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Synthesis and characterization of two novel bimetallic macrocyclic complexes generated from 1,2,4-triazole-containing semi-rigid ligands and $M(NO_3)_2$ units (M = Ni and Zn)

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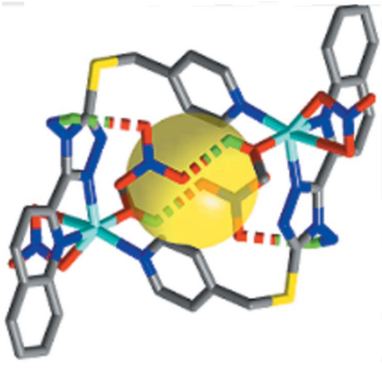
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Keywords: nanotubes; bimetallic rings; nickel(II); zinc(II); two-dimensional network; three-dimensional framework; crystal structure; coordination chemistry; semi-rigid ligands.

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Bimetallic macrocyclic complexes have attracted the attention of chemists and various organic ligands have been used as molecular building blocks, but supramolecular complexes based on semi-rigid organic ligands containing 1,2,4-triazole have remained rare until recently. It is easier to obtain novel topologies by making use of asymmetric semi-rigid ligands in the self-assembly process than by making use of rigid ligands. A new semi-rigid ligand, 3-[(pyridin-4-ylmethyl)-sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine (*L*), has been synthesized and used to generate two novel bimetallic macrocycle complexes, namely bis{μ-3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine}bis-[(methanol-κO)(nitrato-$\kappa^2 O,O'$)nickel(II)] dinitrate, $[Ni_2(NO_3)_2(C_{17}H_{14}N_6S)_2(CH_3OH)_2](NO_3)_2$, (I), and bis{$\mu$-3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine}bis[(methanol-κO)(nitrato-$\kappa^2 O,O'$)zinc(II)] dinitrate, $[Zn_2(NO_3)_2(C_{17}H_{14}N_6S)_2(CH_3OH)_2](NO_3)_2$, (II), by solution reactions with the inorganic salts $M(NO_3)_2$ (M = Ni and Zn, respectively) in mixed solvents. In (I), two Ni^{II} cations with the same coordination environment are linked by *L* ligands through Ni—N bonds to form a bimetallic ring. Compound (I) is extended into a two-dimensional network in the crystallographic *ac* plane *via* N—H···O, O—H···N and O—H···O hydrogen bonds, and neighbouring two-dimensional planes are parallel and form a three-dimensional structure *via* π–π stacking. Compound (II) contains two bimetallic rings with the same coordination environment of the Zn^{II} cations. The Zn^{II} cations are bridged by *L* ligands through Zn—N bonds to form the bimetallic rings. One type of bimetallic ring constructs a one-dimensional nanotube *via* O—H···O and N—H···O hydrogen bonds along the crystallographic *a* direction, and the other constructs zero-dimensional molecular cages *via* O—H···O and N—H···O hydrogen bonds. They are interlinked into a two-dimensional network in the *ac* plane through extensive N—H···O hydrogen bonds, and a three-dimensional supramolecular architecture is formed *via* π–π interactions between the centroids of the benzene rings of the quinoline ring systems.



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1. Introduction

The design and synthesis of functional metal–organic frameworks (MOFs) with novel topologies and structural motifs are of current interest in the field of coordination chemistry, due to their fascinating coordination architectures and potential applications in areas such as catalysis, nonlinear optics, separation, magnetism and molecular recognition, and their fluorescence and biological properties (Kitagawa *et al.*, 2004; Li *et al.*, 2008; Zhang & Xiong, 2012; Li, Yao *et al.*, 2015). To some extent, bimetallic macrocyclic complexes have attracted the attention of chemists for separation processes, recognition,

catalysis and sensor technologies. To date, various organic ligands have been used as molecular building blocks, but supramolecular complexes based on semi-rigid organic ligands containing 1,2,4-triazole have remained rare until recently (Ma *et al.*, 2014). It is easier to obtain novel topologies by making use of asymmetric semi-rigid ligands in the self-assembly process than by making use of rigid ligands. These compounds are good flexible ligands for building supramolecular systems and they have abundant coordination modes due to the introduction of rich nitrogen heterocyclic ligands (Shakir *et al.*, 2003). Meanwhile, amino groups are good hydrogen-bond donors, so they can form various hydrogen-bonded structures. These hydrogen bonds do not only increase the diversity of the complex structures, but also enhance its stability. Therefore, they play an important role in the coordination chemistry of these ligands. What is more, the introduction of a thioether group can not only increase the length but also add to the plasticity and flexibility of the resulting complexes. Previously, our groups have synthesized and studied organometallic coordination frameworks generated from semi-rigid organic ligands containing 1,2,4-triazole (Dong *et al.*, 2005, 2007; Wang *et al.*, 2010). We report here two new bimetallic macrocyclic complexes formed by the bridging of the new semi-rigid ligand 3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine (*L*) and the inorganic salts $M(NO_3)_2$ (*M* = Ni and Zn), namely, $[Ni_2(NO_3)_2(L)_2(CH_3OH)_2](NO_3)_2$, (I), and $[Zn_4(NO_3)_6(L)_4(CH_3OH)_4]$, (II) (see Scheme).

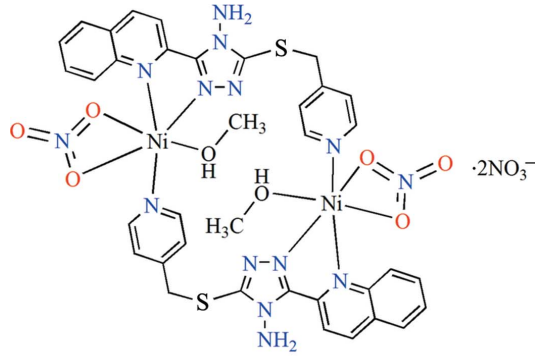
2. Experimental

2.1. Synthesis and crystallization

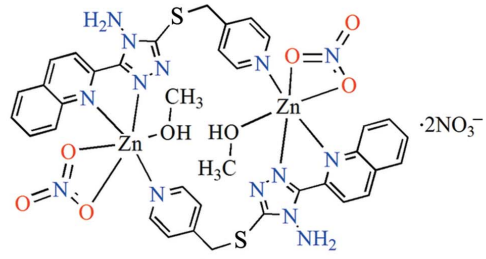
2.1.1. Synthesis of 3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine, *L*. A mixture of 4-amino-5-(quinolin-2-yl)-4*H*-1,2,4-triazole-3-thiol (2.43 g, 10 mmol), K_2CO_3 (6.9 g, 50 mmol) and 4-(chloromethyl)pyridine hydrochloride (1.96 g, 12 mmol) in methanol (60 ml) was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography using dichloromethane (DCM) as eluent to afford *L* (yield 2.27 g, 68.0%). ^{1}H NMR (300 MHz, DMSO, 298 K, TMS): δ 8.56–8.55 (*d*, 2H, $-C_5H_4N$), 8.46 (*d*, 1H, $-C_5H_2N$), 8.06–8.02 (*m*, 2H, $-C_6H_4$), 7.78 (*t*, 1H, $-C_6H_4$), 7.62 (*t*, 1H, $-C_6H_4$), 7.42 (*d*, 1H, $-C_5H_2N$), 7.22 (*m*, 2H, $-C_5H_4N$), 5.74 (*s*, 2H, $-NH_2$), 4.54 (*s*, 2H, $-CH_2-$); IR (KBr pellet, ν, cm^{-1}): 3175 (*w*), 1593 (*m*), 1494 (*w*), 1412 (*s*), 1011 (*s*), 895 (*w*), 832 (*s*), 796 (*m*), 751 (*s*), 562 (*w*), 477 (*s*). Elemental analysis calculated for $C_{17}H_{14}N_6S$: C 61.07, H 4.19, N 25.15%; found: C.60.99, H 4.11, N 25.10%.

2.1.2. Synthesis of (I). A solution of $Ni(NO_3)_2\cdot6H_2O$ (5.82 mg, 0.02 mmol) in methanol (2 ml) was layered onto a solution of *L* (3.34 mg, 0.01 mmol) in DCM (2 ml). The solutions were left for about a week at room temperature, whereupon green crystals of (I) were obtained (yield 3.9 mg, 71%). IR (KBr pellet, ν, cm^{-1}): 3308 (*w*), 3101 (*w*), 2937 (*w*), 2824 (*w*), 1620 (*m*), 1496 (*s*), 1393 (*m*), 1329 (*s*), 1262 (*s*), 1153 (*w*), 1099 (*w*), 1021 (*s*), 955 (*w*), 844 (*m*), 761 (*m*), 728 (*m*), 683 (*m*), 651 (*m*), 568 (*m*), 489 (*m*). Elemental analysis calculated for $C_{36}H_{36}N_{16}Ni_2O_{14}S_2$: C 39.34, H 3.28, N 20.40%; found: C 39.13, H 3.11, N 19.96%.

2.1.3. Synthesis of (II). A solution of $Zn(NO_3)_2\cdot6H_2O$ (5.94 mg, 0.02 mmol) in methanol (2 ml) was layered onto a solution of *L* (3.34 mg, 0.01 mmol) in DCM (2 ml). The solutions were left for about a week at room temperature, whereupon colourless crystals of (II) were obtained (yield 3.6 mg, 65%). IR (KBr pellet, ν, cm^{-1}): 3317 (*w*), 3207 (*w*), 2934 (*w*), 1620 (*m*), 1468 (*s*), 1376 (*m*), 1297 (*s*), 1281 (*w*), 1155 (*w*), 1064 (*w*), 1012 (*s*), 960 (*w*), 831 (*s*), 757 (*s*), 688 (*m*), 645 (*m*), 578 (*s*), 502 (*s*), 438 (*m*). Elemental analysis calculated for $C_{36}H_{36}N_{16}O_{14}S_2Zn_2$: C 38.86, H 3.24, N 20.15%; found: C 38.77, H 3.05, N 20.11%.



(I)



(II)

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93–0.98 Å, N—H = 0.91–0.94 Å and O—H = 0.93 Å, and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C,N,O) or 1.5U_{eq}(C).

3. Results and discussion

Compound (I) crystallizes in the triclinic space group $P\overline{1}$, and the asymmetric unit contains one Ni^{II} centre, one *L* ligand, one coordinated MeOH molecule and two nitrate anions. As depicted in Fig. 1, the complex is binuclear, with two triazole and two pyridine rings linked *via* thioether groups acting as bidentate bridges between pairs of Ni^{II} cations, with an Ni···Ni distance of 8.0158 (6) Å and an S···S distance of

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Ni_2(NO_3)_2(C_{17}H_{14}N_6S)_2(CH_4O)_2](NO_3)_2$	$[Zn_2(NO_3)_2(C_{17}H_{14}N_6S)_2(CH_4O)_2](NO_3)_2$
M_r	1098.34	1111.67
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	100	100
a, b, c (Å)	9.4131 (7), 9.9334 (7), 13.0829 (6)	10.0414 (5), 14.4893 (7), 15.6001 (8)
α, β, γ (°)	77.650 (5), 83.824 (5), 70.284 (6)	88.257 (4), 81.614 (4), 80.184 (4)
V (Å^3)	1124.11 (12)	2212.53 (19)
Z	1	2
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	1.02	2.97
Crystal size (mm)	0.29 × 0.18 × 0.08	0.21 × 0.07 × 0.04
Data collection		
Diffractometer	Agilent SuperNova Dual Source diffractometer with an Eos detector	Agilent SuperNova Dual Source diffractometer with an Eos detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.907, 1.000	0.784, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	7894, 4594, 3976	14520, 7875, 6746
R_{int}	0.023	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.597
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.075, 1.04	0.040, 0.112, 1.05
No. of reflections	4594	7875
No. of parameters	317	633
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.32	0.56, −0.82

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008) and *SHELXL97* (Sheldrick, 2008).

10.4872 (1) Å. Selected bond lengths for (I) are listed in Table 2. Each Ni^{II} cation is six-coordinated and located in a distorted octahedral coordination environment involving three N atoms from one quinoline ring (N1), one triazole ring (N2) and one pyridine ring [N6^i; symmetry code: (i) $-x, -y, -z+1$], and three O atoms from one MeOH molecule (O5) and one nitrate ligand (O2 and O3). The coordination environment of the Ni^{II} cation is similar to that observed in $\{Ni_2(tpyprz)_2\}$ [tpyprz is 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine; Burkholder *et al.*, 2004]. However, the planes of the quinoline and triazole rings are almost coplanar, with a dihedral angle of 11.8 (11)°, while the dihedral angle between the planes of the pyridyl and triazole rings is 86.3 (10)°. The bond angle of the thioether group (C11—S1—C12) is 97.95 (12)°. The above-mentioned angles are in close agreement with previously reported values (Li *et al.*, 2014). The two MeOH ligands point to the interior of the rings.

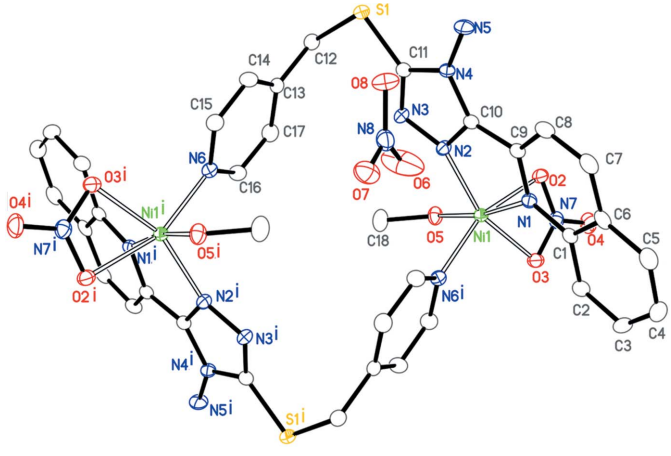


Figure 1
The asymmetric unit and Ni^{II} coordination environment of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, -y, -z+1$.]

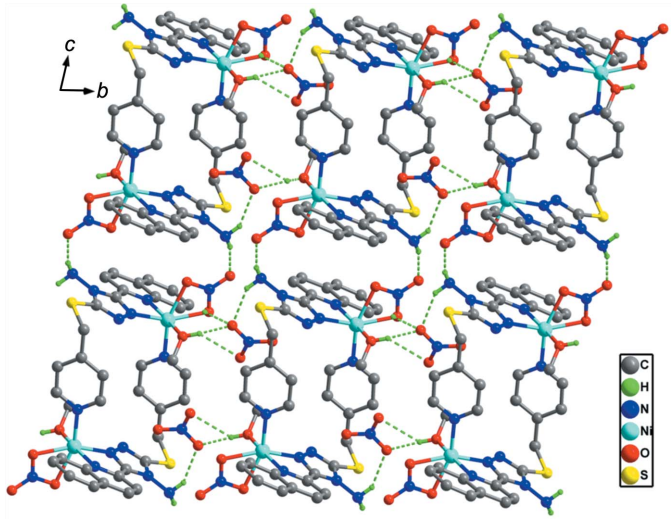


Figure 2
A perspective view of the two-dimensional network of (I), showing the hydrogen bonds (bright-green dashed lines, highlighted in part).

Table 2
Selected bond lengths (Å) for (I).

N1—Ni1	2.1377 (18)	Ni1—O5	2.0290 (15)
N2—Ni1	2.0240 (17)	Ni1—O3	2.1411 (15)
N6—Ni1^{i}	2.0339 (18)	Ni1—O2	2.1908 (15)

Symmetry code: (i) $-x, -y, -z+1$.

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O8	0.89	2.27	3.050 (3)	147
N5—H5B···O4^{ii}	0.89	2.35	3.222 (3)	165
O5—H5C···O8^{iii}	0.85	1.80	2.646 (2)	171
O5—H5C···N8^{iii}	0.85	2.49	3.295 (3)	158
O5—H5C···O7^{iii}	0.85	2.50	3.114 (2)	130

Symmetry codes: (ii) $-x, -y, -z$; (iii) $x, y-1, z$.

Five kinds of hydrogen bonds [N5—H5A···O8, N5—H5B···O4^{ii}, O5—H5C···N8^{iii}, O5—H5C···O8^{iii} and O5—H5C···O7^{iii}; symmetry codes: (ii) $-x, -y, -z$; (iii) $x, y-1, z$] (Table 3) connect neighbouring bimetallic rings into a novel two-dimensional layer parallel to the crystallographic bc plane (Fig. 2). The hydrogen-bond distances are in close agreement with values reported previously (Wang *et al.*, 2009; Kumar *et al.*, 2006). In addition, neighbouring two-dimensional planes are parallel, leading to a three-dimensional framework *via* π–π stacking (Fig. 3).

The construction of (II) is different from that of (I). As shown in Fig. 4, it contains two bimetallic rings with the same coordination environment of the Zn^{II} cations. It crystallizes in the triclinic space group $P\overline{1}$, and each asymmetric unit contains one Zn^{II} centre, one L ligand, one coordinated MeOH molecule and two nitrate anions. The Zn—O and Zn—N distances (Table 4) are comparable with values reported for other Zn^{II}

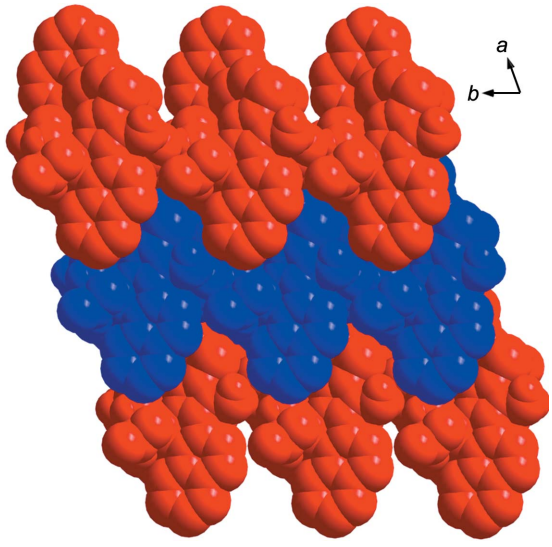


Figure 3
A view of the three-dimensional framework of (I). All H atoms have been omitted for clarity.

Table 4
Selected bond lengths (Å) for (II).

N1—Zn1	2.040 (2)	O1—Zn1	2.0142 (18)
N3—Zn1^{i}	2.018 (2)	O4—Zn1	2.1241 (18)
N6—Zn1^{i}	2.273 (2)	O5—Zn2	2.086 (2)
N7—Zn2	2.272 (2)	O6—Zn2	2.102 (2)
N8—Zn2	2.037 (2)	O7—Zn2	2.415 (3)
N12—Zn2^{ii}	2.047 (2)		

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

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11B···O1^{ii}	0.91	2.65	3.125 (3)	113
N11—H11B···O3^{ii}	0.91	2.19	3.077 (3)	164
O5—H5···N15^{iii}	0.93	2.57	3.348 (3)	141
O5—H5···O9^{iii}	0.93	1.79	2.600 (3)	144
N5—H5B···O8	0.92	2.25	3.113 (3)	156
N5—H5A···O13	0.93	2.55	3.291 (3)	137
N11—H11A···O11	0.95	2.18	3.037 (3)	149
O4—H4A···O14	0.93	2.11	2.655 (3)	116

Symmetry codes: (ii) $-x+1, -y, -z$; (iii) $x+1, y, z$.

compounds (Cui *et al.*, 2014). The Zn1 and Zn2 centres are six-coordinated in a distorted octahedral coordination geometry surrounded by three N atoms from one quinoline ring, one triazole ring and one pyridine ring, and by three O atoms from one methanol molecule and one nitrate ligand. In (II), the essential differences between the two rings are the Zn—O bond lengths involving the nitrate O atoms (Table 4); in (I), the distances from the Ni^{II} cation to the two nitrate O atoms are nearly equal (Table 2). In the Zn1-containing bimetallic

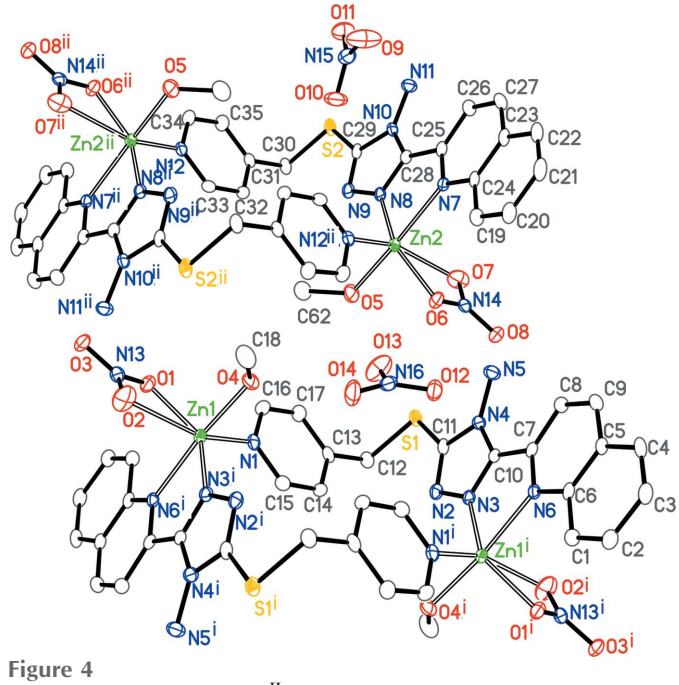


Figure 4
The asymmetric unit and Zn^{II} coordination environment of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $-x+1, -y, -z$; (iii) $x+1, y, z$.]

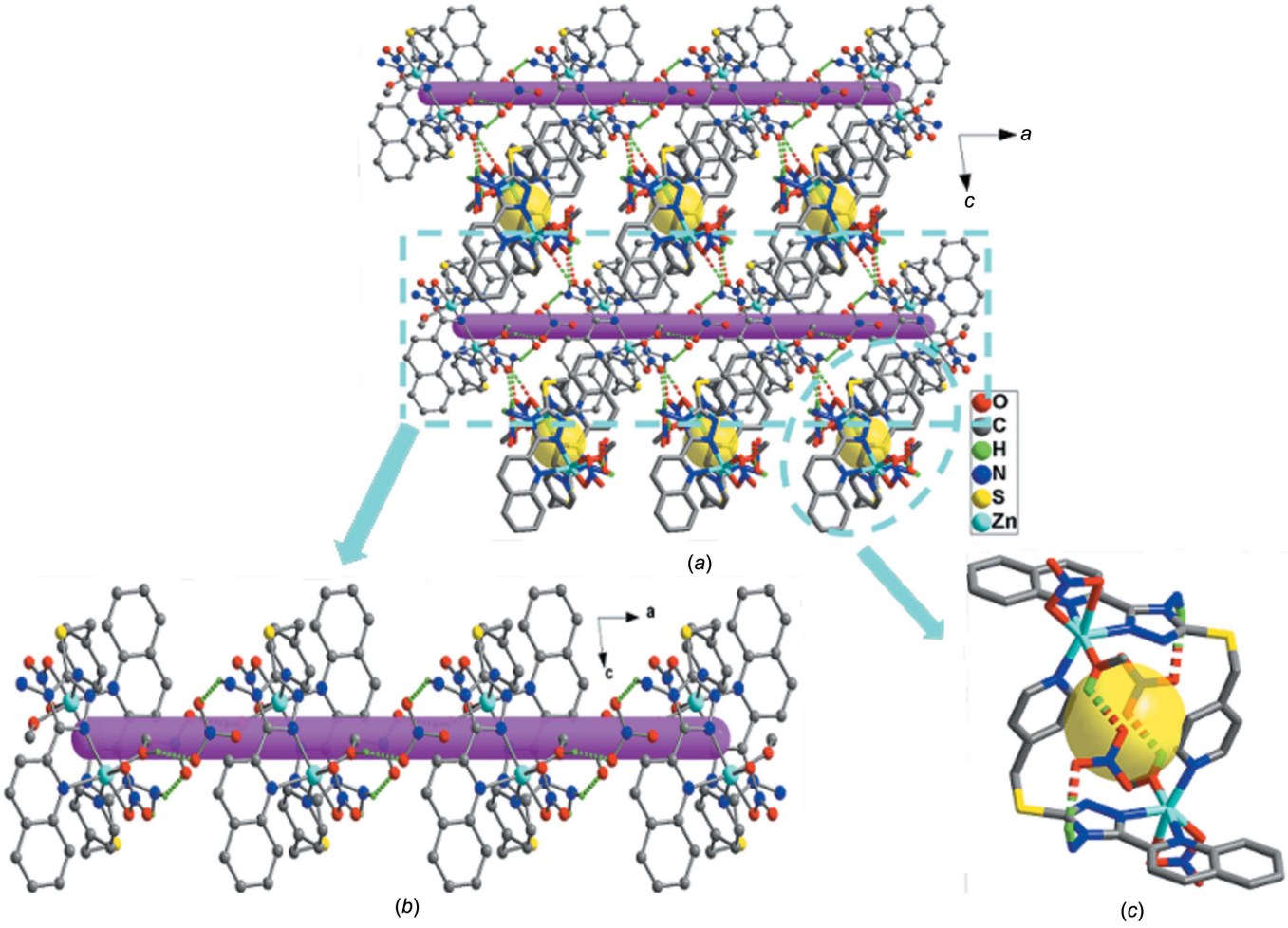


Figure 5
(*a*) The two-dimensional network of (II), linked by hydrogen bonds (green or green–red dashed lines). (*b*) The hydrogen bonds (bright-green dashed lines) in the nanotube composed of the Zn2-containing molecules. (*c*) The hydrogen bonds (bright-green dashed lines) in the zero-dimensional molecular cage composed of the Zn1-containing molecule.

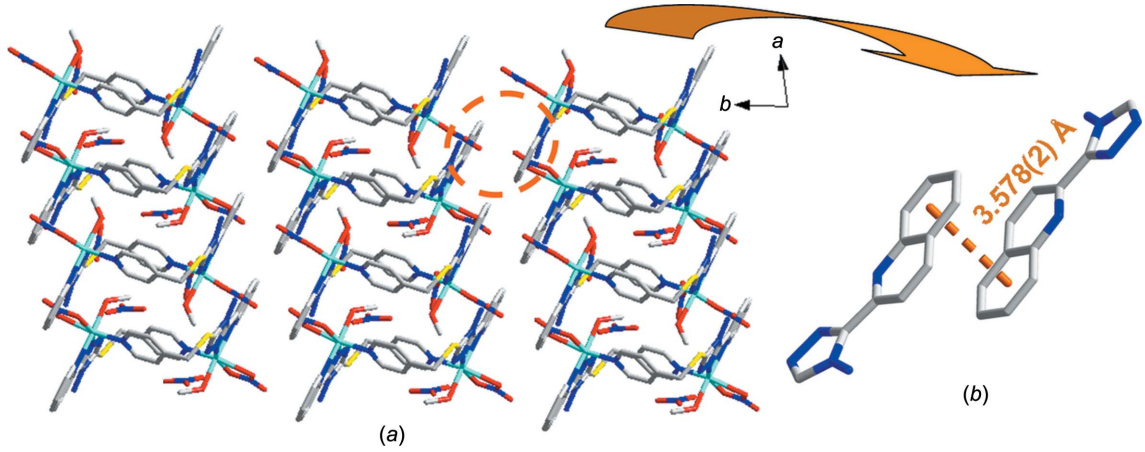


Figure 6
(*a*) The three-dimensional network of (II), viewed along the *c* axis. All H atoms have been omitted for clarity. (*b*) The π–π interaction (orange dashed line) between neighbouring two-dimensional sheets.

ring, the quinoline and triazole rings are almost coplanar, with a dihedral angle of 5.0 (8)° between their planes, while the dihedral angle between the planes of the pyridyl and triazole rings is 88.60 (10)°. However, in the Zn2-containing bimetallic ring, the quinoline and triazole rings are almost coplanar, with a dihedral angle of 9.6 (7)°, while the dihedral angle between

the planes of the pyridyl and triazole rings is 83.05 (10)°. The bond angle of the thioether group (C29—S2—C30) is 99.36 (13)°. What is more, in the Zn1-containing structure, the distance between the two S atoms is 10.343 (2) Å, while in the Zn2-containing structure, the distance is 10.322 (2) Å. Both these values are a little shorter than that between the two S atoms in (I) [S···S = 10.487 (2) Å]. Interestingly, the two coordinated MeOH molecules in the Zn1-containing structure point to the outside of the ring, while in the Zn2-containing structure they point to the interior of the ring.

In the crystal structure of (II), neighbouring Zn2-containing bimetallic rings interact *via* hydrogen bonds (O5—H5···O9^{iii} and N11—H11*A*···O11; see Table 5 for details and symmetry code) to form a one-dimensional nanotube in the direction of the *a* axis (Fig. 5*b*). A similar nanotube structure has been reported previously (Dai *et al.*, 2008; Liu *et al.*, 2013). Strong hydrogen bonds involving methanol O atoms, amino N atoms (as donors) and free nitrate N atoms (as acceptors) (O4—H4*A*···O14 and N5—H5*A*···O13) in the Zn1-containing bimetallic rings lead to the formation of a small zero-dimensional molecular cage (Fig. 5*c*), and these cages are connected to the one-dimensional nanotubes by three kinds of hydrogen bonds [N5—H5*B*···O8, N11—H11*B*···O1^{ii} and N11—H11*B*···O3^{ii}; symmetry code: (ii) $-x+1, -y, -z$], resulting in a novel two-dimensional network in the *ac* plane (Fig. 5*a*). Furthermore, π–π interactions between pairs of quinoline benzene rings in parallel two-dimensional sheets [centroid-to-centroid distance between benzene rings = 3.578 (2) Å] (Fig. 6*b*) facilitate the formation of a three-dimensional framework (Fig. 6*a*).

In summary, the semi-rigid organic ligand 3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine can be used as a polydentate or chelating ligand to coordinate transition metal ions. Two novel bimetallic macrocyclic complexes were obtained. This study has shown that this series of semi-rigid organic ligands coordinated to metal ions afford bimetallic rings easily. We are currently extending this study by preparing new ligands of this type with different substituted functional groups. We anticipate this approach will be useful for constructing novel supramolecular complexes.

Acknowledgements

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Synthesis and characterization of two novel bimetallic macrocyclic complexes generated from 1,2,4-triazole-containing semi-rigid ligands and $M(NO_3)_2$ units (M = Ni and Zn)

Xiang-Wen Wu, Shi Yin, Wan-Fu Wu and Jian-Ping Ma

Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

(I) Bis{μ-3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine}bis[(methanol-κO)(nitrato-κ^2O,O') nickel(II)] dinitrate

Crystal data

$[Ni_2(NO_3)_2(C_{17}H_{14}N_6S)_2(CH_4O)_2](NO_3)_2$
M_r = 1098.34
Triclinic, $P\overline{1}$
a = 9.4131 (7) Å
b = 9.9334 (7) Å
c = 13.0829 (6) Å
α = 77.650 (5)°
β = 83.824 (5)°
γ = 70.284 (6)°
V = 1124.11 (12) Å^3
Z = 1
$F(000)$ = 564
D_x = 1.622 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4292 reflections
θ = 3.9–28.5°
μ = 1.02 mm^{-1}
T = 100 K
Block, clear light green
0.29 × 0.18 × 0.08 mm

Data collection

Agilent SuperNova Dual Source diffractometer with Eos detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 16.0793 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min} = 0.907, T_{max} = 1.000
7894 measured reflections
4594 independent reflections
3976 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 26.4°, θ_{min} = 3.0°
h = −11→10
k = −12→12
l = −16→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.075
S = 1.04
4594 reflections
317 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
$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 0.6343P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Experimental. Absorption correction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34k (release 13–08-2014 CrysAlis171. NET) (compiled Aug 13 2014,16:31:05) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4848 (2)	−0.0812 (2)	0.16190 (16)	0.0154 (5)
C2	0.5749 (2)	−0.2254 (2)	0.20181 (17)	0.0176 (5)
H2	0.5294	−0.2930	0.2368	0.021*
C3	0.7287 (2)	−0.2658 (3)	0.18920 (18)	0.0219 (5)
H3	0.7870	−0.3607	0.2162	0.026*
C4	0.7999 (3)	−0.1648 (3)	0.13556 (18)	0.0231 (5)
H4	0.9045	−0.1943	0.1263	0.028*
C5	0.7157 (2)	−0.0236 (3)	0.09716 (17)	0.0207 (5)
H5	0.7635	0.0422	0.0623	0.025*
C6	0.5570 (2)	0.0221 (3)	0.11040 (16)	0.0165 (5)
C7	0.4648 (2)	0.1677 (3)	0.07468 (16)	0.0182 (5)
H7	0.5086	0.2372	0.0408	0.022*
C8	0.3119 (2)	0.2055 (2)	0.09013 (16)	0.0171 (5)
H8	0.2505	0.3011	0.0685	0.021*
C9	0.2486 (2)	0.0973 (2)	0.13945 (16)	0.0141 (4)
C10	0.0869 (2)	0.1262 (2)	0.16618 (16)	0.0138 (4)
C11	−0.1536 (2)	0.2199 (2)	0.19911 (16)	0.0143 (4)
C12	−0.4301 (2)	0.2576 (3)	0.29624 (16)	0.0181 (5)
H12A	−0.5372	0.3120	0.2952	0.022*
H12B	−0.4173	0.1624	0.2816	0.022*
C13	−0.3757 (2)	0.2383 (2)	0.40446 (16)	0.0155 (5)
C14	−0.3585 (2)	0.3533 (3)	0.44177 (17)	0.0199 (5)
H14	−0.3799	0.4452	0.3994	0.024*
C15	−0.3097 (2)	0.3300 (2)	0.54162 (17)	0.0188 (5)
H15	−0.2992	0.4078	0.5654	0.023*
C16	−0.2939 (2)	0.0881 (2)	0.57046 (17)	0.0179 (5)
H16	−0.2723	−0.0028	0.6142	0.022*

C17	−0.3424 (2)	0.1040 (2)	0.47142 (17)	0.0186 (5)
H17	−0.3528	0.0248	0.4496	0.022*
C18	−0.0525 (3)	−0.2458 (3)	0.40587 (19)	0.0284 (6)
H18A	−0.0101	−0.3223	0.4636	0.043*
H18B	−0.1524	−0.2442	0.3952	0.043*
H18C	−0.0572	−0.1539	0.4210	0.043*
N1	0.32990 (19)	−0.04215 (19)	0.17446 (13)	0.0133 (4)
N2	0.03988 (19)	0.02663 (19)	0.22970 (13)	0.0143 (4)
N3	−0.11398 (19)	0.0846 (2)	0.25144 (14)	0.0155 (4)
N4	−0.03254 (19)	0.25038 (19)	0.14351 (13)	0.0137 (4)
N5	−0.0280 (2)	0.3818 (2)	0.07985 (14)	0.0197 (4)
H5A	−0.0308	0.4446	0.1200	0.030*
H5B	−0.1075	0.4183	0.0394	0.030*
N6	−0.27643 (19)	0.1986 (2)	0.60643 (14)	0.0158 (4)
N7	0.2698 (2)	−0.3583 (2)	0.12778 (14)	0.0174 (4)
N8	0.1402 (2)	0.3740 (2)	0.32742 (15)	0.0225 (4)
Ni1	0.19640 (3)	−0.17424 (3)	0.25010 (2)	0.01265 (8)
O2	0.17321 (16)	−0.23163 (16)	0.10154 (11)	0.0170 (3)
O3	0.33181 (16)	−0.38138 (16)	0.21469 (11)	0.0168 (3)
O4	0.30006 (18)	−0.45156 (18)	0.07358 (12)	0.0250 (4)
O5	0.04041 (16)	−0.27120 (17)	0.31305 (11)	0.0183 (3)
H5C	0.0540	−0.3556	0.3004	0.027*
O6	0.1513 (3)	0.2493 (2)	0.32338 (17)	0.0645 (8)
O7	0.21368 (18)	0.3999 (2)	0.38994 (13)	0.0283 (4)
O8	0.05204 (18)	0.47932 (18)	0.26555 (13)	0.0252 (4)
S1	−0.33258 (6)	0.35160 (6)	0.19261 (4)	0.01745 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0149 (11)	0.0214 (12)	0.0097 (10)	−0.0050 (9)	−0.0022 (8)	−0.0032 (9)
C2	0.0179 (12)	0.0187 (12)	0.0152 (11)	−0.0052 (9)	−0.0026 (8)	−0.0015 (9)
C3	0.0152 (12)	0.0259 (13)	0.0205 (12)	0.0006 (10)	−0.0058 (9)	−0.0053 (10)
C4	0.0125 (11)	0.0357 (15)	0.0215 (12)	−0.0062 (10)	−0.0006 (9)	−0.0089 (11)
C5	0.0203 (12)	0.0327 (14)	0.0153 (11)	−0.0150 (10)	−0.0007 (9)	−0.0070 (10)
C6	0.0212 (12)	0.0230 (12)	0.0093 (10)	−0.0108 (10)	−0.0015 (8)	−0.0047 (9)
C7	0.0241 (12)	0.0215 (12)	0.0126 (11)	−0.0126 (10)	−0.0009 (9)	−0.0026 (9)
C8	0.0225 (12)	0.0147 (11)	0.0144 (11)	−0.0067 (9)	−0.0040 (8)	−0.0004 (9)
C9	0.0152 (11)	0.0154 (11)	0.0111 (10)	−0.0038 (9)	−0.0023 (8)	−0.0026 (9)
C10	0.0162 (11)	0.0125 (11)	0.0118 (10)	−0.0030 (9)	−0.0022 (8)	−0.0024 (9)
C11	0.0142 (11)	0.0157 (11)	0.0126 (11)	−0.0037 (9)	−0.0021 (8)	−0.0029 (9)
C12	0.0131 (11)	0.0223 (12)	0.0171 (11)	−0.0038 (9)	−0.0004 (8)	−0.0035 (10)
C13	0.0106 (10)	0.0204 (12)	0.0137 (11)	−0.0031 (9)	0.0008 (8)	−0.0029 (9)
C14	0.0243 (12)	0.0134 (11)	0.0180 (12)	−0.0015 (9)	−0.0041 (9)	−0.0006 (9)
C15	0.0230 (12)	0.0133 (11)	0.0188 (12)	−0.0030 (9)	−0.0023 (9)	−0.0043 (9)
C16	0.0206 (12)	0.0127 (11)	0.0182 (12)	−0.0044 (9)	−0.0013 (9)	0.0005 (9)
C17	0.0192 (12)	0.0184 (12)	0.0206 (12)	−0.0077 (9)	−0.0001 (9)	−0.0062 (10)
C18	0.0265 (13)	0.0297 (15)	0.0261 (14)	−0.0091 (11)	0.0115 (10)	−0.0052 (11)

N1	0.0125 (9)	0.0154 (10)	0.0122 (9)	−0.0042 (7)	−0.0017 (7)	−0.0029 (7)
N2	0.0114 (9)	0.0147 (10)	0.0156 (9)	−0.0025 (7)	−0.0005 (7)	−0.0034 (8)
N3	0.0114 (9)	0.0157 (10)	0.0171 (9)	−0.0011 (7)	−0.0001 (7)	−0.0037 (8)
N4	0.0154 (9)	0.0098 (9)	0.0136 (9)	−0.0027 (7)	−0.0008 (7)	0.0005 (7)
N5	0.0225 (10)	0.0118 (10)	0.0198 (10)	−0.0028 (8)	−0.0023 (8)	0.0038 (8)
N6	0.0161 (9)	0.0131 (9)	0.0157 (9)	−0.0020 (7)	−0.0006 (7)	−0.0023 (8)
N7	0.0181 (10)	0.0165 (10)	0.0171 (10)	−0.0063 (8)	0.0030 (7)	−0.0031 (8)
N8	0.0293 (11)	0.0181 (11)	0.0171 (10)	−0.0047 (9)	0.0036 (8)	−0.0044 (8)
Ni1	0.01295 (15)	0.01106 (15)	0.01256 (15)	−0.00265 (11)	−0.00092 (10)	−0.00111 (11)
O2	0.0149 (8)	0.0150 (8)	0.0178 (8)	−0.0022 (6)	−0.0012 (6)	−0.0003 (6)
O3	0.0161 (8)	0.0159 (8)	0.0167 (8)	−0.0028 (6)	−0.0034 (6)	−0.0019 (6)
O4	0.0312 (10)	0.0224 (9)	0.0221 (9)	−0.0061 (7)	0.0037 (7)	−0.0118 (7)
O5	0.0202 (8)	0.0167 (8)	0.0186 (8)	−0.0080 (7)	0.0049 (6)	−0.0039 (7)
O6	0.128 (2)	0.0128 (10)	0.0513 (14)	−0.0079 (12)	−0.0434 (13)	−0.0069 (10)
O7	0.0277 (10)	0.0330 (11)	0.0253 (9)	−0.0126 (8)	−0.0054 (7)	−0.0008 (8)
O8	0.0235 (9)	0.0169 (9)	0.0319 (10)	−0.0030 (7)	−0.0098 (7)	0.0008 (7)
S1	0.0148 (3)	0.0165 (3)	0.0159 (3)	0.0007 (2)	−0.0015 (2)	−0.0011 (2)

Geometric parameters (Å, º)

C1—N1	1.377 (3)	C14—H14	0.9300
C1—C2	1.414 (3)	C15—N6	1.353 (3)
C1—C6	1.430 (3)	C15—H15	0.9300
C2—C3	1.367 (3)	C16—N6	1.346 (3)
C2—H2	0.9300	C16—C17	1.380 (3)
C3—C4	1.414 (3)	C16—H16	0.9300
C3—H3	0.9300	C17—H17	0.9300
C4—C5	1.372 (3)	C18—O5	1.434 (2)
C4—H4	0.9300	C18—H18A	0.9600
C5—C6	1.410 (3)	C18—H18B	0.9600
C5—H5	0.9300	C18—H18C	0.9600
C6—C7	1.419 (3)	N1—Ni1	2.1377 (18)
C7—C8	1.364 (3)	N2—N3	1.389 (2)
C7—H7	0.9300	N2—Ni1	2.0240 (17)
C8—C9	1.408 (3)	N4—N5	1.402 (2)
C8—H8	0.9300	N5—H5A	0.8900
C9—N1	1.342 (3)	N5—H5B	0.8900
C9—C10	1.467 (3)	N6—Ni1^{i}	2.0339 (18)
C10—N2	1.315 (3)	N7—O4	1.225 (2)
C10—N4	1.362 (3)	N7—O3	1.276 (2)
C11—N3	1.318 (3)	N7—O2	1.280 (2)
C11—N4	1.371 (3)	N8—O6	1.219 (3)
C11—S1	1.747 (2)	N8—O7	1.243 (3)
C12—C13	1.509 (3)	N8—O8	1.279 (2)
C12—S1	1.822 (2)	Ni1—O5	2.0290 (15)
C12—H12A	0.9700	Ni1—N6^{i}	2.0339 (18)
C12—H12B	0.9700	Ni1—O3	2.1411 (15)
C13—C17	1.386 (3)	Ni1—O2	2.1908 (15)

C13—C14	1.397 (3)	O5—H5C	0.8536
C14—C15	1.378 (3)		
N1—C1—C2	119.7 (2)	C16—C17—H17	120.0
N1—C1—C6	121.26 (19)	C13—C17—H17	120.0
C2—C1—C6	119.04 (19)	O5—C18—H18A	109.5
C3—C2—C1	120.3 (2)	O5—C18—H18B	109.5
C3—C2—H2	119.9	H18A—C18—H18B	109.5
C1—C2—H2	119.9	O5—C18—H18C	109.5
C2—C3—C4	120.7 (2)	H18A—C18—H18C	109.5
C2—C3—H3	119.7	H18B—C18—H18C	109.5
C4—C3—H3	119.7	C9—N1—C1	117.91 (19)
C5—C4—C3	120.5 (2)	C9—N1—Ni1	113.71 (13)
C5—C4—H4	119.8	C1—N1—Ni1	128.32 (15)
C3—C4—H4	119.8	C10—N2—N3	109.34 (17)
C4—C5—C6	120.2 (2)	C10—N2—Ni1	113.40 (13)
C4—C5—H5	119.9	N3—N2—Ni1	136.25 (14)
C6—C5—H5	119.9	C11—N3—N2	105.29 (17)
C5—C6—C7	122.6 (2)	C10—N4—C11	105.28 (17)
C5—C6—C1	119.3 (2)	C10—N4—N5	126.26 (17)
C7—C6—C1	118.14 (19)	C11—N4—N5	128.41 (17)
C8—C7—C6	119.9 (2)	N4—N5—H5A	109.4
C8—C7—H7	120.1	N4—N5—H5B	109.2
C6—C7—H7	120.1	H5A—N5—H5B	109.5
C7—C8—C9	118.8 (2)	C16—N6—C15	117.49 (19)
C7—C8—H8	120.6	C16—N6—Ni1^{i}	123.11 (15)
C9—C8—H8	120.6	C15—N6—Ni1^{i}	119.37 (16)
N1—C9—C8	124.00 (19)	O4—N7—O3	122.17 (18)
N1—C9—C10	112.04 (19)	O4—N7—O2	122.40 (19)
C8—C9—C10	123.79 (19)	O3—N7—O2	115.43 (17)
N2—C10—N4	108.97 (18)	O6—N8—O7	121.1 (2)
N2—C10—C9	120.15 (18)	O6—N8—O8	119.1 (2)
N4—C10—C9	130.6 (2)	O7—N8—O8	119.8 (2)
N3—C11—N4	111.10 (17)	N2—Ni1—O5	92.37 (7)
N3—C11—S1	128.32 (16)	N2—Ni1—N6^{i}	103.63 (7)
N4—C11—S1	120.56 (16)	O5—Ni1—N6^{i}	91.55 (7)
C13—C12—S1	114.12 (16)	N2—Ni1—N1	78.70 (7)
C13—C12—H12A	108.7	O5—Ni1—N1	170.65 (6)
S1—C12—H12A	108.7	N6^{i}—Ni1—N1	93.23 (7)
C13—C12—H12B	108.7	N2—Ni1—O3	158.17 (7)
S1—C12—H12B	108.7	O5—Ni1—O3	86.66 (6)
H12A—C12—H12B	107.6	N6^{i}—Ni1—O3	98.20 (6)
C17—C13—C14	117.4 (2)	N1—Ni1—O3	100.58 (6)
C17—C13—C12	120.5 (2)	N2—Ni1—O2	98.34 (6)
C14—C13—C12	122.1 (2)	O5—Ni1—O2	87.30 (6)
C15—C14—C13	119.7 (2)	N6^{i}—Ni1—O2	158.03 (6)
C15—C14—H14	120.1	N1—Ni1—O2	91.24 (6)
C13—C14—H14	120.1	O3—Ni1—O2	59.83 (5)

N6—C15—C14	122.7 (2)	N7—O2—Ni1	91.08 (11)
N6—C15—H15	118.7	N7—O3—Ni1	93.48 (11)
C14—C15—H15	118.7	C18—O5—Ni1	126.36 (15)
N6—C16—C17	122.8 (2)	C18—O5—H5C	112.1
N6—C16—H16	118.6	Ni1—O5—H5C	116.8
C17—C16—H16	118.6	C11—S1—C12	98.93 (10)
C16—C17—C13	119.9 (2)		

N1—C1—C2—C3	179.5 (2)	S1—C11—N4—C10	179.93 (15)
C6—C1—C2—C3	−1.4 (3)	N3—C11—N4—N5	−179.0 (2)
C1—C2—C3—C4	−0.5 (3)	S1—C11—N4—N5	2.3 (3)
C2—C3—C4—C5	1.3 (3)	C17—C16—N6—C15	0.5 (3)
C3—C4—C5—C6	−0.3 (3)	C17—C16—N6—Ni1^{i}	−177.29 (16)
C4—C5—C6—C7	178.3 (2)	C14—C15—N6—C16	−0.6 (3)
C4—C5—C6—C1	−1.5 (3)	C14—C15—N6—Ni1^{i}	177.32 (16)
N1—C1—C6—C5	−178.54 (19)	C10—N2—Ni1—O5	−164.80 (15)
C2—C1—C6—C5	2.4 (3)	N3—N2—Ni1—O5	2.0 (2)
N1—C1—C6—C7	1.6 (3)	C10—N2—Ni1—N6^{i}	103.02 (16)
C2—C1—C6—C7	−177.5 (2)	N3—N2—Ni1—N6^{i}	−90.1 (2)
C5—C6—C7—C8	−179.7 (2)	C10—N2—Ni1—N1	12.41 (15)
C1—C6—C7—C8	0.1 (3)	N3—N2—Ni1—N1	179.3 (2)
C6—C7—C8—C9	−1.5 (3)	C10—N2—Ni1—O3	−77.9 (2)
C7—C8—C9—N1	1.3 (3)	N3—N2—Ni1—O3	89.0 (2)
C7—C8—C9—C10	176.1 (2)	C10—N2—Ni1—O2	−77.19 (16)
N1—C9—C10—N2	8.7 (3)	N3—N2—Ni1—O2	89.7 (2)
C8—C9—C10—N2	−166.7 (2)	C9—N1—Ni1—N2	−8.05 (14)
N1—C9—C10—N4	−178.3 (2)	C1—N1—Ni1—N2	169.11 (18)
C8—C9—C10—N4	6.3 (4)	C9—N1—Ni1—O5	9.3 (5)
S1—C12—C13—C17	−132.14 (18)	C1—N1—Ni1—O5	−173.5 (3)
S1—C12—C13—C14	48.6 (2)	C9—N1—Ni1—N6^{i}	−111.31 (15)
C17—C13—C14—C15	0.2 (3)	C1—N1—Ni1—N6^{i}	65.85 (18)
C12—C13—C14—C15	179.45 (19)	C9—N1—Ni1—O3	149.72 (14)
C13—C14—C15—N6	0.2 (3)	C1—N1—Ni1—O3	−33.12 (18)
N6—C16—C17—C13	−0.1 (3)	C9—N1—Ni1—O2	90.21 (15)
C14—C13—C17—C16	−0.2 (3)	C1—N1—Ni1—O2	−92.63 (17)
C12—C13—C17—C16	−179.51 (19)	O4—N7—O2—Ni1	175.44 (18)
C8—C9—N1—C1	0.4 (3)	O3—N7—O2—Ni1	−4.15 (16)
C10—C9—N1—C1	−174.93 (17)	N2—Ni1—O2—N7	−177.13 (11)
C8—C9—N1—Ni1	177.91 (16)	O5—Ni1—O2—N7	−85.13 (11)
C10—C9—N1—Ni1	2.5 (2)	N6^{i}—Ni1—O2—N7	2.3 (2)
C2—C1—N1—C9	177.23 (19)	N1—Ni1—O2—N7	104.11 (11)
C6—C1—N1—C9	−1.9 (3)	O3—Ni1—O2—N7	2.58 (10)
C2—C1—N1—Ni1	0.2 (3)	O4—N7—O3—Ni1	−175.34 (17)
C6—C1—N1—Ni1	−178.92 (15)	O2—N7—O3—Ni1	4.26 (17)
N4—C10—N2—N3	−0.6 (2)	N2—Ni1—O3—N7	−1.8 (2)
C9—C10—N2—N3	173.82 (18)	O5—Ni1—O3—N7	86.21 (12)
N4—C10—N2—Ni1	169.81 (13)	N6^{i}—Ni1—O3—N7	177.30 (12)
C9—C10—N2—Ni1	−15.8 (3)	N1—Ni1—O3—N7	−87.83 (12)

N4—C11—N3—N2	1.0 (2)	O2—Ni1—O3—N7	−2.60 (10)
S1—C11—N3—N2	179.59 (16)	N2—Ni1—O5—C18	−60.18 (18)
C10—N2—N3—C11	−0.2 (2)	N6^{i}—Ni1—O5—C18	43.54 (18)
Ni1—N2—N3—C11	−167.45 (16)	N1—Ni1—O5—C18	−77.2 (4)
N2—C10—N4—C11	1.2 (2)	O3—Ni1—O5—C18	141.67 (17)
C9—C10—N4—C11	−172.5 (2)	O2—Ni1—O5—C18	−158.42 (17)
N2—C10—N4—N5	178.84 (19)	N3—C11—S1—C12	10.5 (2)
C9—C10—N4—N5	5.2 (4)	N4—C11—S1—C12	−171.04 (18)
N3—C11—N4—C10	−1.3 (2)	C13—C12—S1—C11	67.03 (18)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···O8	0.89	2.27	3.050 (3)	147
N5—H5*B*···O4^{ii}	0.89	2.35	3.222 (3)	165
O5—H5*C*···O8^{iii}	0.85	1.80	2.646 (2)	171
O5—H5*C*···N8^{iii}	0.85	2.49	3.295 (3)	158
O5—H5*C*···O7^{iii}	0.85	2.50	3.114 (2)	130

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

(II) Bis{*μ*-3-[(pyridin-4-ylmethyl)sulfanyl]-5-(quinolin-2-yl)-4*H*-1,2,4-triazol-4-amine}bis[(methanol-*κO*)(nitrato-*κ*^{2}*O*,*O*′) zinc(II)] dinitrate

Crystal data

$[Zn_2(NO_3)_2(C_{17}H_{14}N_6S)_2(CH_4O)_2](NO_3)_2$
M_r = 1111.67
Triclinic, $P\overline{1}$
a = 10.0414 (5) Å
b = 14.4893 (7) Å
c = 15.6001 (8) Å
α = 88.257 (4)°
β = 81.614 (4)°
γ = 80.184 (4)°
V = 2212.53 (19) Å^3
Z = 2
F(000) = 1136
D_x = 1.669 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54184 Å
Cell parameters from 6413 reflections
θ = 4.2–71.0°
μ = 2.97 mm^{-1}
T = 100 K
Prism, colourless
0.21 × 0.07 × 0.04 mm

Data collection

Agilent SuperNova Dual Source diffractometer with Eos detector
Radiation source: sealed X-ray tube, SuperNova (Cu) X-ray Source
Mirror monochromator
Detector resolution: 16.0793 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min} = 0.784, T_{max} = 1.000
14520 measured reflections
7875 independent reflections
6746 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 67.1°, θ_{min} = 4.2°
h = −11→9
k = −17→17
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.112$
$S = 1.05$
7875 reflections
633 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
$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 1.4194P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Special details

Experimental. Absorption correction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34k (release 13–08-2014 CrysAlis171. NET) (compiled Aug 13 2014,16:31:05) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O9	0.0010 (2)	0.1910 (2)	0.05406 (15)	0.0528 (8)
C1	0.8354 (3)	0.32365 (18)	0.79060 (17)	0.0176 (6)
H1	0.9203	0.2853	0.7870	0.021*
C2	0.7678 (3)	0.35566 (19)	0.86972 (17)	0.0193 (6)
H2A	0.8072	0.3391	0.9196	0.023*
C3	0.6385 (3)	0.41373 (18)	0.87577 (17)	0.0189 (6)
H3A	0.5945	0.4365	0.9295	0.023*
C4	0.5777 (3)	0.43653 (18)	0.80385 (18)	0.0193 (6)
H4	0.4914	0.4732	0.8091	0.023*
C5	0.6444 (3)	0.40510 (18)	0.72091 (17)	0.0164 (6)
C6	0.7761 (3)	0.34889 (17)	0.71442 (17)	0.0149 (5)
C7	0.7882 (3)	0.34246 (17)	0.56490 (16)	0.0141 (5)
C8	0.6579 (3)	0.39678 (18)	0.56588 (18)	0.0180 (6)
H8A	0.6209	0.4114	0.5149	0.022*
C9	0.5870 (3)	0.42751 (18)	0.64442 (18)	0.0193 (6)
H9A	0.5004	0.4634	0.6471	0.023*
C10	0.8741 (3)	0.30341 (17)	0.48531 (17)	0.0140 (5)
C11	0.9589 (3)	0.25187 (17)	0.35641 (16)	0.0149 (5)
C12	1.1115 (3)	0.14148 (18)	0.23094 (17)	0.0170 (6)
H12A	1.1463	0.1344	0.1697	0.020*
H12B	1.1835	0.1572	0.2602	0.020*
C13	1.0732 (3)	0.05090 (18)	0.26652 (16)	0.0159 (5)

C14	1.1180 (3)	0.01082 (18)	0.34141 (17)	0.0168 (5)
H14A	1.1746	0.0395	0.3703	0.020*
C15	1.0782 (3)	−0.07191 (19)	0.37281 (17)	0.0184 (6)
H15	1.1096	−0.0980	0.4228	0.022*
C16	0.9520 (3)	−0.07797 (19)	0.26141 (17)	0.0198 (6)
H16	0.8950	−0.1079	0.2340	0.024*
C17	0.9884 (3)	0.00422 (19)	0.22601 (17)	0.0201 (6)
H17	0.9568	0.0285	0.1754	0.024*
C18	0.6390 (3)	−0.1720 (2)	0.4954 (2)	0.0360 (8)
H18A	0.6119	−0.2275	0.4763	0.054*
H18B	0.5630	−0.1215	0.4994	0.054*
H18C	0.6683	−0.1834	0.5512	0.054*
C19	0.3477 (3)	0.34179 (19)	0.27779 (18)	0.0197 (6)
H19	0.4335	0.3046	0.2736	0.024*
C20	0.2808 (3)	0.37392 (19)	0.35726 (18)	0.0219 (6)
H20	0.3224	0.3588	0.4065	0.026*
C21	0.1495 (3)	0.42958 (19)	0.36513 (18)	0.0236 (6)
H21	0.1051	0.4507	0.4193	0.028*
C22	0.0883 (3)	0.45210 (19)	0.29347 (18)	0.0221 (6)
H22	0.0017	0.4883	0.2991	0.026*
C23	0.1546 (3)	0.42135 (18)	0.20990 (18)	0.0187 (6)
C24	0.2858 (3)	0.36531 (17)	0.20217 (17)	0.0158 (5)
C25	0.2904 (3)	0.35376 (18)	0.05370 (17)	0.0156 (5)
C26	0.1614 (3)	0.40983 (19)	0.05595 (18)	0.0200 (6)
H26	0.1228	0.4240	0.0055	0.024*
C27	0.0938 (3)	0.44319 (19)	0.13474 (19)	0.0225 (6)
H27	0.0079	0.4802	0.1383	0.027*
C28	0.3671 (3)	0.30816 (18)	−0.02562 (16)	0.0147 (5)
C29	0.4354 (3)	0.24557 (17)	−0.15247 (16)	0.0155 (5)
C30	0.5747 (3)	0.12854 (18)	−0.28003 (17)	0.0186 (6)
H30A	0.6001	0.1191	−0.3419	0.022*
H30B	0.6514	0.1466	−0.2574	0.022*
C31	0.5434 (3)	0.03842 (18)	−0.23759 (17)	0.0158 (5)
C32	0.6022 (3)	0.00361 (18)	−0.16546 (17)	0.0169 (6)
H32	0.6623	0.0355	−0.1432	0.020*
C33	0.5710 (3)	−0.07837 (19)	−0.12699 (17)	0.0171 (6)
H33	0.6118	−0.1010	−0.0790	0.021*
C34	0.4268 (3)	−0.09315 (19)	−0.22595 (18)	0.0219 (6)
H34	0.3661	−0.1259	−0.2465	0.026*
C35	0.4543 (3)	−0.01180 (19)	−0.26837 (18)	0.0219 (6)
H35	0.4136	0.0090	−0.3169	0.026*
C62	0.7793 (4)	0.0800 (2)	0.0034 (2)	0.0449 (10)
H62A	0.8322	0.0392	0.0402	0.067*
H62B	0.8290	0.0795	−0.0540	0.067*
H62C	0.6942	0.0588	0.0018	0.067*
N1	0.9960 (2)	−0.11640 (15)	0.33417 (14)	0.0163 (5)
N2	1.0517 (2)	0.22035 (15)	0.40600 (14)	0.0158 (5)
N3	0.9955 (2)	0.25343 (15)	0.48816 (13)	0.0138 (4)

N4	0.8470 (2)	0.30474 (15)	0.40262 (14)	0.0148 (5)
N5	0.7219 (2)	0.34077 (17)	0.37356 (15)	0.0204 (5)
H5A	0.6797	0.2907	0.3638	0.024*
H5B	0.7402	0.3781	0.3257	0.024*
N6	0.8470 (2)	0.31887 (14)	0.63554 (14)	0.0136 (4)
N7	0.3530 (2)	0.33242 (15)	0.12322 (14)	0.0144 (5)
N8	0.4852 (2)	0.25269 (15)	−0.02394 (14)	0.0146 (5)
N9	0.5303 (2)	0.21180 (15)	−0.10474 (14)	0.0167 (5)
N10	0.3332 (2)	0.30683 (15)	−0.10648 (14)	0.0150 (5)
N11	0.2109 (2)	0.35226 (16)	−0.13419 (15)	0.0194 (5)
H11A	0.1625	0.3031	−0.1421	0.023*
H11B	0.2348	0.3792	−0.1865	0.023*
N12	0.4843 (2)	−0.12685 (15)	−0.15610 (14)	0.0163 (5)
N13	0.8108 (2)	−0.37585 (15)	0.35907 (14)	0.0171 (5)
N14	0.6875 (2)	0.37159 (16)	0.14884 (15)	0.0190 (5)
N15	0.0875 (3)	0.17909 (17)	−0.01357 (16)	0.0243 (5)
N16	0.7093 (2)	0.10437 (17)	0.46048 (15)	0.0202 (5)
O1	0.86417 (19)	−0.31119 (13)	0.31515 (12)	0.0191 (4)
O2	0.8159 (3)	−0.38048 (16)	0.43720 (13)	0.0353 (6)
O3	0.7588 (2)	−0.43063 (13)	0.32024 (13)	0.0218 (4)
O4	0.74837 (19)	−0.14797 (13)	0.43490 (12)	0.0205 (4)
H4A	0.7344	−0.0885	0.4102	0.025*
O5	0.7536 (2)	0.17212 (14)	0.03642 (14)	0.0282 (5)
H5	0.8277	0.2033	0.0340	0.034*
O6	0.6529 (2)	0.29791 (13)	0.18695 (13)	0.0235 (4)
O7	0.6601 (2)	0.38603 (17)	0.07346 (13)	0.0331 (5)
O8	0.7415 (2)	0.42477 (14)	0.18700 (13)	0.0232 (4)
O10	0.2092 (2)	0.15304 (16)	−0.00498 (16)	0.0360 (6)
O11	0.0502 (2)	0.19419 (16)	−0.08553 (13)	0.0312 (5)
O12	0.6843 (2)	0.17514 (14)	0.50813 (13)	0.0253 (5)
O13	0.7271 (3)	0.11297 (18)	0.38083 (14)	0.0413 (6)
O14	0.7157 (3)	0.02480 (14)	0.49573 (14)	0.0359 (6)
S1	0.96593 (7)	0.23574 (4)	0.24530 (4)	0.01697 (15)
S2	0.42808 (7)	0.22190 (4)	−0.26045 (4)	0.01849 (16)
Zn1	0.94009 (4)	−0.23344 (2)	0.39500 (2)	0.01448 (11)
Zn2	0.56310 (4)	0.24394 (2)	0.09007 (2)	0.01486 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O9	0.0269 (14)	0.112 (2)	0.0198 (12)	−0.0119 (14)	−0.0026 (10)	−0.0089 (13)
C1	0.0176 (15)	0.0160 (13)	0.0189 (13)	−0.0021 (11)	−0.0019 (11)	−0.0025 (10)
C2	0.0254 (16)	0.0162 (13)	0.0168 (13)	−0.0048 (11)	−0.0031 (11)	−0.0012 (10)
C3	0.0214 (15)	0.0167 (13)	0.0166 (13)	−0.0046 (11)	0.0061 (11)	−0.0058 (10)
C4	0.0172 (15)	0.0131 (13)	0.0248 (14)	−0.0010 (11)	0.0056 (11)	−0.0068 (11)
C5	0.0151 (14)	0.0119 (12)	0.0216 (14)	−0.0028 (10)	0.0012 (11)	−0.0054 (10)
C6	0.0173 (14)	0.0112 (12)	0.0162 (13)	−0.0044 (10)	0.0008 (10)	−0.0046 (10)
C7	0.0151 (14)	0.0121 (12)	0.0158 (13)	−0.0049 (10)	−0.0006 (10)	−0.0044 (10)

C8	0.0186 (15)	0.0169 (13)	0.0184 (13)	−0.0001 (11)	−0.0045 (11)	−0.0046 (10)
C9	0.0143 (14)	0.0155 (13)	0.0265 (15)	0.0010 (11)	−0.0009 (11)	−0.0051 (11)
C10	0.0154 (14)	0.0108 (12)	0.0166 (13)	−0.0023 (10)	−0.0039 (10)	−0.0030 (10)
C11	0.0173 (14)	0.0110 (12)	0.0154 (13)	−0.0024 (10)	0.0022 (10)	−0.0032 (10)
C12	0.0189 (15)	0.0164 (13)	0.0138 (12)	−0.0005 (11)	0.0013 (10)	−0.0017 (10)
C13	0.0142 (14)	0.0143 (13)	0.0155 (13)	0.0039 (10)	0.0042 (10)	−0.0052 (10)
C14	0.0122 (13)	0.0175 (13)	0.0208 (13)	−0.0022 (10)	−0.0021 (10)	−0.0051 (10)
C15	0.0192 (15)	0.0185 (14)	0.0170 (13)	0.0007 (11)	−0.0050 (11)	−0.0023 (10)
C16	0.0203 (15)	0.0204 (14)	0.0200 (14)	−0.0022 (11)	−0.0067 (11)	−0.0059 (11)
C17	0.0251 (16)	0.0184 (14)	0.0163 (13)	−0.0003 (11)	−0.0050 (11)	−0.0033 (10)
C18	0.0198 (17)	0.0251 (17)	0.058 (2)	−0.0014 (13)	0.0073 (15)	−0.0024 (15)
C19	0.0217 (15)	0.0159 (13)	0.0205 (14)	−0.0018 (11)	−0.0009 (11)	−0.0023 (10)
C20	0.0324 (17)	0.0161 (14)	0.0167 (13)	−0.0049 (12)	−0.0003 (12)	−0.0017 (10)
C21	0.0327 (18)	0.0171 (14)	0.0187 (14)	−0.0070 (12)	0.0088 (12)	−0.0073 (11)
C22	0.0248 (16)	0.0154 (14)	0.0238 (15)	−0.0031 (11)	0.0051 (12)	−0.0076 (11)
C23	0.0230 (15)	0.0118 (13)	0.0207 (14)	−0.0032 (11)	0.0000 (11)	−0.0055 (10)
C24	0.0187 (14)	0.0098 (12)	0.0184 (13)	−0.0035 (10)	0.0013 (11)	−0.0046 (10)
C25	0.0192 (15)	0.0116 (12)	0.0158 (13)	−0.0035 (10)	−0.0002 (11)	−0.0034 (10)
C26	0.0223 (15)	0.0180 (14)	0.0189 (14)	0.0017 (11)	−0.0052 (11)	−0.0049 (11)
C27	0.0181 (15)	0.0178 (14)	0.0289 (15)	0.0030 (11)	−0.0002 (12)	−0.0070 (11)
C28	0.0164 (14)	0.0124 (12)	0.0153 (13)	−0.0031 (10)	−0.0012 (10)	−0.0024 (10)
C29	0.0198 (15)	0.0114 (12)	0.0145 (12)	−0.0032 (10)	0.0020 (10)	−0.0053 (10)
C30	0.0241 (15)	0.0140 (13)	0.0156 (13)	0.0007 (11)	0.0006 (11)	−0.0030 (10)
C31	0.0132 (14)	0.0144 (13)	0.0167 (13)	0.0017 (10)	0.0044 (10)	−0.0064 (10)
C32	0.0131 (14)	0.0172 (13)	0.0201 (13)	−0.0022 (10)	−0.0003 (10)	−0.0054 (10)
C33	0.0135 (14)	0.0196 (14)	0.0180 (13)	0.0007 (11)	−0.0043 (10)	−0.0038 (10)
C34	0.0273 (16)	0.0175 (14)	0.0227 (14)	−0.0030 (12)	−0.0096 (12)	−0.0042 (11)
C35	0.0289 (17)	0.0181 (14)	0.0202 (14)	−0.0021 (12)	−0.0102 (12)	−0.0011 (11)
C62	0.039 (2)	0.041 (2)	0.054 (2)	0.0130 (16)	−0.0190 (18)	−0.0311 (18)
N1	0.0173 (12)	0.0131 (11)	0.0171 (11)	0.0011 (9)	−0.0009 (9)	−0.0046 (8)
N2	0.0173 (12)	0.0154 (11)	0.0139 (11)	−0.0024 (9)	0.0005 (9)	−0.0041 (8)
N3	0.0143 (12)	0.0141 (11)	0.0127 (10)	−0.0015 (9)	−0.0008 (8)	−0.0041 (8)
N4	0.0129 (12)	0.0160 (11)	0.0148 (11)	−0.0006 (9)	−0.0009 (9)	−0.0038 (8)
N5	0.0176 (13)	0.0231 (12)	0.0195 (12)	0.0028 (10)	−0.0065 (10)	−0.0024 (9)
N6	0.0121 (11)	0.0116 (10)	0.0166 (11)	−0.0017 (8)	0.0002 (9)	−0.0040 (8)
N7	0.0139 (12)	0.0123 (11)	0.0169 (11)	−0.0021 (9)	−0.0012 (9)	−0.0039 (8)
N8	0.0150 (12)	0.0140 (11)	0.0139 (11)	−0.0008 (9)	0.0004 (9)	−0.0054 (8)
N9	0.0201 (13)	0.0158 (11)	0.0135 (11)	−0.0014 (9)	−0.0008 (9)	−0.0049 (9)
N10	0.0158 (12)	0.0120 (11)	0.0162 (11)	0.0007 (9)	−0.0020 (9)	−0.0035 (8)
N11	0.0159 (12)	0.0235 (12)	0.0182 (11)	0.0007 (10)	−0.0050 (9)	−0.0033 (9)
N12	0.0170 (12)	0.0125 (11)	0.0185 (11)	0.0011 (9)	−0.0027 (9)	−0.0030 (9)
N13	0.0147 (12)	0.0166 (11)	0.0185 (12)	0.0009 (9)	−0.0009 (9)	−0.0053 (9)
N14	0.0135 (12)	0.0206 (12)	0.0211 (12)	0.0030 (9)	−0.0021 (9)	−0.0095 (9)
N15	0.0233 (14)	0.0261 (13)	0.0256 (13)	−0.0067 (10)	−0.0063 (11)	−0.0019 (10)
N16	0.0166 (12)	0.0244 (13)	0.0210 (12)	−0.0045 (10)	−0.0047 (9)	−0.0033 (10)
O1	0.0205 (11)	0.0182 (10)	0.0200 (10)	−0.0059 (8)	−0.0033 (8)	−0.0044 (8)
O2	0.0536 (16)	0.0397 (13)	0.0155 (11)	−0.0135 (11)	−0.0075 (10)	−0.0034 (9)
O3	0.0212 (11)	0.0193 (10)	0.0276 (11)	−0.0078 (8)	−0.0059 (8)	−0.0062 (8)

O4	0.0141 (10)	0.0195 (10)	0.0259 (10)	0.0010 (8)	0.0000 (8)	−0.0024 (8)
O5	0.0193 (11)	0.0252 (11)	0.0371 (12)	0.0000 (9)	0.0041 (9)	−0.0113 (9)
O6	0.0219 (11)	0.0187 (10)	0.0316 (11)	−0.0072 (8)	−0.0044 (9)	−0.0059 (8)
O7	0.0332 (13)	0.0488 (14)	0.0157 (10)	0.0027 (11)	−0.0077 (9)	−0.0070 (9)
O8	0.0249 (11)	0.0196 (10)	0.0277 (11)	−0.0054 (8)	−0.0093 (9)	−0.0048 (8)
O10	0.0177 (12)	0.0400 (14)	0.0524 (15)	−0.0051 (10)	−0.0133 (10)	0.0074 (11)
O11	0.0308 (13)	0.0442 (14)	0.0207 (11)	−0.0080 (10)	−0.0095 (9)	0.0010 (9)
O12	0.0281 (12)	0.0188 (10)	0.0289 (11)	−0.0043 (8)	−0.0017 (9)	−0.0064 (8)
O13	0.0585 (17)	0.0537 (16)	0.0175 (11)	−0.0257 (13)	−0.0051 (11)	−0.0031 (10)
O14	0.0570 (16)	0.0164 (11)	0.0367 (13)	−0.0047 (10)	−0.0157 (11)	−0.0015 (9)
S1	0.0219 (4)	0.0144 (3)	0.0127 (3)	0.0016 (3)	−0.0011 (2)	−0.0030 (2)
S2	0.0270 (4)	0.0139 (3)	0.0129 (3)	0.0019 (3)	−0.0028 (3)	−0.0040 (2)
Zn1	0.0147 (2)	0.01331 (19)	0.01557 (19)	−0.00140 (14)	−0.00285 (14)	−0.00415 (13)
Zn2	0.0161 (2)	0.01338 (19)	0.01497 (18)	−0.00124 (14)	−0.00262 (14)	−0.00371 (13)

Geometric parameters (Å, º)

O9—N15	1.261 (3)	C27—H27	0.9300
C1—C2	1.372 (4)	C28—N8	1.317 (3)
C1—C6	1.417 (4)	C28—N10	1.355 (3)
C1—H1	0.9300	C29—N9	1.315 (3)
C2—C3	1.414 (4)	C29—N10	1.367 (3)
C2—H2A	0.9300	C29—S2	1.744 (3)
C3—C4	1.359 (4)	C30—C31	1.506 (4)
C3—H3A	0.9300	C30—S2	1.818 (3)
C4—C5	1.417 (4)	C30—H30A	0.9700
C4—H4	0.9300	C30—H30B	0.9700
C5—C9	1.405 (4)	C31—C32	1.388 (4)
C5—C6	1.422 (4)	C31—C35	1.389 (4)
C6—N6	1.372 (3)	C32—C33	1.377 (4)
C7—N6	1.334 (3)	C32—H32	0.9300
C7—C8	1.406 (4)	C33—N12	1.343 (3)
C7—C10	1.473 (3)	C33—H33	0.9300
C8—C9	1.370 (4)	C34—N12	1.347 (4)
C8—H8A	0.9300	C34—C35	1.383 (4)
C9—H9A	0.9300	C34—H34	0.9300
C10—N3	1.313 (3)	C35—H35	0.9300
C10—N4	1.356 (3)	C62—O5	1.413 (4)
C11—N2	1.311 (3)	C62—H62A	0.9600
C11—N4	1.368 (3)	C62—H62B	0.9600
C11—S1	1.746 (3)	C62—H62C	0.9600
C12—C13	1.498 (4)	N1—Zn1	2.040 (2)
C12—S1	1.815 (3)	N2—N3	1.387 (3)
C12—H12A	0.9700	N3—Zn1^{i}	2.018 (2)
C12—H12B	0.9700	N4—N5	1.409 (3)
C13—C14	1.389 (4)	N5—H5A	0.9275
C13—C17	1.400 (4)	N5—H5B	0.9235
C14—C15	1.381 (4)	N6—Zn1^{i}	2.273 (2)

C14—H14A	0.9300	N7—Zn2	2.272 (2)
C15—N1	1.346 (4)	N8—N9	1.390 (3)
C15—H15	0.9300	N8—Zn2	2.037 (2)
C16—N1	1.348 (4)	N10—N11	1.411 (3)
C16—C17	1.381 (4)	N11—H11A	0.9485
C16—H16	0.9300	N11—H11B	0.9117
C17—H17	0.9300	N12—Zn2^{ii}	2.047 (2)
C18—O4	1.424 (4)	N13—O2	1.227 (3)
C18—H18A	0.9600	N13—O3	1.238 (3)
C18—H18B	0.9600	N13—O1	1.288 (3)
C18—H18C	0.9600	N14—O8	1.227 (3)
C19—C20	1.375 (4)	N14—O7	1.250 (3)
C19—C24	1.418 (4)	N14—O6	1.281 (3)
C19—H19	0.9300	N15—O11	1.236 (3)
C20—C21	1.414 (4)	N15—O10	1.241 (3)
C20—H20	0.9300	N16—O13	1.235 (3)
C21—C22	1.357 (4)	N16—O12	1.253 (3)
C21—H21	0.9300	N16—O14	1.258 (3)
C22—C23	1.422 (4)	O1—Zn1	2.0142 (18)
C22—H22	0.9300	O4—Zn1	2.1241 (18)
C23—C27	1.403 (4)	O4—H4A	0.9300
C23—C24	1.416 (4)	O5—Zn2	2.086 (2)
C24—N7	1.372 (3)	O5—H5	0.9300
C25—N7	1.334 (3)	O6—Zn2	2.102 (2)
C25—C26	1.403 (4)	O7—Zn2	2.415 (3)
C25—C28	1.470 (3)	Zn1—N3^{i}	2.018 (2)
C26—C27	1.373 (4)	Zn1—N6^{i}	2.273 (2)
C26—H26	0.9300	Zn2—N12^{ii}	2.047 (2)

C2—C1—C6	120.1 (3)	C32—C31—C30	120.6 (2)
C2—C1—H1	120.0	C35—C31—C30	121.4 (2)
C6—C1—H1	120.0	C33—C32—C31	119.7 (3)
C1—C2—C3	120.3 (3)	C33—C32—H32	120.1
C1—C2—H2A	119.9	C31—C32—H32	120.1
C3—C2—H2A	119.9	N12—C33—C32	122.6 (3)
C4—C3—C2	120.6 (2)	N12—C33—H33	118.7
C4—C3—H3A	119.7	C32—C33—H33	118.7
C2—C3—H3A	119.7	N12—C34—C35	122.7 (3)
C3—C4—C5	120.8 (3)	N12—C34—H34	118.6
C3—C4—H4	119.6	C35—C34—H34	118.6
C5—C4—H4	119.6	C34—C35—C31	119.2 (3)
C9—C5—C4	123.1 (3)	C34—C35—H35	120.4
C9—C5—C6	118.2 (2)	C31—C35—H35	120.4
C4—C5—C6	118.6 (2)	O5—C62—H62A	109.5
N6—C6—C1	119.4 (2)	O5—C62—H62B	109.5
N6—C6—C5	121.1 (2)	H62A—C62—H62B	109.5
C1—C6—C5	119.5 (2)	O5—C62—H62C	109.5
N6—C7—C8	124.2 (2)	H62A—C62—H62C	109.5

N6—C7—C10	112.3 (2)	H62B—C62—H62C	109.5
C8—C7—C10	123.5 (2)	C15—N1—C16	117.8 (2)
C9—C8—C7	117.8 (3)	C15—N1—Zn1	116.67 (18)
C9—C8—H8A	121.1	C16—N1—Zn1	125.39 (19)
C7—C8—H8A	121.1	C11—N2—N3	105.0 (2)
C8—C9—C5	120.4 (3)	C10—N3—N2	109.6 (2)
C8—C9—H9A	119.8	C10—N3—Zn1^{i}	117.57 (17)
C5—C9—H9A	119.8	N2—N3—Zn1^{i}	132.71 (17)
N3—C10—N4	108.6 (2)	C10—N4—C11	105.5 (2)
N3—C10—C7	120.9 (2)	C10—N4—N5	126.7 (2)
N4—C10—C7	130.4 (2)	C11—N4—N5	127.1 (2)
N2—C11—N4	111.3 (2)	N4—N5—H5A	108.0
N2—C11—S1	128.3 (2)	N4—N5—H5B	107.7
N4—C11—S1	120.4 (2)	H5A—N5—H5B	115.0
C13—C12—S1	111.22 (19)	C7—N6—C6	118.2 (2)
C13—C12—H12A	109.4	C7—N6—Zn1^{i}	112.87 (16)
S1—C12—H12A	109.4	C6—N6—Zn1^{i}	128.88 (18)
C13—C12—H12B	109.4	C25—N7—C24	118.0 (2)
S1—C12—H12B	109.4	C25—N7—Zn2	112.55 (16)
H12A—C12—H12B	108.0	C24—N7—Zn2	129.41 (18)
C14—C13—C17	117.4 (3)	C28—N8—N9	109.5 (2)
C14—C13—C12	121.6 (2)	C28—N8—Zn2	116.80 (17)
C17—C13—C12	121.0 (2)	N9—N8—Zn2	133.66 (17)
C15—C14—C13	119.6 (3)	C29—N9—N8	105.0 (2)
C15—C14—H14A	120.2	C28—N10—C29	105.7 (2)
C13—C14—H14A	120.2	C28—N10—N11	126.6 (2)
N1—C15—C14	122.9 (3)	C29—N10—N11	127.4 (2)
N1—C15—H15	118.6	N10—N11—H11A	104.5
C14—C15—H15	118.6	N10—N11—H11B	106.7
N1—C16—C17	122.4 (3)	H11A—N11—H11B	109.3
N1—C16—H16	118.8	C33—N12—C34	117.9 (2)
C17—C16—H16	118.8	C33—N12—Zn2^{ii}	119.40 (18)
C16—C17—C13	119.8 (3)	C34—N12—Zn2^{ii}	122.67 (19)
C16—C17—H17	120.1	O2—N13—O3	123.5 (2)
C13—C17—H17	120.1	O2—N13—O1	118.0 (2)
O4—C18—H18A	109.5	O3—N13—O1	118.5 (2)
O4—C18—H18B	109.5	O8—N14—O7	123.5 (3)
H18A—C18—H18B	109.5	O8—N14—O6	120.2 (2)
O4—C18—H18C	109.5	O7—N14—O6	116.4 (2)
H18A—C18—H18C	109.5	O11—N15—O10	122.1 (3)
H18B—C18—H18C	109.5	O11—N15—O9	120.0 (3)
C20—C19—C24	120.0 (3)	O10—N15—O9	117.9 (3)
C20—C19—H19	120.0	O13—N16—O12	120.5 (2)
C24—C19—H19	120.0	O13—N16—O14	121.0 (2)
C19—C20—C21	120.9 (3)	O12—N16—O14	118.4 (2)
C19—C20—H20	119.6	N13—O1—Zn1	109.55 (15)
C21—C20—H20	119.6	C18—O4—Zn1	126.92 (18)
C22—C21—C20	119.8 (3)	C18—O4—H4A	116.5

C22—C21—H21	120.1	Zn1—O4—H4A	116.5
C20—C21—H21	120.1	C62—O5—Zn2	125.4 (2)
C21—C22—C23	121.1 (3)	C62—O5—H5	117.3
C21—C22—H22	119.4	Zn2—O5—H5	117.3
C23—C22—H22	119.4	N14—O6—Zn2	100.56 (16)
C27—C23—C24	118.6 (2)	N14—O7—Zn2	86.72 (17)
C27—C23—C22	122.4 (3)	C11—S1—C12	97.95 (12)
C24—C23—C22	119.0 (3)	C29—S2—C30	99.36 (13)
N7—C24—C23	121.3 (2)	O1—Zn1—N3^{i}	135.43 (8)
N7—C24—C19	119.6 (2)	O1—Zn1—N1	111.59 (8)
C23—C24—C19	119.2 (2)	N3^{i}—Zn1—N1	111.92 (9)
N7—C25—C26	124.0 (2)	O1—Zn1—O4	93.77 (8)
N7—C25—C28	113.0 (2)	N3^{i}—Zn1—O4	98.42 (8)
C26—C25—C28	122.9 (2)	N1—Zn1—O4	85.96 (8)
C27—C26—C25	118.2 (3)	O1—Zn1—N6^{i}	92.05 (8)
C27—C26—H26	120.9	N3^{i}—Zn1—N6^{i}	76.25 (8)
C25—C26—H26	120.9	N1—Zn1—N6^{i}	93.36 (8)
C26—C27—C23	119.9 (3)	O4—Zn1—N6^{i}	173.96 (7)
C26—C27—H27	120.1	N8—Zn2—N12^{ii}	109.00 (9)
C23—C27—H27	120.1	N8—Zn2—O5	94.14 (9)
N8—C28—N10	108.6 (2)	N12^{ii}—Zn2—O5	91.60 (9)
N8—C28—C25	120.8 (2)	N8—Zn2—O6	153.19 (8)
N10—C28—C25	130.5 (2)	N12^{ii}—Zn2—O6	97.28 (8)
N9—C29—N10	111.2 (2)	O5—Zn2—O6	90.19 (8)
N9—C29—S2	128.6 (2)	N8—Zn2—N7	76.29 (8)
N10—C29—S2	120.2 (2)	N12^{ii}—Zn2—N7	95.83 (8)
C31—C30—S2	111.13 (19)	O5—Zn2—N7	169.39 (8)
C31—C30—H30A	109.4	O6—Zn2—N7	96.35 (8)
S2—C30—H30A	109.4	N8—Zn2—O7	97.34 (8)
C31—C30—H30B	109.4	N12^{ii}—Zn2—O7	153.63 (8)
S2—C30—H30B	109.4	O5—Zn2—O7	87.72 (8)
H30A—C30—H30B	108.0	O6—Zn2—O7	56.37 (7)
C32—C31—C35	117.9 (3)	N7—Zn2—O7	88.97 (8)

C6—C1—C2—C3	0.2 (4)	C23—C24—N7—C25	−0.9 (4)
C1—C2—C3—C4	1.8 (4)	C19—C24—N7—C25	178.3 (2)
C2—C3—C4—C5	−2.0 (4)	C23—C24—N7—Zn2	178.96 (18)
C3—C4—C5—C9	−179.2 (3)	C19—C24—N7—Zn2	−1.9 (4)
C3—C4—C5—C6	0.2 (4)	N10—C28—N8—N9	−1.2 (3)
C2—C1—C6—N6	177.9 (2)	C25—C28—N8—N9	174.4 (2)
C2—C1—C6—C5	−2.0 (4)	N10—C28—N8—Zn2	178.62 (16)
C9—C5—C6—N6	1.4 (4)	C25—C28—N8—Zn2	−5.7 (3)
C4—C5—C6—N6	−178.0 (2)	N10—C29—N9—N8	0.8 (3)
C9—C5—C6—C1	−178.8 (2)	S2—C29—N9—N8	−179.4 (2)
C4—C5—C6—C1	1.8 (4)	C28—N8—N9—C29	0.2 (3)
N6—C7—C8—C9	0.1 (4)	Zn2—N8—N9—C29	−179.54 (19)
C10—C7—C8—C9	178.7 (2)	N8—C28—N10—C29	1.6 (3)
C7—C8—C9—C5	0.2 (4)	C25—C28—N10—C29	−173.4 (3)

C4—C5—C9—C8	178.5 (3)	N8—C28—N10—N11	176.0 (2)
C6—C5—C9—C8	−0.9 (4)	C25—C28—N10—N11	0.9 (4)
N6—C7—C10—N3	−1.5 (4)	N9—C29—N10—C28	−1.6 (3)
C8—C7—C10—N3	179.7 (2)	S2—C29—N10—C28	178.64 (19)
N6—C7—C10—N4	174.0 (3)	N9—C29—N10—N11	−175.8 (2)
C8—C7—C10—N4	−4.8 (4)	S2—C29—N10—N11	4.4 (4)
S1—C12—C13—C14	−109.0 (3)	C32—C33—N12—C34	0.3 (4)
S1—C12—C13—C17	69.9 (3)	C32—C33—N12—Zn2^{ii}	−176.59 (19)
C17—C13—C14—C15	−0.1 (4)	C35—C34—N12—C33	0.4 (4)
C12—C13—C14—C15	178.8 (2)	C35—C34—N12—Zn2^{ii}	177.1 (2)
C13—C14—C15—N1	−0.4 (4)	O2—N13—O1—Zn1	−0.9 (3)
N1—C16—C17—C13	−0.5 (4)	O3—N13—O1—Zn1	179.97 (17)
C14—C13—C17—C16	0.5 (4)	O8—N14—O6—Zn2	177.93 (19)
C12—C13—C17—C16	−178.4 (2)	O7—N14—O6—Zn2	−0.3 (2)
C24—C19—C20—C21	0.7 (4)	O8—N14—O7—Zn2	−177.9 (2)
C19—C20—C21—C22	−0.2 (4)	O6—N14—O7—Zn2	0.3 (2)
C20—C21—C22—C23	−0.6 (4)	N2—C11—S1—C12	14.3 (3)
C21—C22—C23—C27	179.7 (3)	N4—C11—S1—C12	−167.1 (2)
C21—C22—C23—C24	0.8 (4)	C13—C12—S1—C11	74.5 (2)
C27—C23—C24—N7	−0.2 (4)	N9—C29—S2—C30	7.0 (3)
C22—C23—C24—N7	178.8 (2)	N10—C29—S2—C30	−173.3 (2)
C27—C23—C24—C19	−179.3 (3)	C31—C30—S2—C29	74.8 (2)
C22—C23—C24—C19	−0.3 (4)	N13—O1—Zn1—N3^{i}	23.2 (2)
C20—C19—C24—N7	−179.6 (2)	N13—O1—Zn1—N1	−170.02 (15)
C20—C19—C24—C23	−0.5 (4)	N13—O1—Zn1—O4	−82.87 (16)
N7—C25—C26—C27	−1.5 (4)	N13—O1—Zn1—N6^{i}	95.55 (16)
C28—C25—C26—C27	175.0 (3)	C15—N1—Zn1—O1	−163.84 (18)
C25—C26—C27—C23	0.4 (4)	C16—N1—Zn1—O1	19.6 (2)
C24—C23—C27—C26	0.4 (4)	C15—N1—Zn1—N3^{i}	6.2 (2)
C22—C23—C27—C26	−178.6 (3)	C16—N1—Zn1—N3^{i}	−170.3 (2)
N7—C25—C28—N8	−0.1 (4)	C15—N1—Zn1—O4	103.70 (19)
C26—C25—C28—N8	−176.9 (2)	C16—N1—Zn1—O4	−72.8 (2)
N7—C25—C28—N10	174.5 (3)	C15—N1—Zn1—N6^{i}	−70.29 (19)
C26—C25—C28—N10	−2.4 (4)	C16—N1—Zn1—N6^{i}	113.2 (2)
S2—C30—C31—C32	−108.9 (2)	C18—O4—Zn1—O1	77.4 (2)
S2—C30—C31—C35	70.4 (3)	C18—O4—Zn1—N3^{i}	−59.6 (2)
C35—C31—C32—C33	0.0 (4)	C18—O4—Zn1—N1	−171.2 (2)
C30—C31—C32—C33	179.3 (2)	C18—O4—Zn1—N6^{i}	−87.4 (8)
C31—C32—C33—N12	−0.5 (4)	C28—N8—Zn2—N12^{ii}	97.6 (2)
N12—C34—C35—C31	−0.8 (4)	N9—N8—Zn2—N12^{ii}	−82.6 (2)
C32—C31—C35—C34	0.6 (4)	C28—N8—Zn2—O5	−169.24 (19)
C30—C31—C35—C34	−178.7 (2)	N9—N8—Zn2—O5	10.5 (2)
C14—C15—N1—C16	0.4 (4)	C28—N8—Zn2—O6	−70.6 (3)
C14—C15—N1—Zn1	−176.4 (2)	N9—N8—Zn2—O6	109.2 (3)
C17—C16—N1—C15	0.1 (4)	C28—N8—Zn2—N7	6.12 (18)
C17—C16—N1—Zn1	176.6 (2)	N9—N8—Zn2—N7	−174.1 (2)
N4—C11—N2—N3	1.0 (3)	C28—N8—Zn2—O7	−81.01 (19)
S1—C11—N2—N3	179.68 (19)	N9—N8—Zn2—O7	98.7 (2)

N4—C10—N3—N2	0.0 (3)	C62—O5—Zn2—N8	−67.1 (3)
C7—C10—N3—N2	176.4 (2)	C62—O5—Zn2—N12^{ii}	42.1 (3)
N4—C10—N3—Zn1^{i}	−176.95 (16)	C62—O5—Zn2—O6	139.3 (3)
C7—C10—N3—Zn1^{i}	−0.6 (3)	C62—O5—Zn2—N7	−92.4 (5)
C11—N2—N3—C10	−0.6 (3)	C62—O5—Zn2—O7	−164.3 (3)
C11—N2—N3—Zn1^{i}	175.75 (18)	N14—O6—Zn2—N8	−12.3 (3)
N3—C10—N4—C11	0.5 (3)	N14—O6—Zn2—N12^{ii}	178.94 (15)
C7—C10—N4—C11	−175.4 (3)	N14—O6—Zn2—O5	87.31 (15)
N3—C10—N4—N5	171.8 (2)	N14—O6—Zn2—N7	−84.32 (15)
C7—C10—N4—N5	−4.1 (4)	N14—O6—Zn2—O7	0.18 (14)
N2—C11—N4—C10	−1.0 (3)	C25—N7—Zn2—N8	−6.14 (17)
S1—C11—N4—C10	−179.79 (19)	C24—N7—Zn2—N8	174.0 (2)
N2—C11—N4—N5	−172.2 (2)	C25—N7—Zn2—N12^{ii}	−114.32 (18)
S1—C11—N4—N5	9.0 (4)	C24—N7—Zn2—N12^{ii}	65.9 (2)
C8—C7—N6—C6	0.3 (4)	C25—N7—Zn2—O5	19.9 (5)
C10—C7—N6—C6	−178.4 (2)	C24—N7—Zn2—O5	−160.0 (4)
C8—C7—N6—Zn1^{i}	−178.7 (2)	C25—N7—Zn2—O6	147.65 (18)
C10—C7—N6—Zn1^{i}	2.6 (3)	C24—N7—Zn2—O6	−32.2 (2)
C1—C6—N6—C7	179.1 (2)	C25—N7—Zn2—O7	91.67 (18)
C5—C6—N6—C7	−1.1 (4)	C24—N7—Zn2—O7	−88.2 (2)
C1—C6—N6—Zn1^{i}	−2.1 (3)	N14—O7—Zn2—N8	174.19 (15)
C5—C6—N6—Zn1^{i}	177.72 (18)	N14—O7—Zn2—N12^{ii}	−2.9 (3)
C26—C25—N7—C24	1.7 (4)	N14—O7—Zn2—O5	−91.93 (15)
C28—C25—N7—C24	−175.1 (2)	N14—O7—Zn2—O6	−0.18 (14)
C26—C25—N7—Zn2	−178.1 (2)	N14—O7—Zn2—N7	98.15 (15)
C28—C25—N7—Zn2	5.1 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*B*···O1^{ii}	0.91	2.65	3.125 (3)	113
N11—H11*B*···O3^{ii}	0.91	2.19	3.077 (3)	164
O5—H5···N15^{iii}	0.93	2.57	3.348 (3)	141
O5—H5···O9^{iii}	0.93	1.79	2.600 (3)	144
N5—H5*B*···O8	0.92	2.25	3.113 (3)	156
N5—H5*A*···O13	0.93	2.55	3.291 (3)	137
N11—H11*A*···O11	0.95	2.18	3.037 (3)	149
O4—H4*A*···O14	0.93	2.11	2.655 (3)	116

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