368 (11)
F3	0.7919 (6)	0.1670 (3)	0.4403 (2)	0.0482 (14)
C18	0.7554 (10)	0.4998 (4)	0.0672 (2)	0.0176 (12)
N3	0.6338 (6)	0.3825 (3)	0.3132 (2)	0.0174 (12)
F6	0.5121 (6)	0.1630 (3)	0.51400 (19)	0.0411 (12)
N5	0.5255 (7)	0.5454 (3)	0.2570 (2)	0.0150 (11)
F4	0.4119 (7)	0.1162 (3)	0.5956 (2)	0.0442 (13)
N6	0.9532 (7)	0.4437 (3)	0.2627 (2)	0.0161 (11)
F2	0.8370 (6)	0.2769 (3)	0.4839 (2)	0.0384 (11)
O6	0.4198 (7)	0.2660 (3)	0.6583 (2)	0.0303 (13)
N2	0.8412 (7)	0.6064 (3)	0.3076 (2)	0.0163 (11)
F5	0.2979 (7)	0.2035 (4)	0.5441 (3)	0.0618 (18)
O1	0.9262 (7)	0.2684 (3)	0.3526 (2)	0.0333 (13)
C12	0.5253 (9)	0.3153 (4)	0.3973 (3)	0.0197 (14)
H12	0.507101	0.312568	0.438778	0.024*
C5	0.6718 (8)	0.4400 (4)	0.4114 (3)	0.0174 (13)
O2	1.1243 (7)	0.2976 (4)	0.4263 (2)	0.0369 (14)
C20	0.8656 (8)	0.4685 (4)	0.1615 (3)	0.0162 (13)
C28	1.2298 (8)	0.3884 (4)	0.2245 (3)	0.0212 (14)
H28	1.322073	0.369520	0.211654	0.025*
C29	1.1960 (7)	0.3915 (4)	0.2852 (3)	0.0189 (14)
H29	1.265285	0.375202	0.314258	0.023*
C24	0.2846 (8)	0.6020 (4)	0.2747 (3)	0.0229 (15)
H24	0.213080	0.619438	0.302129	0.027*
C16	0.6264 (8)	0.5214 (4)	0.1585 (3)	0.0165 (13)
C17	0.6272 (8)	0.5258 (4)	0.0961 (3)	0.0175 (13)
H17	0.545638	0.545277	0.074463	0.021*
C1	0.7991 (8)	0.5595 (4)	0.4083 (3)	0.0185 (14)
C6	0.8651 (8)	0.6192 (4)	0.3676 (3)	0.0160 (13)
O3	1.0984 (9)	0.1662 (3)	0.3834 (3)	0.0455 (17)
C22	0.3669 (8)	0.5775 (4)	0.1736 (3)	0.0180 (14)
H22	0.349975	0.578390	0.131982	0.022*
C15	0.5834 (8)	0.3253 (4)	0.2760 (3)	0.0187 (14)
H15	0.605054	0.328322	0.234802	0.022*
C26	0.9879 (8)	0.4410 (3)	0.2022 (3)	0.0139 (13)
C9	0.9789 (8)	0.7236 (4)	0.2867 (3)	0.0196 (13)
H9	1.015282	0.758818	0.258190	0.023*
C21	0.5004 (8)	0.5490 (4)	0.1966 (3)	0.0149 (13)

C23	0.2574 (8)	0.6051 (4)	0.2134 (3)	0.0203 (13)
H23	0.167547	0.625130	0.198581	0.024*
C3	0.7381 (11)	0.5025 (5)	0.5027 (3)	0.0248 (16)
C11	0.6082 (8)	0.3759 (4)	0.3733 (3)	0.0171 (14)
C19	0.8777 (8)	0.4698 (4)	0.0988 (3)	0.0174 (13)
H19	0.962740	0.451617	0.079014	0.021*
C4	0.6738 (9)	0.4398 (4)	0.4739 (3)	0.0210 (15)
H4	0.632968	0.398490	0.495791	0.025*
C2	0.8041 (9)	0.5644 (4)	0.4712 (3)	0.0241 (16)
H2	0.848764	0.606471	0.491101	0.029*
C30	1.0565 (8)	0.4192 (4)	0.3022 (3)	0.0178 (14)
H30	1.033884	0.420937	0.343356	0.021*
C10	0.8965 (8)	0.6589 (4)	0.2685 (3)	0.0171 (13)
H10	0.878663	0.651626	0.227301	0.021*
C8	1.0062 (8)	0.7350 (4)	0.3471 (3)	0.0222 (15)
H8	1.063614	0.777259	0.360215	0.027*
C14	0.4998 (8)	0.2620 (4)	0.2971 (3)	0.0232 (15)
H14	0.465569	0.223332	0.270748	0.028*
C13	0.4697 (8)	0.2586 (4)	0.3584 (3)	0.0181 (14)
H13	0.411636	0.217943	0.373612	0.022*
C25	0.4210 (8)	0.5724 (4)	0.2951 (3)	0.0206 (14)
H25	0.440334	0.571281	0.336536	0.025*
C7	0.9467 (8)	0.6822 (4)	0.3889 (3)	0.0209 (15)
H7	0.961769	0.689324	0.430330	0.025*
O5	0.6589 (7)	0.2185 (5)	0.6262 (3)	0.059 (2)
O4	0.5307 (13)	0.3215 (4)	0.5698 (3)	0.074 (3)
C27	1.1232 (8)	0.4142 (4)	0.1825 (3)	0.0192 (14)
H27	1.144398	0.413231	0.141203	0.023*
C31	0.9012 (9)	0.2133 (5)	0.4603 (3)	0.0294 (17)
C32	0.4313 (9)	0.1828 (5)	0.5623 (3)	0.0294 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0177 (4)	0.0154 (4)	0.0110 (3)	0.0014 (3)	−0.0032 (4)	0.0000 (3)
S1	0.0294 (9)	0.0212 (9)	0.0211 (8)	−0.0002 (8)	−0.0055 (7)	−0.0027 (6)
Cl2	0.0317 (10)	0.0332 (9)	0.0115 (7)	0.0024 (8)	−0.0014 (7)	0.0009 (6)
S2	0.0413 (11)	0.0276 (10)	0.0195 (8)	−0.0150 (8)	−0.0009 (8)	−0.0006 (6)
Cl1	0.0641 (14)	0.0379 (10)	0.0099 (7)	−0.0228 (10)	−0.0019 (9)	−0.0015 (6)
N4	0.012 (3)	0.017 (3)	0.017 (2)	0.000 (2)	−0.003 (2)	0.0054 (19)
N1	0.028 (3)	0.013 (2)	0.013 (2)	−0.001 (2)	−0.006 (3)	0.0007 (19)
F1	0.049 (3)	0.036 (3)	0.026 (2)	0.000 (2)	−0.006 (2)	0.0077 (17)
F3	0.056 (4)	0.050 (3)	0.039 (3)	−0.031 (3)	−0.014 (2)	0.011 (2)
C18	0.023 (3)	0.016 (3)	0.013 (3)	−0.003 (3)	−0.002 (3)	0.001 (2)
N3	0.014 (3)	0.015 (3)	0.023 (3)	0.003 (2)	−0.006 (2)	−0.003 (2)
F6	0.054 (3)	0.045 (3)	0.025 (2)	−0.006 (3)	0.011 (2)	−0.0151 (19)
N5	0.017 (3)	0.012 (3)	0.016 (2)	0.001 (2)	0.000 (2)	0.0013 (18)
F4	0.064 (4)	0.027 (3)	0.043 (3)	−0.015 (2)	0.007 (3)	−0.0049 (19)

N6	0.019 (3)	0.015 (3)	0.014 (2)	−0.001 (2)	−0.002 (2)	−0.0011 (19)
F2	0.037 (3)	0.045 (3)	0.034 (2)	0.008 (2)	0.002 (2)	−0.0034 (19)
O6	0.047 (4)	0.025 (3)	0.019 (2)	0.000 (2)	−0.004 (2)	−0.0014 (19)
N2	0.020 (3)	0.016 (3)	0.012 (3)	0.005 (2)	0.000 (2)	0.0016 (19)
F5	0.049 (4)	0.076 (4)	0.061 (3)	0.022 (3)	−0.032 (3)	−0.030 (3)
O1	0.036 (3)	0.034 (3)	0.030 (3)	0.000 (3)	−0.009 (2)	0.008 (2)
C12	0.027 (4)	0.016 (3)	0.015 (3)	0.000 (3)	−0.004 (3)	0.003 (2)
C5	0.013 (3)	0.018 (3)	0.021 (3)	−0.002 (3)	−0.004 (3)	0.003 (2)
O2	0.038 (3)	0.040 (4)	0.032 (3)	−0.019 (3)	−0.005 (3)	−0.001 (2)
C20	0.020 (4)	0.009 (3)	0.020 (3)	0.000 (3)	−0.003 (3)	−0.002 (2)
C28	0.021 (4)	0.019 (3)	0.024 (3)	0.002 (3)	−0.006 (3)	−0.002 (2)
C29	0.018 (3)	0.015 (3)	0.024 (3)	0.003 (3)	−0.006 (3)	−0.002 (3)
C24	0.016 (3)	0.020 (3)	0.033 (4)	0.002 (3)	0.006 (3)	0.000 (3)
C16	0.016 (3)	0.015 (3)	0.019 (3)	−0.004 (3)	−0.008 (3)	0.001 (2)
C17	0.017 (3)	0.017 (3)	0.018 (3)	0.001 (3)	−0.007 (3)	0.000 (2)
C1	0.024 (4)	0.016 (3)	0.015 (3)	0.003 (3)	−0.002 (3)	0.001 (2)
C6	0.018 (3)	0.017 (3)	0.012 (3)	0.003 (3)	0.000 (2)	0.000 (2)
O3	0.072 (5)	0.028 (3)	0.036 (3)	0.022 (3)	0.002 (3)	−0.010 (2)
C22	0.019 (4)	0.015 (3)	0.019 (3)	0.002 (3)	0.000 (3)	0.000 (2)
C15	0.025 (4)	0.015 (3)	0.016 (3)	0.005 (3)	−0.010 (3)	−0.004 (2)
C26	0.021 (3)	0.008 (3)	0.012 (3)	−0.002 (3)	−0.003 (3)	0.003 (2)
C9	0.017 (3)	0.016 (3)	0.025 (3)	0.004 (3)	0.003 (3)	0.006 (2)
C21	0.017 (3)	0.012 (3)	0.016 (3)	−0.001 (3)	0.002 (3)	0.000 (2)
C23	0.017 (3)	0.021 (3)	0.024 (3)	0.004 (3)	0.002 (3)	0.002 (3)
C3	0.036 (4)	0.027 (3)	0.012 (3)	−0.005 (3)	−0.001 (3)	−0.001 (2)
C11	0.019 (4)	0.014 (3)	0.018 (3)	0.001 (3)	−0.004 (3)	−0.002 (2)
C19	0.022 (4)	0.017 (3)	0.014 (3)	0.000 (3)	−0.002 (3)	−0.001 (2)
C4	0.024 (4)	0.022 (4)	0.018 (3)	−0.006 (3)	0.000 (3)	0.003 (3)
C2	0.037 (5)	0.020 (4)	0.016 (3)	−0.001 (3)	−0.003 (3)	−0.002 (2)
C30	0.023 (4)	0.017 (3)	0.013 (3)	0.001 (3)	−0.006 (3)	−0.002 (2)
C10	0.019 (4)	0.015 (3)	0.017 (3)	0.005 (3)	0.000 (3)	0.003 (2)
C8	0.014 (3)	0.017 (4)	0.035 (4)	0.000 (3)	−0.002 (3)	0.002 (3)
C14	0.027 (4)	0.016 (3)	0.027 (4)	0.003 (3)	−0.014 (3)	−0.006 (2)
C13	0.024 (3)	0.012 (3)	0.018 (3)	0.000 (3)	−0.001 (3)	0.004 (2)
C25	0.029 (4)	0.016 (3)	0.017 (3)	0.001 (3)	0.003 (3)	0.001 (2)
C7	0.028 (4)	0.018 (3)	0.017 (3)	0.001 (3)	−0.007 (3)	0.003 (2)
O5	0.018 (3)	0.110 (7)	0.049 (4)	−0.002 (4)	−0.001 (3)	−0.025 (4)
O4	0.162 (9)	0.027 (3)	0.032 (3)	−0.033 (5)	0.030 (4)	0.004 (2)
C27	0.023 (4)	0.016 (3)	0.019 (3)	0.000 (3)	−0.003 (3)	0.001 (2)
C31	0.026 (4)	0.032 (4)	0.030 (4)	−0.007 (3)	−0.012 (3)	0.001 (3)
C32	0.029 (4)	0.032 (4)	0.027 (4)	−0.002 (3)	−0.002 (3)	−0.010 (3)

Geometric parameters (Å, º)

Zn1—N4	2.109 (5)	C20—C26	1.486 (9)
Zn1—N1	2.079 (5)	C20—C19	1.387 (9)
Zn1—N3	2.196 (6)	C28—H28	0.9300
Zn1—N5	2.181 (6)	C28—C29	1.375 (10)

Zn1—N6	2.163 (6)	C28—C27	1.396 (9)
Zn1—N2	2.194 (6)	C29—H29	0.9300
S1—O1	1.445 (6)	C29—C30	1.386 (10)
S1—O2	1.439 (6)	C24—H24	0.9300
S1—O3	1.449 (6)	C24—C23	1.373 (10)
S1—C31	1.827 (8)	C24—C25	1.391 (10)
Cl2—C18	1.730 (5)	C16—C17	1.378 (9)
S2—O6	1.428 (6)	C16—C21	1.483 (9)
S2—O5	1.408 (8)	C17—H17	0.9300
S2—O4	1.439 (6)	C1—C6	1.482 (9)
S2—C32	1.810 (8)	C1—C2	1.389 (9)
Cl1—C3	1.728 (6)	C6—C7	1.380 (10)
N4—C20	1.329 (9)	C22—H22	0.9300
N4—C16	1.336 (9)	C22—C21	1.381 (10)
N1—C5	1.353 (9)	C22—C23	1.398 (9)
N1—C1	1.339 (9)	C15—H15	0.9300
F1—C31	1.340 (9)	C15—C14	1.395 (10)
F3—C31	1.328 (9)	C26—C27	1.365 (10)
C18—C17	1.386 (10)	C9—H9	0.9300
C18—C19	1.390 (10)	C9—C10	1.385 (10)
N3—C15	1.351 (8)	C9—C8	1.367 (10)
N3—C11	1.351 (9)	C23—H23	0.9300
F6—C32	1.333 (9)	C3—C4	1.369 (11)
N5—C21	1.352 (8)	C3—C2	1.398 (11)
N5—C25	1.339 (9)	C19—H19	0.9300
F4—C32	1.365 (10)	C4—H4	0.9300
N6—C26	1.372 (8)	C2—H2	0.9300
N6—C30	1.333 (9)	C30—H30	0.9300
F2—C31	1.335 (9)	C10—H10	0.9300
N2—C6	1.355 (8)	C8—H8	0.9300
N2—C10	1.340 (8)	C8—C7	1.395 (10)
F5—C32	1.303 (10)	C14—H14	0.9300
C12—H12	0.9300	C14—C13	1.380 (10)
C12—C11	1.380 (10)	C13—H13	0.9300
C12—C13	1.384 (10)	C25—H25	0.9300
C5—C11	1.490 (9)	C7—H7	0.9300
C5—C4	1.378 (9)	C27—H27	0.9300

N4—Zn1—N3	106.9 (2)	C2—C1—C6	123.5 (6)
N4—Zn1—N5	74.8 (2)	N2—C6—C1	114.7 (6)
N4—Zn1—N6	75.1 (2)	N2—C6—C7	122.6 (6)
N4—Zn1—N2	102.3 (2)	C7—C6—C1	122.7 (6)
N1—Zn1—N4	177.4 (2)	C21—C22—H22	120.2
N1—Zn1—N3	75.7 (2)	C21—C22—C23	119.6 (6)
N1—Zn1—N5	105.4 (2)	C23—C22—H22	120.2
N1—Zn1—N6	104.5 (2)	N3—C15—H15	118.9
N1—Zn1—N2	75.1 (2)	N3—C15—C14	122.3 (6)
N5—Zn1—N3	93.6 (2)	C14—C15—H15	118.9

N5—Zn1—N2	94.0 (2)	N6—C26—C20	114.1 (6)
N6—Zn1—N3	95.9 (2)	C27—C26—N6	121.7 (6)
N6—Zn1—N5	149.97 (18)	C27—C26—C20	124.2 (5)
N6—Zn1—N2	91.3 (2)	C10—C9—H9	120.4
N2—Zn1—N3	150.86 (18)	C8—C9—H9	120.4
O1—S1—O3	113.6 (4)	C8—C9—C10	119.2 (6)
O1—S1—C31	102.6 (4)	N5—C21—C16	115.0 (6)
O2—S1—O1	116.1 (4)	N5—C21—C22	121.0 (6)
O2—S1—O3	115.6 (4)	C22—C21—C16	124.0 (6)
O2—S1—C31	103.2 (3)	C24—C23—C22	119.0 (7)
O3—S1—C31	103.2 (4)	C24—C23—H23	120.5
O6—S2—O4	112.7 (4)	C22—C23—H23	120.5
O6—S2—C32	103.3 (4)	C4—C3—Cl1	119.8 (6)
O5—S2—O6	115.1 (4)	C4—C3—C2	122.5 (6)
O5—S2—O4	117.6 (6)	C2—C3—Cl1	117.6 (6)
O5—S2—C32	103.5 (4)	N3—C11—C12	122.2 (6)
O4—S2—C32	101.9 (4)	N3—C11—C5	115.3 (6)
C20—N4—Zn1	119.5 (4)	C12—C11—C5	122.5 (6)
C20—N4—C16	120.9 (5)	C18—C19—H19	121.9
C16—N4—Zn1	119.5 (5)	C20—C19—C18	116.1 (6)
C5—N1—Zn1	119.4 (4)	C20—C19—H19	121.9
C1—N1—Zn1	120.1 (4)	C5—C4—H4	121.1
C1—N1—C5	120.5 (5)	C3—C4—C5	117.7 (7)
C17—C18—Cl2	118.8 (6)	C3—C4—H4	121.1
C17—C18—C19	122.4 (5)	C1—C2—C3	116.1 (7)
C19—C18—Cl2	118.8 (6)	C1—C2—H2	122.0
C15—N3—Zn1	126.4 (5)	C3—C2—H2	122.0
C15—N3—C11	118.6 (6)	N6—C30—C29	123.3 (6)
C11—N3—Zn1	114.8 (4)	N6—C30—H30	118.3
C21—N5—Zn1	116.1 (5)	C29—C30—H30	118.3
C25—N5—Zn1	124.6 (4)	N2—C10—C9	122.9 (6)
C25—N5—C21	119.3 (6)	N2—C10—H10	118.5
C26—N6—Zn1	116.3 (4)	C9—C10—H10	118.5
C30—N6—Zn1	125.8 (4)	C9—C8—H8	120.5
C30—N6—C26	117.9 (6)	C9—C8—C7	119.0 (7)
C6—N2—Zn1	115.1 (4)	C7—C8—H8	120.5
C10—N2—Zn1	126.9 (4)	C15—C14—H14	121.1
C10—N2—C6	117.6 (6)	C13—C14—C15	117.8 (6)
C11—C12—H12	120.7	C13—C14—H14	121.1
C11—C12—C13	118.5 (6)	C12—C13—H13	119.8
C13—C12—H12	120.7	C14—C13—C12	120.5 (7)
N1—C5—C11	114.3 (6)	C14—C13—H13	119.8
N1—C5—C4	121.1 (6)	N5—C25—C24	122.3 (6)
C4—C5—C11	124.4 (6)	N5—C25—H25	118.8
N4—C20—C26	114.8 (5)	C24—C25—H25	118.8
N4—C20—C19	122.1 (6)	C6—C7—C8	118.7 (6)
C19—C20—C26	123.1 (6)	C6—C7—H7	120.7
C29—C28—H28	120.6	C8—C7—H7	120.7

C29—C28—C27	118.9 (7)	C28—C27—H27	120.2
C27—C28—H28	120.6	C26—C27—C28	119.7 (6)
C28—C29—H29	120.7	C26—C27—H27	120.2
C28—C29—C30	118.6 (6)	F1—C31—S1	112.4 (6)
C30—C29—H29	120.7	F3—C31—S1	111.0 (5)
C23—C24—H24	120.6	F3—C31—F1	108.2 (6)
C23—C24—C25	118.8 (7)	F3—C31—F2	107.3 (7)
C25—C24—H24	120.6	F2—C31—S1	110.9 (5)
N4—C16—C17	121.8 (7)	F2—C31—F1	106.8 (6)
N4—C16—C21	114.5 (5)	F6—C32—S2	112.9 (6)
C17—C16—C21	123.8 (6)	F6—C32—F4	106.8 (6)
C18—C17—H17	121.6	F4—C32—S2	108.3 (5)
C16—C17—C18	116.8 (6)	F5—C32—S2	113.9 (6)
C16—C17—H17	121.6	F5—C32—F6	108.7 (6)
N1—C1—C6	114.5 (5)	F5—C32—F4	105.8 (7)
N1—C1—C2	122.0 (6)		

Zn1—N4—C20—C26	1.4 (7)	C16—N4—C20—C26	178.3 (5)
Zn1—N4—C20—C19	−177.6 (5)	C16—N4—C20—C19	−0.8 (10)
Zn1—N4—C16—C17	177.1 (5)	C17—C18—C19—C20	−1.1 (11)
Zn1—N4—C16—C21	−1.3 (8)	C17—C16—C21—N5	−175.0 (6)
Zn1—N1—C5—C11	1.6 (8)	C17—C16—C21—C22	4.1 (11)
Zn1—N1—C5—C4	177.8 (6)	C1—N1—C5—C11	179.9 (6)
Zn1—N1—C1—C6	−0.8 (9)	C1—N1—C5—C4	−3.9 (11)
Zn1—N1—C1—C2	−178.7 (6)	C1—C6—C7—C8	179.2 (7)
Zn1—N3—C15—C14	−170.6 (5)	C6—N2—C10—C9	1.7 (10)
Zn1—N3—C11—C12	170.7 (5)	C6—C1—C2—C3	−179.2 (7)
Zn1—N3—C11—C5	−7.4 (8)	O3—S1—C31—F1	54.5 (6)
Zn1—N5—C21—C16	−3.7 (7)	O3—S1—C31—F3	−66.9 (7)
Zn1—N5—C21—C22	177.1 (5)	O3—S1—C31—F2	174.0 (5)
Zn1—N5—C25—C24	−177.2 (5)	C15—N3—C11—C12	−3.7 (10)
Zn1—N6—C26—C20	−3.7 (7)	C15—N3—C11—C5	178.1 (6)
Zn1—N6—C26—C27	177.0 (5)	C15—C14—C13—C12	−2.0 (11)
Zn1—N6—C30—C29	−176.6 (5)	C26—N6—C30—C29	−0.1 (10)
Zn1—N2—C6—C1	−7.7 (7)	C26—C20—C19—C18	−177.8 (6)
Zn1—N2—C6—C7	171.2 (5)	C9—C8—C7—C6	1.5 (11)
Zn1—N2—C10—C9	−170.5 (5)	C21—N5—C25—C24	2.1 (10)
Cl2—C18—C17—C16	−179.4 (5)	C21—C16—C17—C18	178.0 (6)
Cl2—C18—C19—C20	178.9 (5)	C21—C22—C23—C24	−0.9 (10)
Cl1—C3—C4—C5	−179.5 (6)	C23—C24—C25—N5	−1.3 (10)
Cl1—C3—C2—C1	178.6 (6)	C23—C22—C21—N5	1.7 (10)
N4—C20—C26—N6	1.6 (8)	C23—C22—C21—C16	−177.4 (6)
N4—C20—C26—C27	−179.1 (6)	C11—N3—C15—C14	3.2 (10)
N4—C20—C19—C18	1.1 (10)	C11—C12—C13—C14	1.4 (11)
N4—C16—C17—C18	−0.2 (10)	C11—C5—C4—C3	179.1 (7)
N4—C16—C21—N5	3.3 (8)	C19—C18—C17—C16	0.6 (11)
N4—C16—C21—C22	−177.5 (6)	C19—C20—C26—N6	−179.4 (6)
N1—C5—C11—N3	4.1 (9)	C19—C20—C26—C27	−0.1 (10)

N1—C5—C11—C12	−174.1 (7)	C4—C5—C11—N3	−172.0 (7)
N1—C5—C4—C3	3.3 (12)	C4—C5—C11—C12	9.9 (11)
N1—C1—C6—N2	5.8 (9)	C4—C3—C2—C1	0.9 (13)
N1—C1—C6—C7	−173.1 (7)	C2—C1—C6—N2	−176.4 (7)
N1—C1—C2—C3	−1.4 (12)	C2—C1—C6—C7	4.8 (11)
N3—C15—C14—C13	−0.3 (10)	C2—C3—C4—C5	−1.8 (13)
N6—C26—C27—C28	0.3 (10)	C30—N6—C26—C20	179.4 (5)
O6—S2—C32—F6	−179.0 (6)	C30—N6—C26—C27	0.1 (9)
O6—S2—C32—F4	−60.9 (6)	C10—N2—C6—C1	179.1 (6)
O6—S2—C32—F5	56.5 (7)	C10—N2—C6—C7	−2.0 (10)
N2—C6—C7—C8	0.4 (11)	C10—C9—C8—C7	−1.7 (10)
O1—S1—C31—F1	172.7 (5)	C8—C9—C10—N2	0.1 (10)
O1—S1—C31—F3	51.3 (7)	C13—C12—C11—N3	1.5 (11)
O1—S1—C31—F2	−67.8 (5)	C13—C12—C11—C5	179.5 (7)
C5—N1—C1—C6	−179.1 (6)	C25—N5—C21—C16	176.9 (6)
C5—N1—C1—C2	2.9 (11)	C25—N5—C21—C22	−2.3 (9)
O2—S1—C31—F1	−66.3 (6)	C25—C24—C23—C22	0.7 (10)
O2—S1—C31—F3	172.3 (6)	O5—S2—C32—F6	−58.6 (7)
O2—S1—C31—F2	53.2 (6)	O5—S2—C32—F4	59.5 (6)
C20—N4—C16—C17	0.3 (10)	O5—S2—C32—F5	176.9 (7)
C20—N4—C16—C21	−178.1 (5)	O4—S2—C32—F6	63.9 (8)
C20—C26—C27—C28	−178.9 (6)	O4—S2—C32—F4	−178.0 (6)
C28—C29—C30—N6	−0.3 (10)	O4—S2—C32—F5	−60.6 (8)
C29—C28—C27—C26	−0.7 (10)	C27—C28—C29—C30	0.7 (10)