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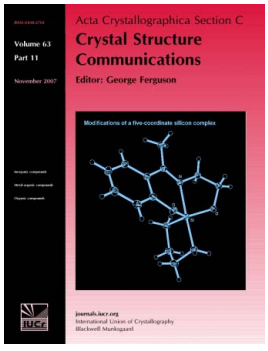

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Monodentate and bridging behaviour of the sulfur-containing ligand 4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4″-terpyridine in two discrete zinc(II) complexes with acetylacetonate

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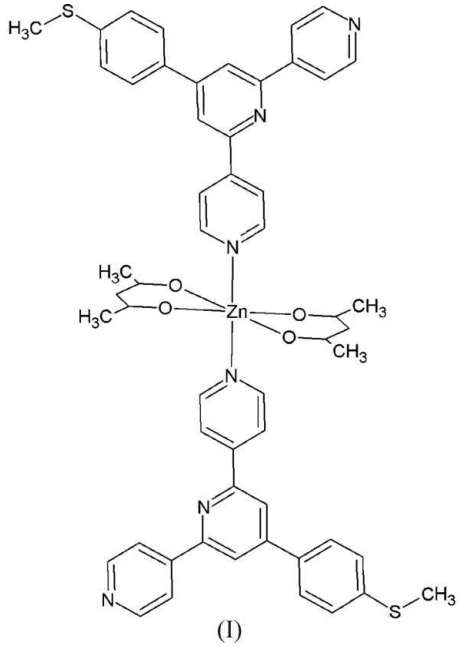
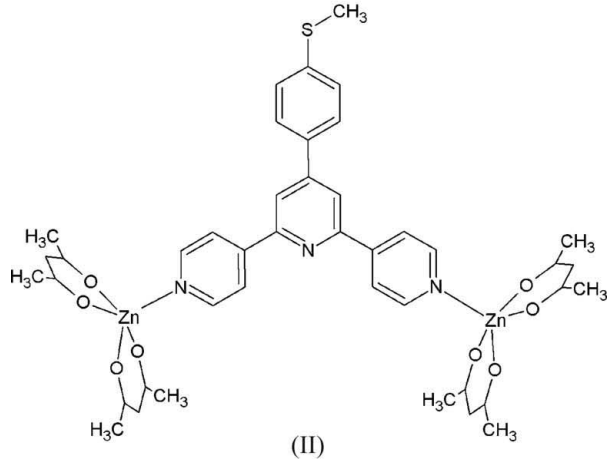
The Zn complexes bis(acetylacetonato-κ^2O,O')bis{4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4″-terpyridine-κN^1}zinc(II), $[Zn(C_5H_7O_2)_2(C_{22}H_{17}N_3S)_2]$, (I), and {$\mu$-4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4″-terpyridine-$\kappa^2N^1:N^{1''}$}bis[bis(acetylacetonato-κ^2O,O')zinc(II)], $[Zn_2(C_5H_7O_2)_4(C_{22}H_{17}N_3S)]$, (II), are discrete entities with different nuclearities. Compound (I) consists of two centrosymmetrically related monodentate 4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4″-terpyridine (*L*1) ligands binding to one Zn^{II} atom sitting on an inversion centre and two centrosymmetrically related chelating acetylacetonate (acac) groups which bind *via* carbonyl O-atom donors, giving an N_2O_4 octahedral environment for Zn^{II}. Compound (II), however, consists of a bis-monodentate *L*1 ligand bridging two Zn^{II} atoms from two different $Zn(acac)_2$ fragments. Intra- and intermolecular interactions are weak, mainly of the C—H$\cdots\pi$ and π–π types, mediating similar layered structures. In contrast to related structures in the literature, sulfur-mediated nonbonding interactions in (II) do not seem to have any significant influence on the supramolecular structure.

Comment

The study of the coordination chemistry of 2,2′:6′,2″-terpyridine and its derivatives has been directed more commonly to their behaviour as chelating ligands, *i.e.* in systems in which they present a convergent disposition of their pyridine N-donor atoms to link to metal centres (Constable, 2007; Eryazici *et al.*, 2008). In contrast, 4′-aryl-substituted terpyridine-based ligands with divergent coordinating geometry, able to



(I)



(II)

bridge at least two metal centres, have been scarce and structural reports on their complexes are relatively recent. The pioneering work of Cave & Raston (2002) was based on the 4′-(4-octyloxyphenyl)-4,2′:6′,4″-terpyridine (*L*2) ligand, which in its reaction with $ZnCl_2$ produced the helical coordination polymer $[ZnCl_2(L2)]_n$, in which the ligand bridges two Zn^{II} centres *via* only its terminal pyridine N atoms. The remaining reports using this type of functionalized 4,2′:6′,4″-terpyridine are very recent, from 2008 onward (Li *et al.*, 2008; Constable, Zhang, Coronado *et al.*, 2010; Constable, Zhang, Housecroft *et al.*, 2010; Constable *et al.*, 2011; Li *et al.* 2011). A common feature in all of these compounds is the bridging behaviour of the terpyridine-based derivatives, which gives rise to polymeric structures ranging from one- to three-dimensional, with the sole exception of a discrete molecular metallohexacycle obtained from the reaction of $ZnCl_2$ and 4′-(4-ethynylphenyl)-4,2′:6′,4″-terpyridine (Constable *et al.*, 2011).

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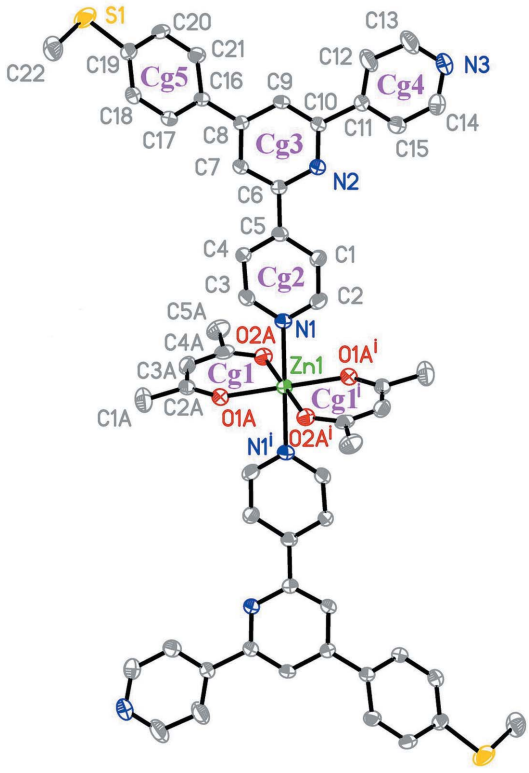

Figure 1
The molecular structure of (I), showing the atom and ring labelling, and drawn with 40% probability displacement ellipsoids. H atoms are not shown. [Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$.]

We report herein two Zn^{II} complexes containing a ligand of this type, namely 4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4″-terpyridine (*L*1), along with the acetylacetonate (acac) anion. Both complexes have unusual discrete molecular character, *viz*. $[Zn(acac)_2(L1)_2]$, (I), is mononuclear and $[Zn_2(acac)_4(\mu\text{-}L1)]$, (II), is dinuclear. To our knowledge, (I) is the first reported complex with monodentate coordination for a functionalized 4′-aryl-substituted 4,2′:6′,4″-terpyridine ligand. This is in contrast to the three known complexes involving the *L*1 ligand, which are polymers, one (one-dimensional) obtained by reacting *L*1 with $Zn(NO_3)_2$ (Constable, Zhang, Coronado *et al.*, 2010) and the other two (one- and two-dimensional) with $Cd(NO_3)_2$ (Constable, Zhang, Housecroft *et al.*, 2010).

Compound (I) (Fig. 1) consists of two centrosymmetrically related monodentate *L*1 ligands bound to atom Zn1, which sits on an inversion centre, and two (also centrosymmetrically related) chelating acac groups which bind laterally *via* carbonyl O-atom donors to provide a nearly regular N_2O_4 octahedral environment [Zn1—O2*A* = 2.0448 (13) Å, Zn1—O1*A* = 2.0667 (12) Å and Zn1—N1 = 2.2607 (14) Å; *cis* angles are in the range 90±2.05 (5)°].

Sharing with (I) its novel discrete character, but differing from it in being a binuclear structure, compound (II) consists of a bis-monodentate *L*1 ligand bridging two Zn^{II} atoms (Zn1 and Zn2) from two different $Zn(acac)_2$ fragments (Fig. 2). Each Zn^{II} centre has an NO_4 coordination sphere; four sites are provided by two different acac groups [Zn—O = 1.9663 (16)–2.0894 (15) Å] coordinated in the usual chelating mode through their carbonyl O-atom donors, with the planar rings forming dihedral angles of 52.00 (9) and 52.60 (10)° for Zn1 and Zn2, respectively. This contrasts markedly with the rigorous coplanarity of the acac ligands in (I), related by the centre of symmetry. The fifth site of the coordination polyhedron in (II) is occupied by a pyridine N atom from the *L*1 ligand [Zn1—N1 = 2.0793 (16) Å and Zn2—N3 = 2.0538 (16) Å]. The geometry around each Zn^{II} atom is trigonal bipyramidal, with O2*A*—Zn1—O2*B* and O1*C*—Zn2—O1*D* angles of 175.17 (7) and 172.91 (7)°, respectively, and apical and equatorial angles in the ranges 90±4.96 (7) and 90±3.89 (7)°, respectively.

In both structures, the *L*1 ligand deviates from planarity, involving rotation of neighbouring six-membered rings. In (I), the N2/C6–C10 and N3/C11–C16 pyridine rings are almost coplanar [dihedral angle = 1.92 (6)°], while the N1/C1–C5 pyridine ring and the methylsulfanyl-substituted benzene ring (C16–C21) deviate significantly from this disposition [dihedral angle = 54.95 (9)°]. Compound (II), instead, presents all three lateral rings, *viz*. pyridine N1/C1–C5, pyridine N2/C6–C10 and benzene C16–C21 (Fig. 2), rotated with respect to the central N3/C11–C15 pyridine ring by dihedral angles of 18.20 (12), 12.91 (11) and 7.37 (11)°, respectively.

Nonbonding interactions in (I) and (II) (C—H$\cdots\pi$ and π–π) are very weak and could probably be assigned the character of London forces and/or dipole-induced dipole interactions. In spite of their weakness, however, they play an esential role in crystal stability, which will be discussed below.

In (I), two intramolecular C—H$\cdots\pi$ contacts (Table 1, first and second entries, and Fig. 3*a*) serve to limit the free rotation of the N1/C1–C5 pyridine ring around the Zn1—N1 bond. The N1/C1–C5 pyridine ring and its symmetry equivalent partner at $(-x+\frac{1}{2}, -y+\frac{1}{2}, -z)$ are rigorously parallel by symmetry. The remaining C—H$\cdots\pi$ (Table 1, third entry and Fig. 3*b*) and

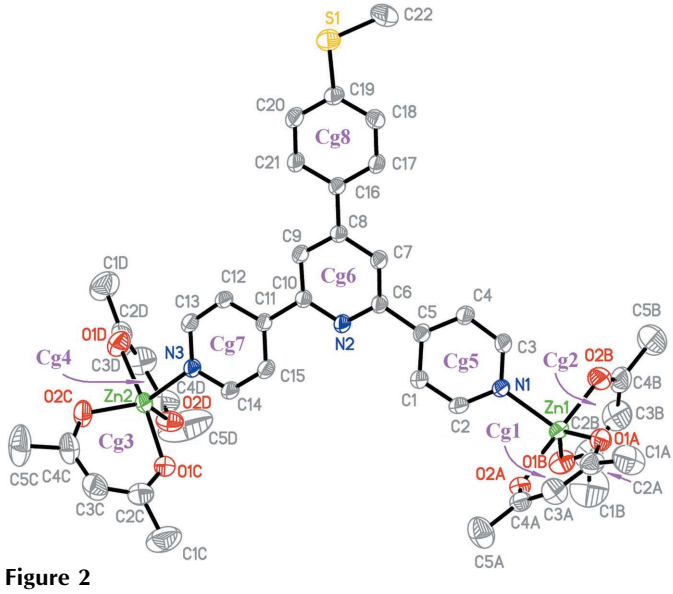

Figure 2
The molecular structure of (II), showing the atom and ring labelling, and drawn with 40% probability displacement ellipsoids. H atoms are not shown.

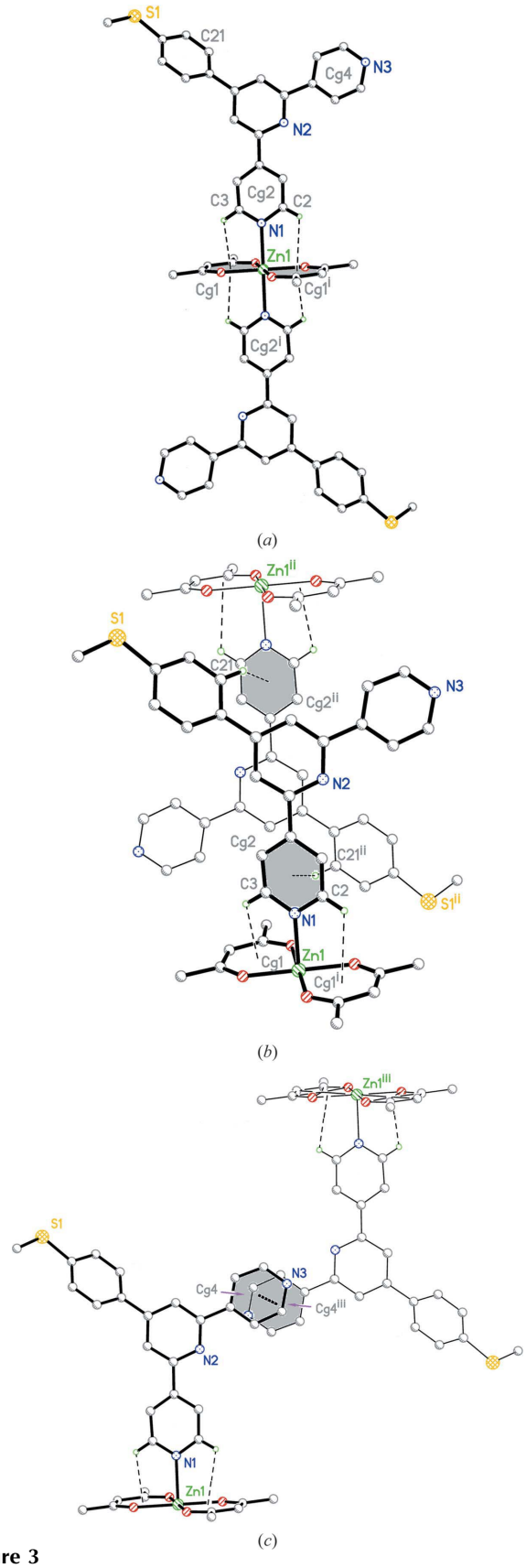

Figure 3
The different noncovalent interaction types in (I). For details in (*a*), see Table 1 (first and second entries), in (*b*), see Table 1 (third entry), and in (*c*), see Table 2 (unique entry). [Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $-x, -y+1, -z$; (iii) $-x, -y+2, -z$.]

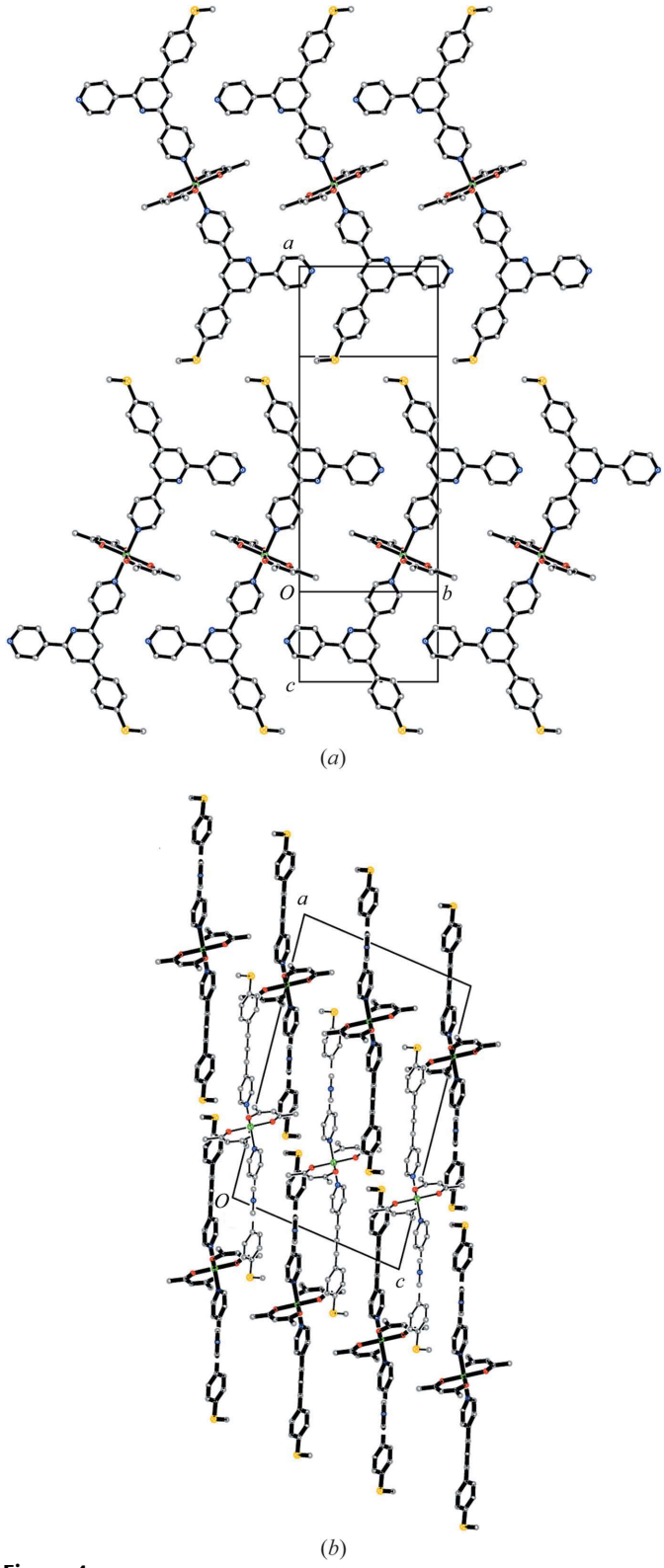

Figure 4
The packing in (I), (*a*) showing two parallel strands extending in the *b* direction and (*b*) a view perpendicular to that shown in (*a*), showing the stacking of consecutive (102) planes (alternating light and dark lines).

π–π (Table 2 and Fig. 3*c*) contacts complete the intermolecular interaction scheme. The final result is the formation of planar arrays of $Zn(L1)_2$ groups parallel to (102) (Fig. 4*a*) formed by

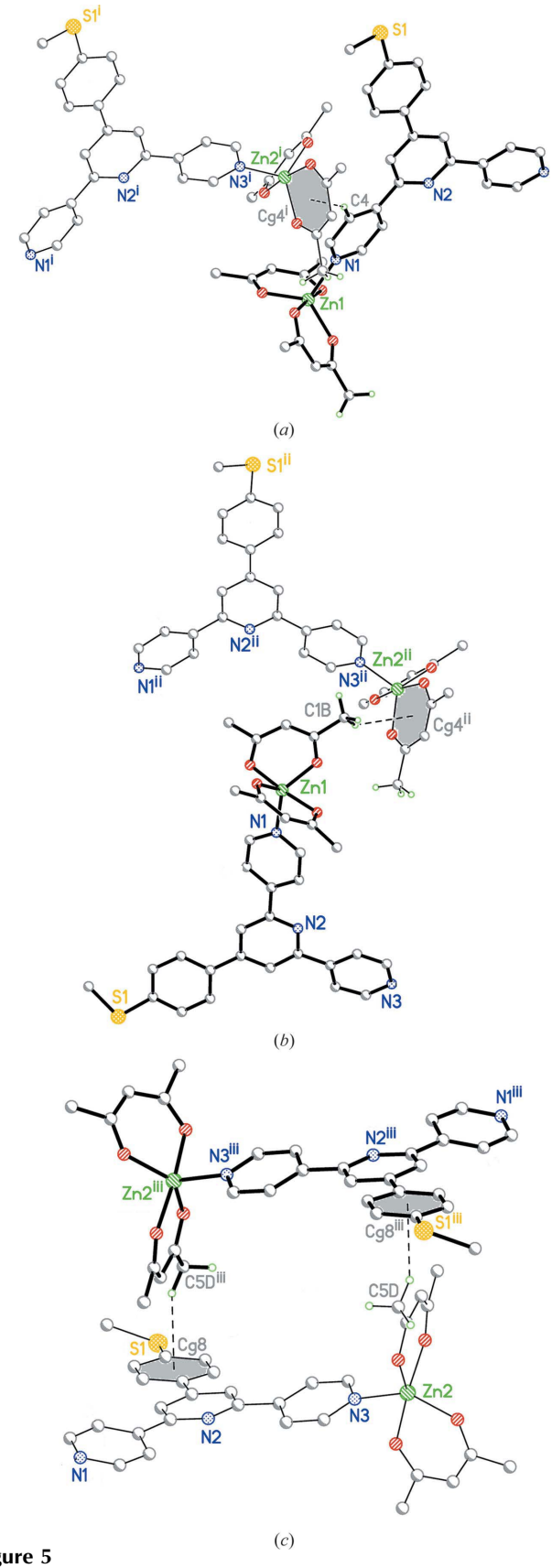

Figure 5
The different noncovalent interactions in (II). For details in (*a*), see Table 3 (first entry), in (*b*), see Table 3 (second entry), and in (*c*), see Table 3 (third entry). [Symmetry codes: (i) $x, y-1, z$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y+1, -z$.]

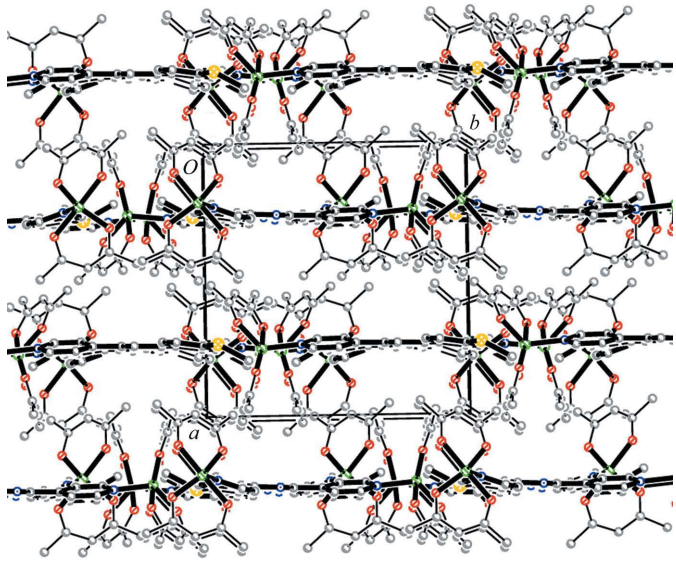

Figure 6
The packing in (II), showing the planar arrays of $Zn_2(L1)$ fragments (bold lines) and the protruding acac anions (lighter lines).

parallel molecules extending along *b*, with the acac anions roughly perpendicular to the principal plane of the array. These planes have the peculiarity of not presenting any direct 'in-plane' interaction, but rather of being connected only through indirect 'interplanar' contacts mediated by molecules in neighbouring planes, in the staggered pattern shown in Fig. 4*b*.

In (II), the most significant intermolecular interactions are three weak C—H$\cdots\pi$ contacts (Table 3 and Fig. 5). The overall arrangement is again a pattern of planar arrays [formed by the $Zn_2(L1)$ groups] parallel to (100) (Fig. 6). As in (I), there are no direct 'in-plane' interactions present, cohesion being achieved through indirect zigzag contacts between molecules in neighbouring planes. What appear to be voids in Fig. 6 are in fact visual artifacts – the locus of unrepresented H atoms – as can be seen in a space-filling drawing (see *Supplementary materials*). *PLATON* (Spek, 2009) was used to confirm the absence of voids.

Compound (II) is similar to a recently published dinuclear analogue, *viz*. $[Zn_2(acac)_4(\mu\text{-}L3)]$ {*L*3 is 4′-[4-(methylsulfanyl)-phenyl]-3,2′:6′,3″-terpyridine; Granifo *et al.*, 2011}, (III), displaying a similar dinuclear configuration despite an important difference in that the pyridine N-donor atoms have a convergent disposition in *L*3. The point to be highlighted, however, is the significant influence that sulfur-mediated nonbonded interactions have in (III), while their influence appears almost non-existent in the structures of (I) and (II) reported here.

Experimental

The ligand *L*1 was synthesized as reported previously (Constable, Zhang, Coronado *et al.*, 2010). To a hot solution (using an oil bath at 337–341 K) of *L*1 (8.6 mg, 0.024 mmol) in MeCN (7 ml) contained in a closed volumetric flask (25 ml) was added an excess of $Zn(acac)_2$ (63.8 mg, 0.242 mmol). The resulting solution was heated in the oil

bath for 10 h. Block-like colourless crystals were obtained after removal of the hot solvent and washing with MeCN (3 × 5 ml) and diethyl ether (2 × 4 ml) (yield: 12 mg, 56.6%). Analysis calculated for $C_{42}H_{45}N_3O_8SZn_2$: C 57.15, H 5.14, N 4.76, S 3.63%; found: C 57.32, H 5.26, N 4.63, S 3.68%. Careful examination of the solid product identified two slightly different kinds of crystals; the major fraction corresponding to compound (II) and a second strictly minor fraction corresponding to compound (I). The latter appear recurrently, though in trace amounts, during the synthesis described above, irrespective of reaction conditions.

Compound (I)

Crystal data

$[Zn(C_5H_7O_2)_2(C_{22}H_{17}N_3S)_2]$
M_r = 974.47
Monoclinic, $C2/c$
a = 26.6479 (7) Å
b = 10.7706 (3) Å
c = 16.4983 (5) Å
β = 99.187 (3)°
V = 4674.5 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 295 K
0.26 × 0.20 × 0.12 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.83, T_{max} = 0.92
9886 measured reflections
5288 independent reflections
3620 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.099
S = 1.00
5288 reflections
307 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Compound (II)

Crystal data

$[Zn_2(C_5H_7O_2)_4(C_{22}H_{17}N_3S)]$
M_r = 882.61
Monoclinic, $P2_1/c$
a = 14.1522 (3) Å
b = 13.4408 (3) Å
c = 23.3887 (5) Å
β = 101.342 (2)°
V = 4362.05 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.20 mm^{-1}
T = 295 K
0.32 × 0.16 × 0.14 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.80, T_{max} = 0.85
27845 measured reflections
9862 independent reflections
6308 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.087
S = 0.98
9862 reflections
505 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

H atoms bonded to C atoms were found in a difference Fourier map, but were further idealized and refined as riding atoms [aromatic C—H = 0.93 Å, with U_{iso}(H) = 1.2U_{eq}(C); methyl C—H = 0.97 Å, with U_{iso}(H) = 1.5U_{eq}(C)].

Table 1
C—H···π contacts (Å, °) in (I).

*Cg*1 is the centroid of the Zn1/O1*A*/C2*A*/C3*A*/C4*A*/O2*A* chelate ring and *Cg*2 is the centroid of the N1/C1–C5 pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···*Cg*1^{i}	0.93	2.66	3.187 (2)	116
C3—H3···*Cg*1	0.93	2.43	3.001 (2)	120
C21—H21···*Cg*2^{ii}	0.93	2.87	3.560 (2)	132

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $-x, -y+1, -z$.

Table 2
π–π contacts (Å, °) in (I).

*Cg*4 is the centroid of the N3/C11–C15 pyridine ring.

Group 1/Group 2	ccd (Å)	da (°)	ipd (Å)	sa (°)
*Cg*4···*Cg*4^{iii}	3.945 (2)	0	3.7822 (14)	16.48

Symmetry code: (iii) $-x, -y+1, -z$. Notes: ccd is the centre-to-centre distance (distance between ring centroids); da is the dihedral angle between rings; ipd is the interplanar distance (distance from one plane to the neighbouring centroid), sa is the slippage angle (angle subtended by the intercentroid vector to the plane normal). For details, see Janiak (2000).

Table 3
C—H···π contacts (Å, °) in (II).

*Cg*4 is the centroid of the Zn2/O1*D*/C2*D*/C3*D*/C4*D*/O2*D* chelate ring and *Cg*8 is the centroid of the C16–C21 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···*Cg*4^{i}	0.93	2.85	3.712 (3)	155
C1*B*—H1*BC*···*Cg*4^{ii}	0.96	2.78	3.563 (4)	140
C5*D*—H5*DB*···*Cg*8^{iii}	0.96	2.67	3.549 (5)	152

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y+1, -z$.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3281). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2012). C**68**, m269–m274 [doi:10.1107/S010827011203483X]

Monodentate and bridging behaviour of the sulfur-containing ligand 4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4′′-terpyridine in two discrete zinc(II) complexes with acetylacetonate

Juan Granifo, Rubén Gaviño, Eleonora Freire and Ricardo Baggio

(I) bis(acetylacetonato-κ^2O,O')bis{4′-[4-(methylsulfanyl)phenyl]- 4,2′:6′,4′′-terpyridine-κN^1}zinc(II)

Crystal data

$[Zn(C_5H_7O_2)_2(C_{22}H_{17}N_3S)_2]$
$M_r = 974.47$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 26.6479$ (7) Å
$b = 10.7706$ (3) Å
$c = 16.4983$ (5) Å
$\beta = 99.187$ (3)°
$V = 4674.5$ (2) Å^3
$Z = 4$
$F(000) = 2032$
$D_x = 1.385$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9886 reflections
$\theta = 3.8$–28.9°
$\mu = 0.67$ mm^{-1}
$T = 295$ K
Block, colourless
0.26 × 0.20 × 0.12 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans, thick slices
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{min} = 0.83$, $T_{max} = 0.92$
9886 measured reflections
5288 independent reflections
3620 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 28.9°$, $\theta_{min} = 3.8°$
$h = -20\rightarrow35$
$k = -14\rightarrow13$
$l = -22\rightarrow18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.00$
5288 reflections
307 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.2500	0.2500	0.0000	0.03104 (10)
S1	−0.22969 (2)	0.25503 (6)	0.20448 (5)	0.0654 (2)
N1	0.18461 (6)	0.33489 (14)	0.05266 (9)	0.0338 (4)
N2	0.05064 (6)	0.63117 (14)	0.11045 (10)	0.0349 (4)
N3	0.01939 (8)	1.08964 (18)	0.11689 (15)	0.0706 (6)
C1	0.14304 (7)	0.50523 (19)	0.10663 (13)	0.0438 (5)
H1	0.1457	0.5843	0.1295	0.053*
C2	0.18550 (7)	0.4475 (2)	0.08669 (13)	0.0446 (5)
H2	0.2164	0.4891	0.0975	0.054*
C3	0.13966 (8)	0.27750 (17)	0.04058 (13)	0.0367 (5)
H3	0.1381	0.1983	0.0179	0.044*
C4	0.09553 (7)	0.32755 (17)	0.05944 (11)	0.0339 (4)
H4	0.0654	0.2824	0.0500	0.041*
C5	0.09622 (7)	0.44535 (16)	0.09254 (11)	0.0312 (4)
C6	0.04921 (7)	0.50658 (17)	0.11032 (11)	0.0308 (4)
C7	0.00698 (7)	0.43913 (17)	0.12383 (11)	0.0332 (4)
H7	0.0076	0.3528	0.1224	0.040*
C8	−0.03643 (6)	0.50110 (16)	0.13962 (11)	0.0307 (4)
C9	−0.03453 (7)	0.63055 (17)	0.13924 (12)	0.0362 (4)
H9	−0.0625	0.6761	0.1493	0.043*
C10	0.00861 (7)	0.69151 (18)	0.12412 (12)	0.0339 (4)
C11	0.01171 (7)	0.82965 (17)	0.12092 (12)	0.0375 (5)
C12	−0.02682 (12)	0.9052 (2)	0.1351 (3)	0.1119 (15)
H12	−0.0568	0.8709	0.1474	0.134*
C13	−0.02166 (13)	1.0334 (3)	0.1314 (3)	0.1182 (15)
H13	−0.0492	1.0822	0.1398	0.142*
C14	0.05544 (10)	1.0158 (2)	0.10173 (18)	0.0715 (8)
H14	0.0850	1.0523	0.0896	0.086*
C15	0.05338 (9)	0.8878 (2)	0.10226 (16)	0.0563 (6)
H15	0.0806	0.8416	0.0898	0.068*
C16	−0.08256 (7)	0.43551 (16)	0.15548 (11)	0.0310 (4)
C17	−0.08026 (7)	0.32421 (17)	0.19845 (11)	0.0336 (4)
H17	−0.0488	0.2879	0.2163	0.040*
C18	−0.12371 (7)	0.26613 (16)	0.21532 (12)	0.0363 (4)
H18	−0.1211	0.1922	0.2448	0.044*
C19	−0.17111 (7)	0.31761 (18)	0.18844 (12)	0.0358 (4)
C20	−0.17422 (7)	0.42817 (19)	0.14415 (12)	0.0410 (5)
H20	−0.2058	0.4633	0.1250	0.049*
C21	−0.13062 (7)	0.48542 (18)	0.12868 (12)	0.0382 (5)
H21	−0.1333	0.5596	0.0995	0.046*

C22	−0.21480 (9)	0.1278 (2)	0.27307 (14)	0.0592 (7)
H22A	−0.1993	0.0627	0.2459	0.089*
H22B	−0.2454	0.0973	0.2899	0.089*
H22C	−0.1916	0.1547	0.3204	0.089*
O1A	0.22421 (5)	0.07433 (12)	0.02249 (8)	0.0365 (3)
O2A	0.20393 (5)	0.24688 (12)	−0.11169 (8)	0.0370 (3)
C1A	0.18303 (10)	−0.1193 (2)	0.00482 (15)	0.0593 (6)
H1AA	0.2130	−0.1697	0.0077	0.089*
H1AB	0.1557	−0.1568	−0.0320	0.089*
H1AC	0.1737	−0.1124	0.0585	0.089*
C2A	0.19366 (7)	0.00850 (17)	−0.02625 (12)	0.0358 (4)
C3A	0.16957 (7)	0.04515 (19)	−0.10402 (12)	0.0397 (5)
H3A	0.1471	−0.0111	−0.1331	0.048*
C4A	0.17611 (7)	0.15876 (19)	−0.14219 (11)	0.0370 (5)
C5A	0.14763 (8)	0.1800 (2)	−0.22755 (13)	0.0527 (6)
H5AA	0.1342	0.2629	−0.2316	0.079*
H5AB	0.1202	0.1216	−0.2387	0.079*
H5AC	0.1703	0.1692	−0.2667	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02582 (16)	0.02878 (16)	0.03907 (18)	0.00138 (14)	0.00684 (12)	−0.00130 (14)
S1	0.0357 (3)	0.0678 (4)	0.0976 (5)	−0.0049 (3)	0.0255 (3)	0.0256 (4)
N1	0.0287 (8)	0.0311 (8)	0.0429 (9)	0.0038 (7)	0.0100 (7)	−0.0008 (7)
N2	0.0294 (8)	0.0283 (8)	0.0481 (9)	0.0011 (7)	0.0099 (7)	−0.0034 (7)
N3	0.0581 (13)	0.0297 (10)	0.126 (2)	−0.0050 (10)	0.0202 (13)	−0.0022 (11)
C1	0.0313 (10)	0.0363 (11)	0.0657 (14)	−0.0031 (9)	0.0139 (10)	−0.0183 (10)
C2	0.0264 (10)	0.0452 (12)	0.0634 (14)	−0.0027 (9)	0.0107 (9)	−0.0156 (10)
C3	0.0364 (11)	0.0272 (10)	0.0492 (12)	0.0019 (8)	0.0149 (9)	−0.0014 (8)
C4	0.0278 (9)	0.0281 (10)	0.0480 (11)	−0.0005 (8)	0.0125 (8)	0.0010 (8)
C5	0.0277 (9)	0.0301 (10)	0.0373 (10)	0.0034 (8)	0.0095 (8)	0.0013 (8)
C6	0.0264 (9)	0.0295 (10)	0.0370 (10)	0.0017 (8)	0.0065 (8)	−0.0013 (8)
C7	0.0300 (10)	0.0251 (9)	0.0457 (11)	0.0041 (8)	0.0101 (8)	−0.0008 (8)
C8	0.0247 (9)	0.0291 (10)	0.0385 (10)	0.0010 (8)	0.0058 (8)	0.0010 (8)
C9	0.0264 (9)	0.0289 (10)	0.0550 (12)	0.0061 (8)	0.0117 (9)	−0.0012 (9)
C10	0.0296 (10)	0.0264 (9)	0.0467 (11)	0.0026 (9)	0.0089 (9)	−0.0014 (9)
C11	0.0321 (10)	0.0263 (10)	0.0550 (12)	−0.0002 (9)	0.0092 (9)	−0.0016 (9)
C12	0.079 (2)	0.0289 (13)	0.251 (4)	−0.0045 (14)	0.097 (3)	−0.013 (2)
C13	0.087 (2)	0.0301 (13)	0.257 (5)	−0.0003 (15)	0.088 (3)	−0.017 (2)
C14	0.0485 (14)	0.0383 (13)	0.130 (2)	−0.0086 (12)	0.0225 (15)	0.0136 (15)
C15	0.0395 (12)	0.0360 (12)	0.0974 (19)	0.0035 (10)	0.0230 (13)	0.0088 (12)
C16	0.0261 (9)	0.0279 (9)	0.0404 (10)	0.0025 (8)	0.0092 (8)	−0.0028 (8)
C17	0.0282 (9)	0.0291 (10)	0.0431 (11)	0.0039 (8)	0.0046 (8)	0.0000 (8)
C18	0.0381 (11)	0.0269 (10)	0.0441 (11)	−0.0004 (9)	0.0074 (9)	0.0037 (8)
C19	0.0301 (10)	0.0354 (11)	0.0443 (11)	−0.0022 (9)	0.0127 (8)	−0.0015 (9)
C20	0.0241 (9)	0.0400 (11)	0.0597 (13)	0.0045 (9)	0.0097 (9)	0.0056 (10)
C21	0.0315 (10)	0.0339 (10)	0.0504 (12)	0.0047 (9)	0.0102 (9)	0.0106 (9)
C22	0.0713 (16)	0.0497 (13)	0.0650 (15)	−0.0122 (13)	0.0367 (13)	0.0003 (12)
O1A	0.0344 (7)	0.0313 (7)	0.0438 (7)	0.0009 (6)	0.0061 (6)	−0.0001 (6)

O2A	0.0331 (7)	0.0374 (7)	0.0400 (7)	0.0010 (7)	0.0048 (6)	0.0012 (6)
C1A	0.0687 (16)	0.0401 (12)	0.0701 (16)	−0.0137 (12)	0.0140 (13)	−0.0011 (12)
C2A	0.0309 (10)	0.0303 (10)	0.0502 (12)	0.0009 (9)	0.0185 (9)	−0.0071 (9)
C3A	0.0319 (10)	0.0418 (11)	0.0459 (11)	−0.0060 (9)	0.0079 (9)	−0.0102 (10)
C4A	0.0255 (9)	0.0482 (12)	0.0390 (11)	0.0061 (9)	0.0105 (8)	−0.0070 (10)
C5A	0.0404 (12)	0.0725 (17)	0.0439 (12)	0.0010 (12)	0.0023 (10)	0.0009 (12)

Geometric parameters (Å, º)

Zn1—O2A^{i}	2.0448 (13)	C12—C13	1.390 (3)
Zn1—O2A	2.0448 (13)	C12—H12	0.9300
Zn1—O1A^{i}	2.0667 (12)	C13—H13	0.9300
Zn1—O1A	2.0667 (12)	C14—C15	1.380 (3)
Zn1—N1^{i}	2.2607 (14)	C14—H14	0.9300
Zn1—N1	2.2607 (14)	C15—H15	0.9300
S1—C19	1.7586 (18)	C16—C17	1.389 (2)
S1—C22	1.781 (2)	C16—C21	1.394 (2)
N1—C3	1.334 (2)	C17—C18	1.383 (2)
N1—C2	1.335 (2)	C17—H17	0.9300
N2—C6	1.342 (2)	C18—C19	1.386 (3)
N2—C10	1.345 (2)	C18—H18	0.9300
N3—C14	1.302 (3)	C19—C20	1.393 (3)
N3—C13	1.306 (3)	C20—C21	1.375 (2)
C1—C2	1.376 (2)	C20—H20	0.9300
C1—C5	1.391 (2)	C21—H21	0.9300
C1—H1	0.9300	C22—H22A	0.9600
C2—H2	0.9300	C22—H22B	0.9600
C3—C4	1.374 (2)	C22—H22C	0.9600
C3—H3	0.9300	O1A—C2A	1.266 (2)
C4—C5	1.380 (2)	O2A—C4A	1.259 (2)
C4—H4	0.9300	C1A—C2A	1.511 (3)
C5—C6	1.486 (2)	C1A—H1AA	0.9600
C6—C7	1.387 (2)	C1A—H1AB	0.9600
C7—C8	1.396 (2)	C1A—H1AC	0.9600
C7—H7	0.9300	C2A—C3A	1.397 (3)
C8—C9	1.395 (2)	C3A—C4A	1.400 (3)
C8—C16	1.477 (2)	C3A—H3A	0.9300
C9—C10	1.381 (2)	C4A—C5A	1.507 (3)
C9—H9	0.9300	C5A—H5AA	0.9600
C10—C11	1.492 (3)	C5A—H5AB	0.9600
C11—C15	1.353 (3)	C5A—H5AC	0.9600
C11—C12	1.359 (3)		

O2A^{i}—Zn1—O2A	180.00 (9)	N3—C13—C12	124.1 (3)
O2A^{i}—Zn1—O1A^{i}	88.72 (5)	N3—C13—H13	117.9
O2A—Zn1—O1A^{i}	91.28 (5)	C12—C13—H13	117.9
O2A^{i}—Zn1—O1A	91.28 (5)	N3—C14—C15	125.3 (2)
O2A—Zn1—O1A	88.72 (5)	N3—C14—H14	117.4
O1A^{i}—Zn1—O1A	180.00 (8)	C15—C14—H14	117.4
O2A^{i}—Zn1—N1^{i}	87.95 (5)	C11—C15—C14	119.9 (2)

O2A—Zn1—N1^{i}	92.05 (5)	C11—C15—H15	120.0
O1A^{i}—Zn1—N1^{i}	90.14 (5)	C14—C15—H15	120.0
O1A—Zn1—N1^{i}	89.86 (5)	C17—C16—C21	117.25 (17)
O2A^{i}—Zn1—N1	92.05 (5)	C17—C16—C8	122.22 (16)
O2A—Zn1—N1	87.95 (5)	C21—C16—C8	120.52 (16)
O1A^{i}—Zn1—N1	89.86 (5)	C18—C17—C16	121.54 (17)
O1A—Zn1—N1	90.14 (5)	C18—C17—H17	119.2
N1^{i}—Zn1—N1	180.00 (7)	C16—C17—H17	119.2
C19—S1—C22	106.11 (11)	C17—C18—C19	120.28 (17)
C3—N1—C2	116.04 (16)	C17—C18—H18	119.9
C3—N1—Zn1	118.94 (12)	C19—C18—H18	119.9
C2—N1—Zn1	124.46 (13)	C18—C19—C20	118.99 (17)
C6—N2—C10	117.34 (16)	C18—C19—S1	125.74 (15)
C14—N3—C13	114.7 (2)	C20—C19—S1	115.27 (15)
C2—C1—C5	120.03 (18)	C21—C20—C19	119.99 (18)
C2—C1—H1	120.0	C21—C20—H20	120.0
C5—C1—H1	120.0	C19—C20—H20	120.0
N1—C2—C1	123.42 (18)	C20—C21—C16	121.93 (17)
N1—C2—H2	118.3	C20—C21—H21	119.0
C1—C2—H2	118.3	C16—C21—H21	119.0
N1—C3—C4	124.40 (17)	S1—C22—H22A	109.5
N1—C3—H3	117.8	S1—C22—H22B	109.5
C4—C3—H3	117.8	H22A—C22—H22B	109.5
C3—C4—C5	119.50 (17)	S1—C22—H22C	109.5
C3—C4—H4	120.2	H22A—C22—H22C	109.5
C5—C4—H4	120.2	H22B—C22—H22C	109.5
C4—C5—C1	116.57 (16)	C2A—O1A—Zn1	126.67 (12)
C4—C5—C6	121.86 (16)	C4A—O2A—Zn1	127.10 (12)
C1—C5—C6	121.55 (16)	C2A—C1A—H1AA	109.5
N2—C6—C7	123.14 (17)	C2A—C1A—H1AB	109.5
N2—C6—C5	114.80 (16)	H1AA—C1A—H1AB	109.5
C7—C6—C5	122.04 (16)	C2A—C1A—H1AC	109.5
C6—C7—C8	119.83 (16)	H1AA—C1A—H1AC	109.5
C6—C7—H7	120.1	H1AB—C1A—H1AC	109.5
C8—C7—H7	120.1	O1A—C2A—C3A	125.43 (17)
C9—C8—C7	116.45 (16)	O1A—C2A—C1A	115.52 (19)
C9—C8—C16	120.70 (16)	C3A—C2A—C1A	119.04 (19)
C7—C8—C16	122.85 (16)	C2A—C3A—C4A	126.04 (19)
C10—C9—C8	120.52 (17)	C2A—C3A—H3A	117.0
C10—C9—H9	119.7	C4A—C3A—H3A	117.0
C8—C9—H9	119.7	O2A—C4A—C3A	125.94 (19)
N2—C10—C9	122.70 (17)	O2A—C4A—C5A	115.83 (19)
N2—C10—C11	115.07 (16)	C3A—C4A—C5A	118.24 (19)
C9—C10—C11	122.22 (16)	C4A—C5A—H5AA	109.5
C15—C11—C12	115.62 (19)	C4A—C5A—H5AB	109.5
C15—C11—C10	121.49 (17)	H5AA—C5A—H5AB	109.5
C12—C11—C10	122.89 (18)	C4A—C5A—H5AC	109.5
C11—C12—C13	120.3 (2)	H5AA—C5A—H5AC	109.5

C11—C12—H12	119.9	H5AB—C5A—H5AC	109.5
C13—C12—H12	119.9		

Symmetry code: (i) −*x*+1/2, −*y*+1/2, −*z*.

Hydrogen-bond geometry (Å, º)

Table 1. C—H···π contacts in (I) (Å, °).

*Cg*1 is the centroid of the Zn1/O1A/C2A/C3A/C4A/O2A chelate ring and *Cg*2 is the centroid of the N1/C1–C5 pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···*Cg*1^{i}	0.93	2.66	3.187 (2)	116
C3—H3···*Cg*1	0.93	2.43	3.001 (2)	120
C21—H21···*Cg*2^{ii}	0.93	2.87	3.560 (2)	132

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*; (ii) −*x*, −*y*+1, −*z*.

(II) {μ-4′-[4-(methylsulfanyl)phenyl]-4,2′:6′,4′′-terpyridine-$\kappa^2N^1:N^{1''}$}bis[bis(acetylacetonato-κ^2O,O')zinc(II)]

Crystal data

$[Zn_2(C_5H_7O_2)_4(C_{22}H_{17}N_3S)]$
M_r = 882.61
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 14.1522 (3) Å
b = 13.4408 (3) Å
c = 23.3887 (5) Å
β = 101.342 (2)°
V = 4362.05 (16) Å^3
Z = 4
$F(000)$ = 1832
D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 27845 reflections
θ = 3.9–29.0°
μ = 1.20 mm^{-1}
T = 295 K
Polyhedra, colourless
0.32 × 0.16 × 0.14 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans, thick slices
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.80, T_{max} = 0.85
27845 measured reflections
9862 independent reflections
6308 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 29.0°, θ_{min} = 3.9°
h = −17→18
k = −15→18
l = −30→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.087
S = 0.98
9862 reflections
505 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.218436 (19)	−0.023500 (19)	0.349827 (10)	0.04179 (8)
Zn2	0.249447 (19)	0.788509 (17)	0.095196 (11)	0.04252 (8)
S1	0.26203 (8)	−0.04367 (6)	−0.22174 (3)	0.0864 (3)
N1	0.23827 (13)	0.03543 (12)	0.27084 (7)	0.0402 (4)
N2	0.26390 (13)	0.27281 (12)	0.11112 (7)	0.0384 (4)
N3	0.26336 (12)	0.63883 (12)	0.08122 (7)	0.0377 (4)
C1	0.2783 (2)	0.17360 (18)	0.21648 (9)	0.0622 (7)
H1	0.3006	0.2388	0.2170	0.075*
C2	0.2695 (2)	0.12781 (17)	0.26771 (9)	0.0654 (8)
H2	0.2863	0.1638	0.3022	0.079*
C3	0.2163 (2)	−0.01285 (16)	0.22092 (10)	0.0577 (7)
H3	0.1953	−0.0783	0.2215	0.069*
C4	0.2229 (2)	0.02835 (16)	0.16801 (10)	0.0609 (7)
H4	0.2055	−0.0090	0.1341	0.073*
C5	0.25462 (16)	0.12378 (14)	0.16501 (9)	0.0376 (5)
C6	0.25986 (15)	0.17335 (15)	0.10865 (8)	0.0357 (5)
C7	0.25918 (16)	0.12118 (15)	0.05764 (8)	0.0403 (5)
H7	0.2567	0.0520	0.0579	0.048*
C8	0.26220 (14)	0.17133 (14)	0.00593 (8)	0.0347 (5)
C9	0.26433 (16)	0.27450 (14)	0.00884 (9)	0.0387 (5)
H9	0.2649	0.3117	−0.0246	0.046*
C10	0.26559 (15)	0.32220 (14)	0.06159 (8)	0.0347 (5)
C11	0.26723 (15)	0.43249 (14)	0.06757 (8)	0.0356 (5)
C12	0.25005 (16)	0.49616 (14)	0.01986 (9)	0.0394 (5)
H12	0.2400	0.4705	−0.0178	0.047*
C13	0.24805 (15)	0.59650 (15)	0.02846 (9)	0.0404 (5)
H13	0.2354	0.6377	−0.0041	0.049*
C14	0.28264 (18)	0.57757 (15)	0.12719 (9)	0.0492 (6)
H14	0.2954	0.6052	0.1644	0.059*
C15	0.28448 (19)	0.47635 (16)	0.12209 (9)	0.0495 (6)
H15	0.2974	0.4369	0.1554	0.059*
C16	0.26189 (15)	0.11671 (14)	−0.04945 (8)	0.0355 (5)
C17	0.24822 (17)	0.01453 (15)	−0.05372 (9)	0.0433 (5)
H17	0.2403	−0.0210	−0.0208	0.052*
C18	0.24604 (17)	−0.03592 (16)	−0.10542 (9)	0.0475 (6)
H18	0.2360	−0.1043	−0.1069	0.057*
C19	0.25856 (18)	0.01415 (16)	−0.15492 (9)	0.0463 (6)
C20	0.27351 (19)	0.11550 (17)	−0.15099 (10)	0.0544 (6)
H20	0.2826	0.1505	−0.1838	0.065*
C21	0.27534 (18)	0.16609 (17)	−0.09943 (9)	0.0498 (6)

H21	0.2858	0.2344	−0.0981	0.060*
C22	0.2009 (3)	−0.1586 (2)	−0.21953 (13)	0.0987 (12)
H22A	0.2369	−0.2000	−0.1895	0.148*
H22B	0.1946	−0.1915	−0.2565	0.148*
H22C	0.1380	−0.1464	−0.2113	0.148*
O1A	0.29796 (13)	−0.13868 (11)	0.38313 (7)	0.0583 (4)
O2A	0.32724 (11)	0.07003 (11)	0.39319 (6)	0.0442 (4)
C1A	0.4306 (3)	−0.2400 (2)	0.42020 (16)	0.1062 (13)
H1AA	0.4051	−0.2677	0.4519	0.159*
H1AB	0.4993	−0.2341	0.4315	0.159*
H1AC	0.4148	−0.2828	0.3868	0.159*
C2A	0.3871 (2)	−0.13828 (19)	0.40509 (11)	0.0607 (7)
C3A	0.4441 (2)	−0.0551 (2)	0.41636 (12)	0.0673 (7)
H3A	0.5097	−0.0655	0.4294	0.081*
C4A	0.41288 (18)	0.04379 (18)	0.41012 (10)	0.0496 (6)
C5A	0.4852 (2)	0.1264 (2)	0.42386 (16)	0.0896 (10)
H5AA	0.5053	0.1469	0.3888	0.134*
H5AB	0.5402	0.1034	0.4516	0.134*
H5AC	0.4565	0.1817	0.4400	0.134*
O1B	0.13151 (12)	0.05352 (13)	0.38961 (7)	0.0612 (4)
O2B	0.10714 (13)	−0.11416 (14)	0.31358 (7)	0.0686 (5)
C1B	0.0021 (3)	0.0937 (3)	0.4345 (2)	0.1332 (16)
H1BA	0.0508	0.1150	0.4668	0.200*
H1BB	−0.0463	0.0563	0.4487	0.200*
H1BC	−0.0270	0.1508	0.4135	0.200*
C2B	0.0472 (2)	0.0294 (3)	0.39461 (14)	0.0772 (9)
C3B	−0.0035 (2)	−0.0486 (3)	0.36671 (17)	0.0913 (10)
H3B	−0.0644	−0.0592	0.3749	0.110*
C4B	0.0249 (2)	−0.1140 (2)	0.32762 (13)	0.0753 (9)
C5B	−0.0453 (3)	−0.1923 (3)	0.29922 (16)	0.1174 (14)
H5BA	−0.0819	−0.1669	0.2632	0.176*
H5BB	−0.0882	−0.2093	0.3248	0.176*
H5BC	−0.0105	−0.2505	0.2915	0.176*
O1C	0.33071 (13)	0.78156 (11)	0.17868 (7)	0.0557 (4)
O2C	0.34574 (12)	0.87955 (12)	0.07399 (8)	0.0602 (5)
C1C	0.4520 (3)	0.8109 (3)	0.26122 (14)	0.1178 (14)
H1CA	0.4077	0.8336	0.2847	0.177*
H1CB	0.5109	0.8479	0.2710	0.177*
H1CC	0.4651	0.7415	0.2685	0.177*
C2C	0.4079 (2)	0.8261 (2)	0.19713 (11)	0.0637 (7)
C3C	0.4542 (2)	0.8875 (2)	0.16381 (15)	0.0792 (9)
H3C	0.5121	0.9159	0.1824	0.095*
C4C	0.4228 (2)	0.9106 (2)	0.10598 (15)	0.0695 (8)
C5C	0.4834 (2)	0.9787 (3)	0.07552 (19)	0.1181 (15)
H5CA	0.5158	0.9398	0.0508	0.177*
H5CB	0.5302	1.0127	0.1042	0.177*
H5CC	0.4423	1.0266	0.0523	0.177*
O1D	0.16383 (14)	0.81287 (13)	0.01464 (7)	0.0643 (5)
O2D	0.13678 (13)	0.81541 (13)	0.13117 (7)	0.0612 (5)

C1D	0.0275 (2)	0.8421 (3)	−0.05845 (13)	0.1007 (11)
H1DA	0.0682	0.8756	−0.0806	0.151*
H1DB	−0.0323	0.8775	−0.0619	0.151*
H1DC	0.0150	0.7756	−0.0730	0.151*
C2D	0.0774 (2)	0.83809 (19)	0.00505 (12)	0.0621 (7)
C3D	0.0246 (2)	0.8601 (3)	0.04699 (15)	0.0855 (9)
H3D	−0.0368	0.8861	0.0343	0.103*
C4D	0.0549 (2)	0.8469 (3)	0.10617 (14)	0.0808 (9)
C5D	−0.0148 (3)	0.8663 (5)	0.14618 (18)	0.178 (3)
H5DA	−0.0336	0.8042	0.1609	0.267*
H5DB	−0.0708	0.8997	0.1249	0.267*
H5DC	0.0157	0.9073	0.1781	0.267*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.04805 (16)	0.04775 (16)	0.03023 (13)	−0.00284 (12)	0.00929 (11)	0.00155 (11)
Zn2	0.05416 (17)	0.02841 (13)	0.04535 (15)	−0.00145 (12)	0.01067 (12)	0.00171 (11)
S1	0.1568 (8)	0.0639 (5)	0.0494 (4)	−0.0240 (5)	0.0473 (5)	−0.0213 (3)
N1	0.0592 (12)	0.0317 (10)	0.0301 (9)	−0.0006 (9)	0.0098 (8)	0.0002 (8)
N2	0.0548 (11)	0.0292 (9)	0.0330 (9)	−0.0001 (8)	0.0130 (8)	0.0009 (7)
N3	0.0507 (11)	0.0297 (9)	0.0343 (9)	0.0014 (8)	0.0126 (8)	0.0011 (8)
C1	0.111 (2)	0.0370 (12)	0.0348 (13)	−0.0201 (14)	0.0054 (13)	0.0020 (10)
C2	0.124 (2)	0.0419 (14)	0.0273 (12)	−0.0168 (15)	0.0075 (14)	−0.0045 (10)
C3	0.108 (2)	0.0307 (12)	0.0384 (12)	−0.0150 (13)	0.0236 (13)	−0.0036 (10)
C4	0.121 (2)	0.0328 (12)	0.0343 (12)	−0.0124 (14)	0.0277 (14)	−0.0076 (10)
C5	0.0529 (13)	0.0287 (11)	0.0335 (11)	0.0050 (10)	0.0145 (10)	0.0017 (9)
C6	0.0464 (12)	0.0290 (10)	0.0334 (11)	0.0026 (10)	0.0121 (9)	0.0026 (9)
C7	0.0605 (14)	0.0268 (11)	0.0358 (11)	0.0019 (10)	0.0146 (10)	0.0005 (9)
C8	0.0429 (12)	0.0309 (11)	0.0316 (10)	0.0006 (9)	0.0100 (9)	−0.0003 (9)
C9	0.0549 (14)	0.0317 (12)	0.0316 (11)	0.0005 (10)	0.0139 (10)	0.0030 (9)
C10	0.0443 (12)	0.0295 (11)	0.0317 (11)	0.0002 (9)	0.0110 (9)	0.0012 (9)
C11	0.0473 (12)	0.0297 (11)	0.0322 (11)	−0.0005 (10)	0.0133 (9)	0.0018 (9)
C12	0.0591 (14)	0.0316 (11)	0.0280 (10)	0.0012 (10)	0.0098 (10)	−0.0006 (8)
C13	0.0533 (14)	0.0365 (12)	0.0320 (11)	0.0013 (10)	0.0095 (10)	0.0061 (9)
C14	0.0880 (18)	0.0310 (12)	0.0300 (11)	−0.0034 (12)	0.0146 (11)	−0.0018 (10)
C15	0.0857 (18)	0.0324 (12)	0.0313 (11)	0.0009 (12)	0.0140 (11)	0.0049 (10)
C16	0.0462 (12)	0.0319 (11)	0.0302 (10)	0.0008 (9)	0.0114 (9)	0.0005 (8)
C17	0.0671 (16)	0.0307 (11)	0.0344 (11)	−0.0009 (11)	0.0160 (11)	0.0030 (9)
C18	0.0687 (16)	0.0324 (12)	0.0445 (12)	−0.0020 (11)	0.0188 (12)	−0.0067 (10)
C19	0.0644 (15)	0.0427 (13)	0.0350 (12)	−0.0003 (12)	0.0178 (11)	−0.0049 (10)
C20	0.0902 (19)	0.0416 (13)	0.0371 (12)	−0.0052 (13)	0.0263 (12)	0.0015 (10)
C21	0.0827 (18)	0.0316 (12)	0.0385 (12)	−0.0055 (12)	0.0203 (12)	0.0004 (10)
C22	0.155 (3)	0.074 (2)	0.071 (2)	−0.033 (2)	0.033 (2)	−0.0329 (17)
O1A	0.0686 (12)	0.0476 (10)	0.0546 (10)	−0.0011 (9)	0.0021 (9)	0.0064 (8)
O2A	0.0454 (9)	0.0482 (9)	0.0375 (8)	−0.0003 (8)	0.0044 (7)	−0.0012 (7)
C1A	0.121 (3)	0.0625 (19)	0.116 (3)	0.030 (2)	−0.023 (2)	0.000 (2)
C2A	0.0713 (19)	0.0572 (16)	0.0502 (15)	0.0129 (15)	0.0034 (13)	0.0033 (12)
C3A	0.0494 (16)	0.0669 (18)	0.0803 (19)	0.0096 (14)	0.0000 (14)	0.0039 (15)
C4A	0.0460 (15)	0.0612 (16)	0.0408 (12)	−0.0044 (12)	0.0070 (11)	−0.0001 (11)

C5A	0.0578 (18)	0.083 (2)	0.121 (3)	−0.0132 (16)	0.0003 (17)	0.009 (2)
O1B	0.0530 (11)	0.0768 (12)	0.0559 (10)	0.0093 (9)	0.0160 (8)	−0.0014 (9)
O2B	0.0654 (12)	0.0812 (13)	0.0585 (11)	−0.0264 (10)	0.0101 (9)	−0.0053 (9)
C1B	0.096 (3)	0.154 (4)	0.168 (4)	0.044 (3)	0.069 (3)	−0.013 (3)
C2B	0.0530 (18)	0.100 (2)	0.082 (2)	0.0240 (18)	0.0224 (16)	0.0166 (19)
C3B	0.0545 (19)	0.123 (3)	0.100 (3)	−0.007 (2)	0.0243 (18)	0.004 (2)
C4B	0.0608 (19)	0.094 (2)	0.0652 (19)	−0.0268 (18)	−0.0027 (15)	0.0240 (17)
C5B	0.088 (2)	0.143 (3)	0.112 (3)	−0.061 (2)	−0.003 (2)	0.007 (2)
O1C	0.0653 (11)	0.0541 (10)	0.0454 (9)	−0.0117 (9)	0.0051 (8)	0.0002 (8)
O2C	0.0584 (11)	0.0524 (10)	0.0694 (11)	−0.0072 (9)	0.0112 (9)	0.0201 (9)
C1C	0.093 (3)	0.185 (4)	0.066 (2)	−0.024 (3)	−0.0092 (18)	0.002 (2)
C2C	0.0586 (17)	0.0739 (18)	0.0560 (16)	0.0018 (15)	0.0053 (13)	−0.0048 (14)
C3C	0.0532 (17)	0.087 (2)	0.092 (2)	−0.0222 (16)	0.0011 (16)	0.0018 (18)
C4C	0.0488 (17)	0.0579 (17)	0.103 (2)	−0.0007 (14)	0.0177 (16)	0.0238 (17)
C5C	0.066 (2)	0.125 (3)	0.165 (4)	−0.021 (2)	0.025 (2)	0.069 (3)
O1D	0.0656 (12)	0.0698 (12)	0.0556 (11)	0.0053 (10)	0.0075 (9)	0.0172 (9)
O2D	0.0557 (11)	0.0717 (12)	0.0562 (10)	0.0030 (9)	0.0112 (9)	−0.0194 (9)
C1D	0.084 (2)	0.131 (3)	0.076 (2)	−0.007 (2)	−0.0116 (17)	0.028 (2)
C2D	0.0652 (19)	0.0494 (15)	0.0649 (17)	−0.0096 (14)	−0.0036 (15)	0.0109 (13)
C3D	0.0575 (18)	0.107 (3)	0.086 (2)	0.0180 (18)	−0.0005 (17)	0.0000 (19)
C4D	0.062 (2)	0.105 (2)	0.074 (2)	0.0068 (18)	0.0116 (17)	−0.0230 (18)
C5D	0.080 (3)	0.362 (8)	0.096 (3)	0.056 (4)	0.027 (2)	−0.039 (4)

Geometric parameters (Å, º)

Zn1—O1B	1.9752 (17)	C22—H22B	0.9600
Zn1—O1A	1.9812 (16)	C22—H22C	0.9600
Zn1—O2B	2.0394 (17)	O1A—C2A	1.265 (3)
Zn1—N1	2.0793 (16)	O2A—C4A	1.250 (3)
Zn1—O2A	2.0894 (15)	C1A—C2A	1.513 (4)
Zn2—O2C	1.9663 (16)	C1A—H1AA	0.9600
Zn2—O2D	1.9770 (17)	C1A—H1AB	0.9600
Zn2—N3	2.0538 (16)	C1A—H1AC	0.9600
Zn2—O1D	2.0560 (17)	C2A—C3A	1.373 (4)
Zn2—O1C	2.0641 (16)	C3A—C4A	1.399 (3)
S1—C19	1.755 (2)	C3A—H3A	0.9300
S1—C22	1.777 (3)	C4A—C5A	1.502 (3)
N1—C3	1.318 (3)	C5A—H5AA	0.9600
N1—C2	1.325 (3)	C5A—H5AB	0.9600
N2—C6	1.339 (3)	C5A—H5AC	0.9600
N2—C10	1.340 (2)	O1B—C2B	1.264 (3)
N3—C13	1.337 (2)	O2B—C4B	1.270 (3)
N3—C14	1.339 (3)	C1B—C2B	1.503 (4)
C1—C5	1.361 (3)	C1B—H1BA	0.9600
C1—C2	1.375 (3)	C1B—H1BB	0.9600
C1—H1	0.9300	C1B—H1BC	0.9600
C2—H2	0.9300	C2B—C3B	1.363 (5)
C3—C4	1.375 (3)	C3B—C4B	1.383 (4)
C3—H3	0.9300	C3B—H3B	0.9300
C4—C5	1.365 (3)	C4B—C5B	1.509 (4)

C4—H4	0.9300	C5B—H5BA	0.9600
C5—C6	1.492 (3)	C5B—H5BB	0.9600
C6—C7	1.382 (3)	C5B—H5BC	0.9600
C7—C8	1.393 (3)	O1C—C2C	1.246 (3)
C7—H7	0.9300	O2C—C4C	1.266 (3)
C8—C9	1.388 (3)	C1C—C2C	1.520 (4)
C8—C16	1.488 (3)	C1C—H1CA	0.9600
C9—C10	1.387 (3)	C1C—H1CB	0.9600
C9—H9	0.9300	C1C—H1CC	0.9600
C10—C11	1.489 (3)	C2C—C3C	1.385 (4)
C11—C15	1.382 (3)	C3C—C4C	1.374 (4)
C11—C12	1.389 (3)	C3C—H3C	0.9300
C12—C13	1.365 (3)	C4C—C5C	1.523 (4)
C12—H12	0.9300	C5C—H5CA	0.9600
C13—H13	0.9300	C5C—H5CB	0.9600
C14—C15	1.366 (3)	C5C—H5CC	0.9600
C14—H14	0.9300	O1D—C2D	1.247 (3)
C15—H15	0.9300	O2D—C4D	1.264 (3)
C16—C17	1.388 (3)	C1D—C2D	1.515 (4)
C16—C21	1.389 (3)	C1D—H1DA	0.9600
C17—C18	1.381 (3)	C1D—H1DB	0.9600
C17—H17	0.9300	C1D—H1DC	0.9600
C18—C19	1.380 (3)	C2D—C3D	1.377 (4)
C18—H18	0.9300	C3D—C4D	1.377 (4)
C19—C20	1.379 (3)	C3D—H3D	0.9300
C20—C21	1.380 (3)	C4D—C5D	1.509 (4)
C20—H20	0.9300	C5D—H5DA	0.9600
C21—H21	0.9300	C5D—H5DB	0.9600
C22—H22A	0.9600	C5D—H5DC	0.9600

O1B—Zn1—O1A	125.64 (7)	H22A—C22—H22C	109.5
O1B—Zn1—O2B	90.42 (8)	H22B—C22—H22C	109.5
O1A—Zn1—O2B	91.67 (7)	C2A—O1A—Zn1	126.89 (16)
O1B—Zn1—N1	115.11 (7)	C4A—O2A—Zn1	124.07 (15)
O1A—Zn1—N1	118.78 (7)	C2A—C1A—H1AA	109.5
O2B—Zn1—N1	94.96 (7)	C2A—C1A—H1AB	109.5
O1B—Zn1—O2A	85.63 (7)	H1AA—C1A—H1AB	109.5
O1A—Zn1—O2A	88.39 (6)	C2A—C1A—H1AC	109.5
O2B—Zn1—O2A	175.17 (7)	H1AA—C1A—H1AC	109.5
N1—Zn1—O2A	89.24 (6)	H1AB—C1A—H1AC	109.5
O2C—Zn2—O2D	130.58 (7)	O1A—C2A—C3A	125.6 (2)
O2C—Zn2—N3	118.46 (7)	O1A—C2A—C1A	114.7 (3)
O2D—Zn2—N3	110.95 (7)	C3A—C2A—C1A	119.6 (3)
O2C—Zn2—O1D	88.99 (7)	C2A—C3A—C4A	126.3 (2)
O2D—Zn2—O1D	88.94 (7)	C2A—C3A—H3A	116.9
N3—Zn2—O1D	93.89 (7)	C4A—C3A—H3A	116.9
O2C—Zn2—O1C	88.96 (7)	O2A—C4A—C3A	124.6 (2)
O2D—Zn2—O1C	87.23 (7)	O2A—C4A—C5A	115.9 (2)
N3—Zn2—O1C	93.05 (6)	C3A—C4A—C5A	119.5 (2)

O1D—Zn2—O1C	172.91 (7)	C4A—C5A—H5AA	109.5
C19—S1—C22	105.07 (12)	C4A—C5A—H5AB	109.5
C3—N1—C2	115.83 (18)	H5AA—C5A—H5AB	109.5
C3—N1—Zn1	123.36 (14)	C4A—C5A—H5AC	109.5
C2—N1—Zn1	120.71 (14)	H5AA—C5A—H5AC	109.5
C6—N2—C10	117.73 (16)	H5AB—C5A—H5AC	109.5
C13—N3—C14	116.73 (17)	C2B—O1B—Zn1	126.6 (2)
C13—N3—Zn2	124.09 (13)	C4B—O2B—Zn1	124.3 (2)
C14—N3—Zn2	119.03 (13)	C2B—C1B—H1BA	109.5
C5—C1—C2	120.1 (2)	C2B—C1B—H1BB	109.5
C5—C1—H1	119.9	H1BA—C1B—H1BB	109.5
C2—C1—H1	119.9	C2B—C1B—H1BC	109.5
N1—C2—C1	123.8 (2)	H1BA—C1B—H1BC	109.5
N1—C2—H2	118.1	H1BB—C1B—H1BC	109.5
C1—C2—H2	118.1	O1B—C2B—C3B	124.8 (3)
N1—C3—C4	123.6 (2)	O1B—C2B—C1B	115.7 (3)
N1—C3—H3	118.2	C3B—C2B—C1B	119.4 (3)
C4—C3—H3	118.2	C2B—C3B—C4B	127.6 (3)
C5—C4—C3	120.4 (2)	C2B—C3B—H3B	116.2
C5—C4—H4	119.8	C4B—C3B—H3B	116.2
C3—C4—H4	119.8	O2B—C4B—C3B	124.9 (3)
C1—C5—C4	116.31 (19)	O2B—C4B—C5B	116.2 (3)
C1—C5—C6	121.03 (18)	C3B—C4B—C5B	118.8 (3)
C4—C5—C6	122.61 (18)	C4B—C5B—H5BA	109.5
N2—C6—C7	122.46 (17)	C4B—C5B—H5BB	109.5
N2—C6—C5	114.64 (16)	H5BA—C5B—H5BB	109.5
C7—C6—C5	122.89 (17)	C4B—C5B—H5BC	109.5
C6—C7—C8	120.52 (18)	H5BA—C5B—H5BC	109.5
C6—C7—H7	119.7	H5BB—C5B—H5BC	109.5
C8—C7—H7	119.7	C2C—O1C—Zn2	126.40 (16)
C9—C8—C7	116.43 (17)	C4C—O2C—Zn2	127.99 (17)
C9—C8—C16	122.11 (17)	C2C—C1C—H1CA	109.5
C7—C8—C16	121.46 (17)	C2C—C1C—H1CB	109.5
C10—C9—C8	120.09 (18)	H1CA—C1C—H1CB	109.5
C10—C9—H9	120.0	C2C—C1C—H1CC	109.5
C8—C9—H9	120.0	H1CA—C1C—H1CC	109.5
N2—C10—C9	122.74 (17)	H1CB—C1C—H1CC	109.5
N2—C10—C11	114.50 (16)	O1C—C2C—C3C	124.8 (3)
C9—C10—C11	122.75 (17)	O1C—C2C—C1C	116.0 (3)
C15—C11—C12	116.71 (18)	C3C—C2C—C1C	119.2 (3)
C15—C11—C10	120.54 (17)	C4C—C3C—C2C	126.3 (3)
C12—C11—C10	122.74 (17)	C4C—C3C—H3C	116.9
C13—C12—C11	119.71 (18)	C2C—C3C—H3C	116.9
C13—C12—H12	120.1	O2C—C4C—C3C	125.5 (2)
C11—C12—H12	120.1	O2C—C4C—C5C	114.9 (3)
N3—C13—C12	123.53 (18)	C3C—C4C—C5C	119.6 (3)
N3—C13—H13	118.2	C4C—C5C—H5CA	109.5
C12—C13—H13	118.2	C4C—C5C—H5CB	109.5
N3—C14—C15	123.13 (19)	H5CA—C5C—H5CB	109.5

N3—C14—H14	118.4	C4C—C5C—H5CC	109.5
C15—C14—H14	118.4	H5CA—C5C—H5CC	109.5
C14—C15—C11	120.15 (19)	H5CB—C5C—H5CC	109.5
C14—C15—H15	119.9	C2D—O1D—Zn2	126.08 (18)
C11—C15—H15	119.9	C4D—O2D—Zn2	127.40 (19)
C17—C16—C21	116.91 (18)	C2D—C1D—H1DA	109.5
C17—C16—C8	121.82 (17)	C2D—C1D—H1DB	109.5
C21—C16—C8	121.27 (18)	H1DA—C1D—H1DB	109.5
C18—C17—C16	121.83 (19)	C2D—C1D—H1DC	109.5
C18—C17—H17	119.1	H1DA—C1D—H1DC	109.5
C16—C17—H17	119.1	H1DB—C1D—H1DC	109.5
C19—C18—C17	120.69 (19)	O1D—C2D—C3D	125.5 (3)
C19—C18—H18	119.7	O1D—C2D—C1D	115.9 (3)
C17—C18—H18	119.7	C3D—C2D—C1D	118.5 (3)
C20—C19—C18	117.98 (19)	C2D—C3D—C4D	125.7 (3)
C20—C19—S1	117.78 (17)	C2D—C3D—H3D	117.2
C18—C19—S1	124.18 (16)	C4D—C3D—H3D	117.2
C19—C20—C21	121.4 (2)	O2D—C4D—C3D	125.7 (3)
C19—C20—H20	119.3	O2D—C4D—C5D	115.0 (3)
C21—C20—H20	119.3	C3D—C4D—C5D	119.3 (3)
C20—C21—C16	121.2 (2)	C4D—C5D—H5DA	109.5
C20—C21—H21	119.4	C4D—C5D—H5DB	109.5
C16—C21—H21	119.4	H5DA—C5D—H5DB	109.5
S1—C22—H22A	109.5	C4D—C5D—H5DC	109.5
S1—C22—H22B	109.5	H5DA—C5D—H5DC	109.5
H22A—C22—H22B	109.5	H5DB—C5D—H5DC	109.5
S1—C22—H22C	109.5		

Hydrogen-bond geometry (Å, º)

Table 3. C—H···π contacts in (II) (Å, °).

*Cg*4 is the centroid of the Zn2/O1D/C2D/C3D/C4D/O2D chelate ring and *Cg*8 is the centroid of the C16–C21 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···*Cg*4^{i}	0.93	2.85	3.712 (3)	155
C1*B*—H1*BC*···*Cg*4^{ii}	0.96	2.78	3.563 (4)	140
C5*D*—H5*DB*···*Cg*8^{iii}	0.96	2.67	3.549 (5)	152

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) −*x*, −*y*+1, −*z*.

Table 2. π–π contacts in (I) (Å, °)

Cg4 is the centroid of the N3/C11-C15 pyridine ring.

Group 1/Group 2	ccd (Å)	da (°)	ipd (Å)	sa (°)
*Cg*4···*Cg*4^{iii}	3.945 (2)	0	3.7822 (14)	16.48

Symmetry code: (iii) -x, -y+1, -z. Notes: ccd is the center-to-center distance (distance between ring centroids); da is the dihedral angle between rings; ipd is the interplanar distance (distance from one plane to the neighbouring centroid), sa is the slippage angle (angle subtended by the intercentroid vector to the plane normal). For details, see Janiak (2000).