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Crystal structures and photophysical properties of mono- and dinuclear Zn^{II} complexes flanked by triethylammonium

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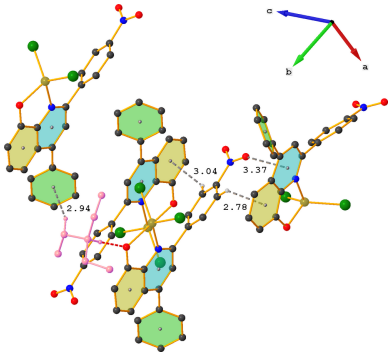
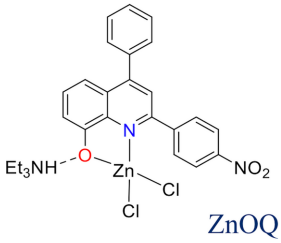
Two new zinc(II) complexes, triethylammonium dichlorido[2-(4-nitrophenyl)-4-phenylquinolin-8-olato]zinc(II), $(C_6H_{16}N)\{Zn(C_{21}H_{13}N_2O_3)Cl_2\}$ (**ZnOQ**), and bis(triethylammonium) {2,2′-[1,4-phenylenebis(nitrilomethylidyne)]diphenolato}bis[dichloridozinc(II)], $(C_6H_{16}N)_2[Zn_2(C_{20}H_{14}N_2O_2)Cl_4]$ (**ZnBS**), were synthesized and their structures were determined using ESI–MS spectrometry, ^{1}H NMR spectroscopy, and single-crystal X-ray diffraction. The results showed that the ligands 2-(4-nitrophenyl)-4-phenylquinolin-8-ol (**HOQ**) and *N*,*N*′-bis(2-hydroxybenzylidene)benzene-1,4-diamine (**H_2BS**) were deprotonated by triethyl-amine, forming the counter-ion Et_3NH^+, which interacts *via* an N—H···O hydrogen bond with the ligand. The Zn^{II} atoms have a distorted trigonal–pyramidal (**ZnOQ**) and distorted tetrahedral (**ZnBS**) geometries with a coordination number of four, coordinating with the ligands *via* N and O atoms. The N atoms coordinating with Zn^{II} correspond to the heterocyclic nitrogen for the **HOQ** ligand, while for the **H_2BS** ligand, it is the nitrogen of the imine (CH═N). The crystal packing of **ZnOQ** is characterized by C—H···π interactions, while that of **ZnBS** by C—H···Cl interactions. The emission spectra showed that **ZnBS** complex exhibits green fluorescence in the solid state with a small band-gap energy, and the **ZnOQ** complex does exhibit non-fluorescence.

1. Chemical context

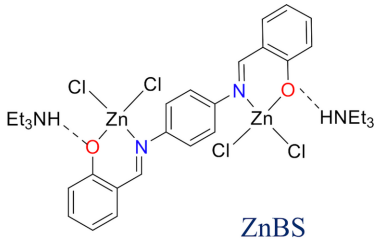
Numerous Zn^{II} complexes have attracted interest from many scientists and have been used in various applications, such as biological sensors (Liu *et al.*, 2020; He *et al.*, 2020), antimicrobial agents (Kargar *et al.*, 2021*ab*), anticancer drugs (Du *et al.*, 2023) and particularly in luminescent materials for organic light-emitting diode (OLED) devices (Gusev *et al.*, 2019, 2021; Rashamuse *et al.*, 2023). Zn^{II} complexes are noted for their impressive fluorescence and cost-effectiveness in OLED applications. Among all ligands, 8-hydroxyquinoline is a classical one. It has the ability to form a five-membered ring with the metal center *via* N and O atoms, which appeals to many scientists from all over the world (Côrte-Real *et al.*, 2023; Harmošová *et al.*, 2023). In order to improve the photophysical properties of Zn^{II} complexes with 8-hydroxyquinoline, many strategies have been conducted to synthesize new neutral Zn^{II} complexes including different substituents at various positions on 8-hydroxyquinoline (Singh *et al.*, 2018), with the approach of extending the π-conjugation system with aryl substituents to increase photoluminiscence quantum yield (PLQY) and to shift the emission to blue yielding potential results (Harmošová *et al.*, 2023; Jianbo *et al.*, 2018; Hien *et al.*, 2024). In particular, a series of six new Zn^{II} complexes bearing



diaryl-8-hydroxyquinoline were synthesized, indicating that electron-donating groups (like OCH_3) enhance the PLQY, while electron-withdrawing groups (like NO_2) show the opposite result (Hien *et al.*, 2024). These complexes are synthesized by direct reaction between $ZnCl_2$ and the ligands to obtain neutral complexes $[Zn(OQ)_2]$, in which Zn^{II} coordinates with deprotonated 8-hydroxyquinoline *via* N and O atoms, as in previous publications. However, in this work, upon the reaction of 2-(4-nitrophenyl)-4-phenylquinolin-8-ol (**HOQ**) with $ZnCl_2$ in the presence of triethylamine, an ionic complex with the molecular formula $[Et_3NH][Zn(OQ)Cl_2]$ (**ZnOQ**) was obtained, in which the ratio of Zn^{II} and ligand is 1:1 instead of 1:2 as in the published Zn^{II} complexes (Singh *et al.*, 2018; Hien *et al.*, 2024). Furthermore, the same reaction condition between $ZnCl_2$ and a similar NO-Schiff base ligand, namely *N*,*N*′-bis(2-hydroxybenzylidine)benzene-1,4-diamine (**H_2BS**) gives a similar ion complex $[Zn_2(BS)Cl_2][Et_3NH]_2$ (**ZnBS**).



ZnOQ



ZnBS

In this report, the ligands **HOQ** and **H_2BS** were successfully prepared, and characterized. Furthermore, two complexes **ZnOQ** and **ZnBS** were also successfully prepared, isolated and characterized by ESI–MS and ^{1}H NMR, and the crystal structures of the complexes were elucidated. The optical properties of the ligands and complexes were studied using absorption and emission spectra in both solid state and in solution in dimethylsulfoxide (DMSO) or tetrahydrofuran (THF) solvents.

2. Structural commentary

The mononuclear complex **ZnOQ** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 1). The Zn^{II} atom coordinates to the N and O atoms of a deprotonated 8-hydoxyquinoline derivative and two chlorine atoms with a distorted trigonal–pyramidal geometry (τ_4 parameter is 0.86; Yang *et al.*, 2007). The negative charge of the complex is compensated by the interaction with triethylammonium *via* an N—H···O hydrogen bond (Table 1). The Zn atom is part of a five-membered ring and is located 0.081 (1) Å above the planar quinoline plane (r.m.s. deviation = 0.058 Å), which makes dihedral angles of 50.88 (12) and 46.95 (13)° with the C10–C15 and C16-C21 phenyl rings, respectively. The mutual angle between the two phenyl rings is 79.42 (16)°. The plane of the nitro group makes an angle of 14.38 (19)° with the C10–C15 phenyl ring.

The dinuclear complex **ZnBS** also crystallizes in the monoclinic space group $P2_1/c$ but with half a molecule in the asymmetric unit (Fig. 2). The second half is generated by inversion symmetry. The complex is flanked at both ends by a triethylammonium moiety *via* an N—H···O interaction (Table 2). The Zn^{II} coordination sphere resembles that observed in **ZnOQ**, but is now intermediate between trigonal–pyramidal and tetragonal geometries (τ_4 parameter is 0.91).

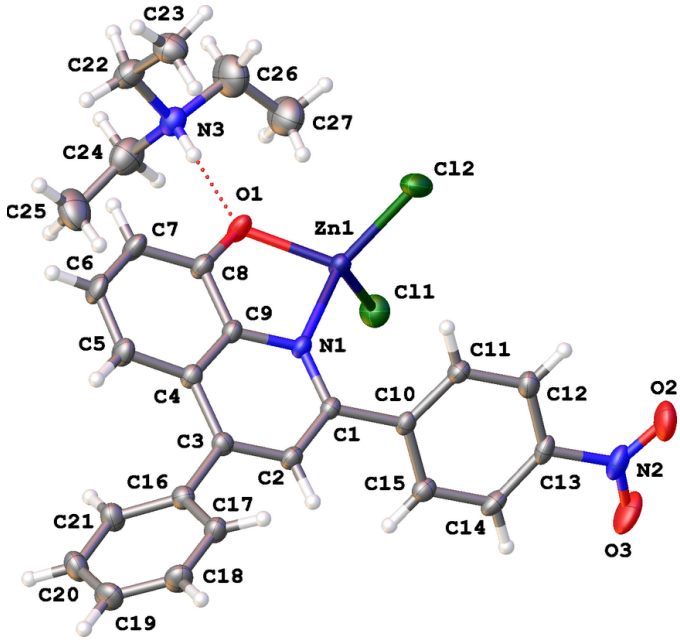


Figure 1
The molecular structure of **ZnOQ** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level. The N—H···O hydrogen bond is shown as a red dashed line.

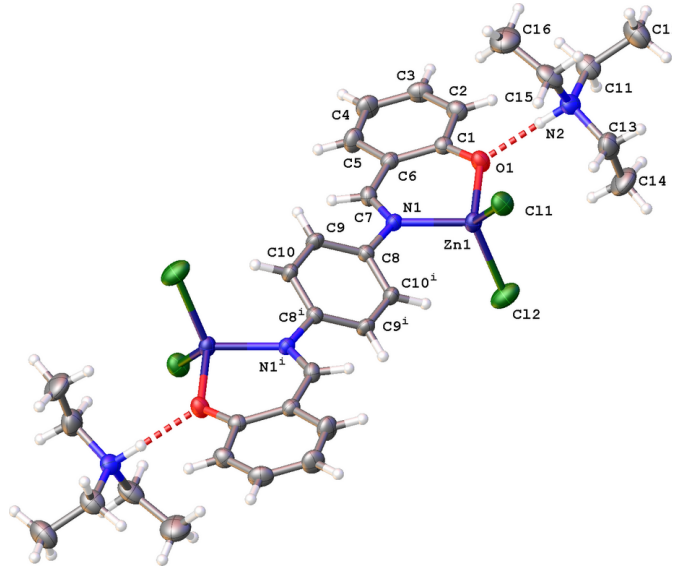


Figure 2
The molecular structure of **ZnBS** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level. The N—H···O hydrogen bonds are shown as a red dashed line. Symmetry code: (i) $-x+1, -y+1, -z+2$.

Table 1
Hydrogen-bond geometry (Å, °) for **ZnOQ**.

*Cg*3 and *Cg*5 are the centroids of C4-C9 and C16-C21, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1	0.88 (4)	1.92 (4)	2.807 (4)	178 (4)
C12—H12···*Cg*3^{i}	0.93	2.78	3.553 (4)	141
C14—H14···*Cg*3^{ii}	0.93	3.04	3.837 (4)	145
C24—H24*B*···*Cg*5^{iii}	0.97	2.94	3.809 (5)	149

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

Table 2
Hydrogen-bond geometry (Å, °) for **ZnBS**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.96 (4)	1.84 (4)	2.782 (4)	165 (4)
C9—H9···Cl1^{i}	0.93	2.83	3.752 (4)	171
C11—H11···Cl2^{ii}	0.97	2.68	3.625 (6)	164
C13—H13···Cl2^{iii}	0.97	2.68	3.562 (6)	151
C15—H15*A*···Cl1	0.97	2.80	3.684 (5)	152
C15—H15*B*···Cl1^{iii}	0.97	2.81	3.769 (5)	169

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, -y+1, -z+1$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

The Zn^{II} atom is part of a six-membered ring and is located 0.405 (3) Å above the best plane through atoms C1–C7/O1/N1 (r.m.s. deviation = 0.027 Å). The interplanar angle between the aromatic rings is 33.4 (2)°. The stereochemistry of the C7═N1 bond is *E*, as illustrated by the torsion angle C6—C7═N1—C8 of 176.9 (4)°.

3. Supramolecular features

Despite the presence of aromatic rings in **ZnOQ**, no π–π stacking is observed in the crystal packing. However, the phenyl part of the quinoline ring system (C4–C9) and one of the phenyl rings (C16–C21) participate in three C—H···π interactions (Table 1, Fig. 3). Centrosymmetric dimers are

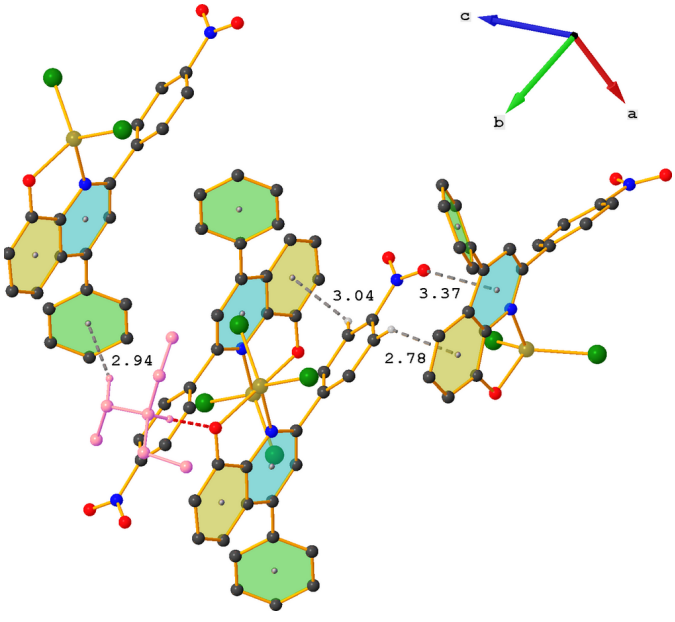


Figure 3
Partial crystal packing of **ZnOQ** showing the C—H···π and N—O···π interactions as gray dashed lines. The N—H···O hydrogen bond is shown as a red dashed line. Further details are given in Table 1. For clarity, hydrogen atoms not involved in hydrogen bonding are omitted and the triethylammonium ion is shown in pink.

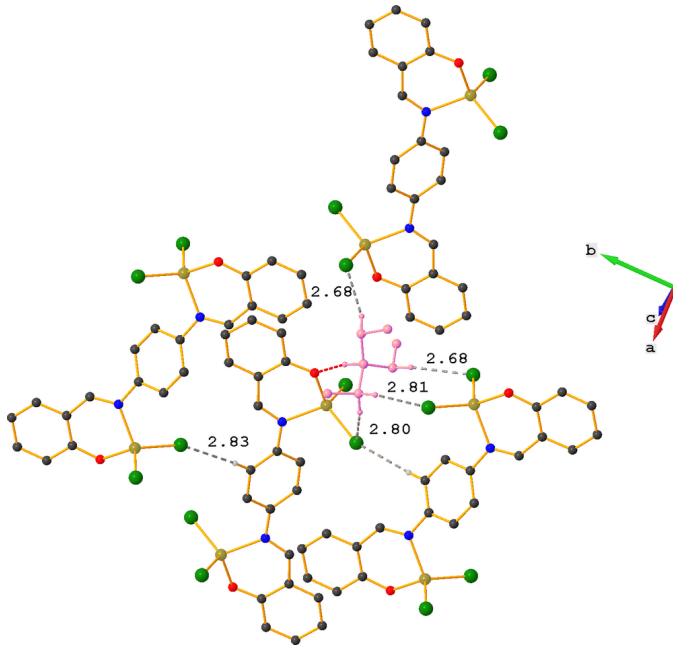


Figure 4
Partial crystal packing of **ZnBS** showing the C—H···Cl interactions as gray dashed lines. The N—H···O hydrogen bond is shown as a red dashed line. Further details are given in Table 2. For clarity, hydrogen atoms not involved in hydrogen bonding are omitted and the triethylammonium ion is shown in pink.

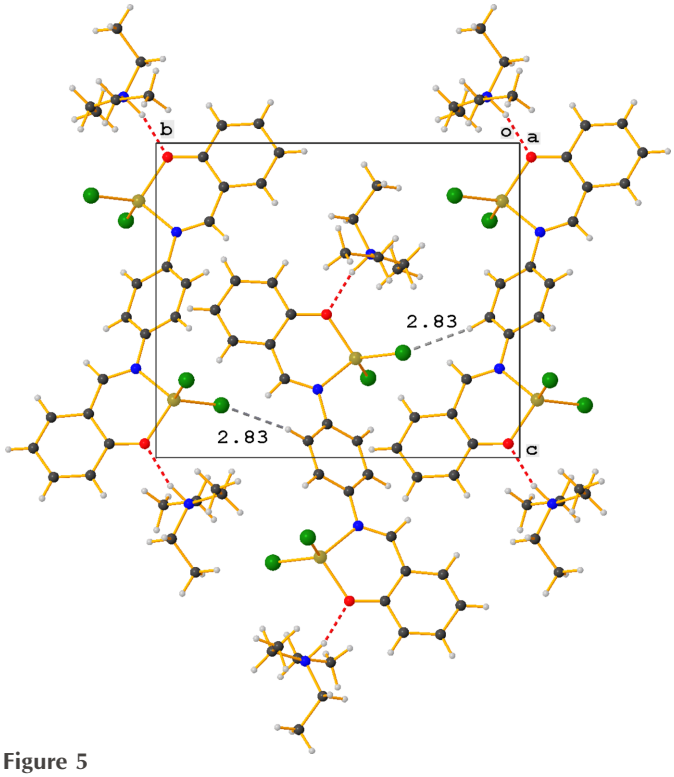


Figure 5
Chain formation in the *b*-axis direction by C—H···Cl interactions (gray dashed lines) in the crystal packing of **ZnBS**.

Table 3
Photophysical data of the examined compounds at room temperature.

Compound	Solvent (polarity)	λ_{ABS} (nm) / ε (M^{-1}.cm^{-1}.10^3)	λ_{em} (nm)	Stokes shift (cm^{-1})	$\lambda_{em}{}^{b}$ (nm)/Intensity
H2BS	DMSO (3.96)	371 (35)	531	8122	575 / 34624
	THF (1.73)	371 (56)	534	8228	
ZnBS	DMSO (3.96)	372 (32)	520	7651	515 / 10616
	THF (1.73)	372 (12)	551	8878	
HOQ	DMSO (3.96)	264 (34); 312 (32)	528	13112	
	THF (1.73)	247 (60); 295 (56)	533	15136	
ZnOQ	DMSO (3.96)	265 (25); 297 (35); 450 (3)^{a}	518	2917	
	THF (1.73)	243 (48); 307 (35); 380 (6)^{a}	467	4902	

Notes: (*a*) shoulder excited; (*b*) in the solid state.

formed by interaction of C14—H14 with a nearby C4–C9 ring. In addition, the other side of the nitrophenyl ring (C12—H12) also interacts with a close by C4–C9 ring. The last interaction involves the triethylammonium ion, with C24—H24*A* interacting with a neighboring C16–C21 ring, resulting in chain formation along the *a*-axis direction. One of the nitro oxygen atoms (O2) shows an O$\cdots\pi$ interaction with the pyridine part of the quinoline ring system [O2$\cdots$*Cg*2^{i} = 3.372 (3) Å; *Cg*2 is the centroid of the N1/C1–C4/C9 ring; symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$].

In contrast to **ZnOQ**, the crystal packing in **ZnBS** is characterized by C—H$\cdots$Cl interactions (Table 2, Fig. 4). The triethylammonium ion plays an important role in these interactions and acts as a stabilizing glue between three complexes *via* one N—H$\cdots$O and four C—H$\cdots$Cl interactions. The fifth C—H$\cdots$Cl interaction is between an H atom of the central phenyl ring (H9) and a nearby chlorine atom (Cl1), which results in the formation of chains running in the *b*-axis direction (Fig. 5).

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.45, last update September 2024; Groom *et al.*, 2016) for the five-membered ring fragment shown in Fig. 6*a* (comparable to a part of **ZnOQ**) resulted in three hits, CSD refcodes MOXFOX, MOXPEX and MOXPIB (Samanta *et al.*, 2019). In these structures, the deviation of the Zn^{II} atom from the best plane through the C, N and O atoms of the fragment (ranging between 0.145 and 0.195 Å) is comparable to that observed for **ZnOQ** [0.203 (3) Å]. The negative charge of the complexes is compensated by a second protonated ligand.

A similar search for the six-membered ring fragment shown in Fig. 6*b* (comparable to a part of **ZnBS**) resulted in 63 hits. The deviation of the Zn^{II} atom from the best plane through the C, N and O atoms of the fragment shows a large variation between 0.003 and 0.927 Å [mean value is 0.327 Å, 0.405 (3) Å for **ZnBS**].

Of the 1876 crystal structures containing a triethylammonium ion in the CSD, the N—H group interacts with an O atom in 383 structures (133 organic and 250 coordination compounds).

A quick search for a nitro group interaction with a phenyl groups gives 6252 hits for an O$\cdots$*Cg* distance shorter than 3.5 Å (*Cg* is the centroid of the phenyl ring).

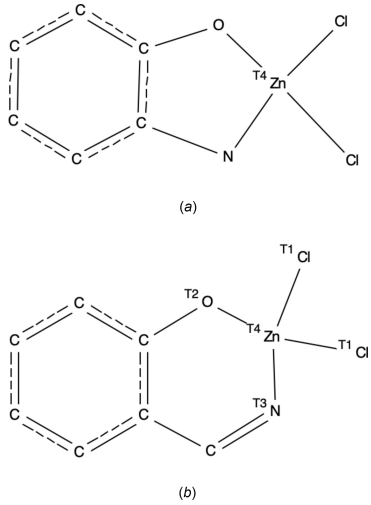


Figure 6
Search fragments used in Conquest to perform the CSD survey: (*a*) five-membered ring fragment present in **ZnOQ**, (*b*) six-membered ring fragment present in **ZnBS**.

5. Photophysical properties

The absorption and emission spectra at room temperature of both ligands and complexes in DMSO or THF solvents at a concentration of 10 µ*M* (**H$_2$BS**, **ZnBS**); 50 µ*M* (**HOQ; ZnOQ**) and in the solid state (**H$_2$BS**, **ZnBS**) are listed in Table 3. In the absorption spectra, **H$_2$BS** and **ZnBS** (Fig. S9) show an absorption band at 371–372nm in both solvents, while two absorption bands were observed at 243–265nm and 295–312nm for **HOQ** and **ZnOQ** (Fig. S4), corresponding to $\pi\rightarrow\pi^*$ or n$\rightarrow\pi^*$ transitions. The results of the solid-state electron absorption spectrum of **H$_2$BS** and **ZnBS** (Fig. 7*a*) show that the band-gap energies of **H$_2$BS** and **ZnBS**, calculated according to the equation $E_{gap} = hc/\lambda_{onset}$ (UV–vis) (Chiyindiko *et al.*, 2022) are approximately 1.8 eV and 2.0 eV, respectively, which has potential for applications in OLED devices (Dumur, 2014; Lakshmanan *et al.*, 2018).

The emission spectra of the examined complexes in DMSO and THF solvents demonstrate that all compounds show no fluorescence (Figs. S5 and S10). However, in the solid state, **H$_2$BS** fluorescences at 575 nm with an intensity of approximately 35000 a.u., while the emission wavelength of **ZnBS** is 515 nm with an intensity of about 10000 a.u., showing a blue

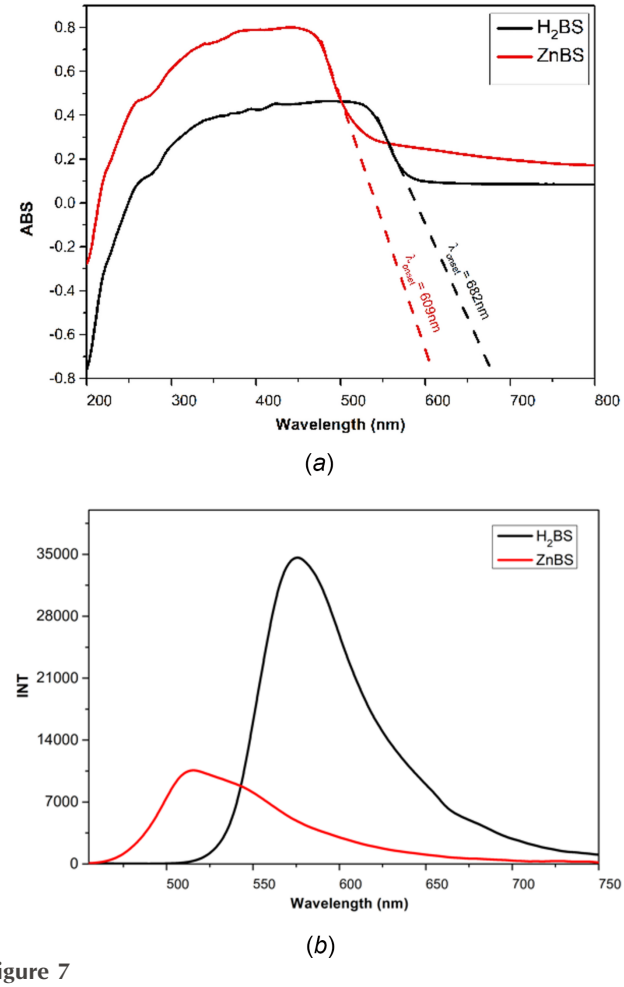


Figure 7
(*a*) Absorption and (*b*) emission spectra in the solid state at λ_{ex} = 425 nm of **H_2BS** and **ZnBS**.

shift compared to the ligand with $\Delta\lambda$ = 60 nm (Fig. 7*b* and S11).

6. Synthesis and crystallization

The reaction sequence for **ZnOQ** and **ZnBS** is shown in Fig. 8. The ligands **HOQ** and **H_2BS** were synthesized according to modified procedures described by Yu *et al.* (2018; for **HOQ**) and Das & Ghosh (1998; for **H_2BS**).

Synthesis of HOQ

A mixture of *ortho*-aminophenol (120 mg, 1.1 mmol), 4-nitrobenzaldehyde (151 mg, 1 mmol), phenylacetylene (139 mg, 1.2 mmol), AgOTf (13 mg, 0.5 mol%) and TFA (456 mg, 400 mol%) in 4 mL of dichloroethane was heated to 353 K for 24 h. After cooling, the reaction mixture was diluted with 15 mL of ethyl acetate and extracted three times with 10 mL of saturated $NaHCO_3$ solution. Then, it was dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography using hexane/ethyl acetate (*v*/*v* = 19:1) as eluent. **HOQ** was obtained as a yellow solid with a yield of 52%.

^{1}H NMR (600 MHz, chloroform-d_1, δ ppm): 8.41 (*br*, 1H, OH), 8.39 [*d*, ^3J(H,H) = 9.0 Hz, 2H, Ar-H], 8.36 [*d*, ^3J(H,H) = 9.0 Hz, 2H, Ar-H], 7.90 (*s*, 1H, Ar-H), 7.57 [*d*, ^3J(H,H) = 4.5 Hz, 4H, Ar-H], 7.56–7.54 (*m*, 1H, Ar-H), 7.48–7.43 (*m*, 2H, Ar-H), 7.26 (*ov*, 1H, Ar-H).

The ^{1}H NMR spectrum of **HOQ** is given in Fig. S1.

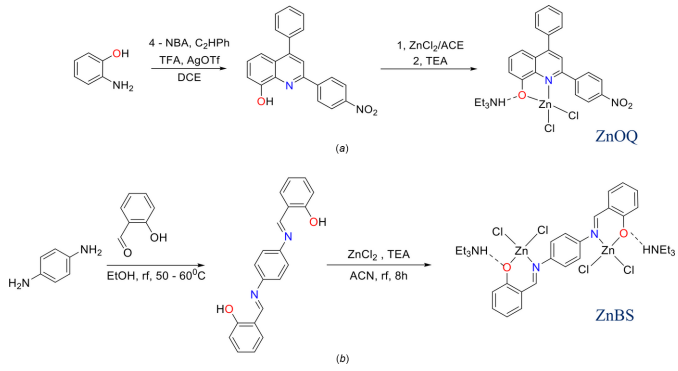


Figure 8
Synthesis of the complexes (*a*) **ZnOQ** and (*b*) **ZnBS**.

Synthesis of $[(Et_3NH)ZnCl_2(OQ)]$ (ZnOQ)

A reaction mixture consisting of ligand **HOQ** (32 mg, 0.1 mmol), zinc(II) chloride (55 mg, 0.1 mmol) and 5 mL of acetone was stirred at room temperature and 25 µL of triethylamine were added to the reaction vessel and stirred for 6 h to obtain an orange solution. Evaporation of the solution gave orange crystals (yield 67%).

^{1}H NMR (600 MHz, d_6–DMSO, δ ppm): 8.44 (*m*, 4H, Ar-H), 7.64 (*s*, 1H, Ar-H), 7.55 (*m*, 6H, Ar-H), 7.43 (*m*, 1H, Ar-H), 7.15 (*d*, 1H, Ar-H), 6.85 (*m*, 1H, NH), 3.31 (*q*, 6H, CH_2), 1,40 (*t*, 9H, CH_3). ESI–MS: 787.5 (100%, $Zn(OQ)_2$ + ACN + H^+).

The ^{1}H NMR and ESI–MS spectra of **ZnOQ** are given in Figs. S2 and S3, respectively.

Synthesis of H_2BS

A mixture of *p*-phenylenediamine (108 mg, 1 mmol) and salicylaldehyde (122 mg, 1 mmol) in 10 mL of ethanol was heated to 333 K for 5 h to obtain the red–orange solid **H_2BS**, which was washed with hot ethanol, with a yield of 85%.

^{1}H NMR (600 MHz, DMSO-d_6, δ ppm): 13.00 (*s*, 1H, OH), 9.00 (*s*, 1H, CH_{imine}), 7.68 (*dd*, 1H, Ar-H), 7.54 (*s*, 2H, Ar-H), 7.43 (*m*, 1H, Ar-H), 6.95 (*m*, 2H, Ar-H).

The ^{1}H NMR spectrum of **H_2BS** is given in Fig. S6.

Synthesis of $[(Et_3NH)_2Zn_2Cl_4(BS)]$ (ZnBS)

A reaction mixture consisting of ligand **H_2BS** (32 mg, 0.1 mmol), zinc(II) chloride (55 mg, 0.4 mmol) and 5 mL of acetonitrile was stirred for 4 h at room temperature to obtain an orange–red solid. To dissolve the precipitate, 40 µL of triethylamine were added to the reaction vessel, forming a yellow solution. After filtering the solution and slow evaporation, transparent yellow–green crystals were obtained (yield 68%).

^{1}H NMR (600 MHz, d_6–DMSO, δ ppm): 9.03 (*s*, 1H, CH_{imine}); 8.63 (*s*, 1H, $NH_{amminium\ salt}$), 7.73 (*m*, 2H, Ar-H), 7.50 (*m*, 1H, Ar-H), 7.27 (*m*, 1H, Ar-H), 7.00 (*m*, 1H, Ar-H), 6.50 (*m*, 1H, Ar-H), 3.30 (*m*, 6H, CH_2), 1.10 (*m*, 9H, CH_3). ESI–MS: 653.3 (100%, *M* – Et_3NH – Cl).

The ^{1}H NMR and ESI–MS spectra of **ZnBS** are given in Figs. S7 and S8, respectively.

Table 4
Experimental details.

	ZnOQ	**ZnBS**
Crystal data		
Chemical formula	$(C_6H_{16}N)\{Zn(C_{21}H_{13}N_2O_3)Cl_2\}$	$(C_6H_{16}N)_2[Zn_2(C_{20}H_{14}N_2O_2)Cl_4]$
M_r	579.80	791.24
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	293	293
a, b, c (Å)	10.4571 (5), 13.9115 (5), 18.5703 (10)	11.9843 (9), 13.4570 (7), 11.9944 (11)
β (°)	100.372 (5)	103.838 (9)
V (Å^3)	2657.4 (2)	1878.2 (3)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.16	1.59
Crystal size (mm)	0.5 × 0.3 × 0.2	0.5 × 0.5 × 0.5
Data collection		
Diffractometer	SuperNova, Single source at offset/far, Eos	SuperNova, Single source at offset/far, Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.728, 1.000	0.473, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27564, 5416, 4166	10514, 3814, 2836
R_{int}	0.042	0.044
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.113, 1.03	0.053, 0.158, 1.05
No. of reflections	5416	3814
No. of parameters	331	206
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.70, −0.38	0.93, −0.39

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2016/4* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Hydrogen atom H2 was located in a difference Fourier map for **ZnBS** and subsequently refined freely. All other H atoms were placed in idealized positions and refined in riding mode with N—H distance of 0.89 Å, C—H distances of 0.93 (aromatic), 0.97 (CH_2) and 0.96 Å (CH_3). Non-hydrogen atoms were refined anisotropically and hydrogen atoms with isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 for methyl groups).

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Crystal structures and photophysical properties of mono- and dinuclear Zn^{II} complexes flanked by triethylammonium

Hai Le Thi Hong, Hien Nguyen, Duong Trinh Hong, Ninh Nguyen Hoang, Khanh Nguyen Nhat and Luc Van Meervelt

Computing details

Dichlorido[2-(4-nitrophenyl)-4-phenylquinolin-8-olato]zinc(II) (ZnOQ)

Crystal data

$(C_6H_{16}N)\{Zn(C_{21}H_{13}N_2O_3)Cl_2]$
M_r = 579.80
Monoclinic, $P2_1/c$
a = 10.4571 (5) Å
b = 13.9115 (5) Å
c = 18.5703 (10) Å
β = 100.372 (5)°
V = 2657.4 (2) Å^3
Z = 4
$F(000)$ = 1200
D_x = 1.449 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8040 reflections
θ = 2.8–25.8°
μ = 1.16 mm^{-1}
T = 293 K
Block, brown
0.5 × 0.3 × 0.2 mm

Data collection

SuperNova, Single source at offset/far, Eos diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 15.9631 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
T_{min} = 0.728, T_{max} = 1.000
27564 measured reflections
5416 independent reflections
4166 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 26.4°, θ_{min} = 2.5°
h = −13→13
k = −17→17
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.113
S = 1.03
5416 reflections
331 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 2.5402P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.28872 (3)	0.61247 (2)	0.31683 (2)	0.03891 (12)
Cl1	0.17475 (9)	0.51997 (7)	0.37894 (5)	0.0576 (2)
O1	0.2901 (2)	0.75402 (14)	0.33465 (14)	0.0497 (6)
N1	0.4792 (2)	0.62069 (15)	0.37204 (12)	0.0310 (5)
C1	0.5666 (3)	0.55364 (19)	0.39637 (15)	0.0309 (6)
Cl2	0.25071 (10)	0.58325 (7)	0.19686 (5)	0.0625 (3)
O2	0.3841 (3)	0.14048 (19)	0.26870 (18)	0.0795 (9)
N2	0.4125 (3)	0.16534 (19)	0.3326 (2)	0.0556 (8)
C2	0.6879 (3)	0.5769 (2)	0.43761 (16)	0.0353 (6)
H2	0.744674	0.527740	0.456108	0.042*
O3	0.4033 (3)	0.11346 (17)	0.38411 (19)	0.0855 (10)
C3	0.7251 (3)	0.6709 (2)	0.45149 (15)	0.0338 (6)
C4	0.6353 (3)	0.7449 (2)	0.42257 (16)	0.0346 (6)
C5	0.6627 (3)	0.8446 (2)	0.42810 (19)	0.0442 (8)
H5	0.745372	0.865861	0.449013	0.053*
C6	0.5672 (3)	0.9091 (2)	0.4026 (2)	0.0500 (8)
H6	0.586516	0.974437	0.405572	0.060*
C7	0.4418 (3)	0.8802 (2)	0.3722 (2)	0.0483 (8)
H7	0.378430	0.926606	0.357652	0.058*
C8	0.4088 (3)	0.7843 (2)	0.36310 (18)	0.0402 (7)
C9	0.5106 (3)	0.71540 (19)	0.38649 (15)	0.0328 (6)
C10	0.5301 (3)	0.45145 (19)	0.37934 (15)	0.0320 (6)
C11	0.4760 (3)	0.4245 (2)	0.30856 (17)	0.0386 (7)
H11	0.463670	0.470366	0.271535	0.046*
C12	0.4404 (3)	0.3306 (2)	0.29243 (18)	0.0440 (7)
H12	0.405316	0.312273	0.244813	0.053*
C13	0.4580 (3)	0.26455 (19)	0.34855 (18)	0.0405 (7)
C14	0.5133 (3)	0.2881 (2)	0.41919 (18)	0.0433 (7)
H14	0.524837	0.241872	0.455936	0.052*
C15	0.5514 (3)	0.3825 (2)	0.43439 (17)	0.0381 (7)
H15	0.591252	0.399781	0.481491	0.046*
C16	0.8549 (3)	0.6934 (2)	0.49497 (16)	0.0373 (7)
C17	0.9647 (3)	0.6483 (2)	0.47914 (18)	0.0426 (7)
H17	0.956210	0.602554	0.442039	0.051*
C18	1.0869 (3)	0.6706 (2)	0.5180 (2)	0.0540 (9)
H18	1.160042	0.640609	0.506368	0.065*
C19	1.1004 (3)	0.7367 (3)	0.5737 (2)	0.0567 (9)
H19	1.182556	0.752005	0.599441	0.068*
C20	0.9924 (3)	0.7802 (3)	0.59125 (19)	0.0544 (9)

H20	1.001479	0.824286	0.629504	0.065*
C21	0.8703 (3)	0.7590 (2)	0.55239 (17)	0.0462 (8)
H21	0.797671	0.788795	0.564764	0.055*
N3	0.0767 (3)	0.87944 (19)	0.31940 (17)	0.0474 (7)
H3	0.145 (4)	0.841 (3)	0.3240 (19)	0.057*
C22	0.1087 (4)	0.9707 (3)	0.2842 (2)	0.0616 (10)
H22A	0.170320	1.007137	0.319001	0.074*
H22B	0.030357	1.008919	0.271428	0.074*
C23	0.1659 (4)	0.9534 (3)	0.2159 (2)	0.0664 (10)
H23A	0.098712	0.931949	0.176996	0.100*
H23B	0.232443	0.905184	0.225731	0.100*
H23C	0.202762	1.012092	0.201695	0.100*
C24	0.0430 (5)	0.8986 (3)	0.3938 (3)	0.0767 (12)
H24A	−0.025594	0.946422	0.388551	0.092*
H24B	0.009135	0.839939	0.411421	0.092*
C25	0.1544 (5)	0.9329 (4)	0.4497 (2)	0.0923 (15)
H25A	0.225333	0.888423	0.452799	0.139*
H25B	0.127844	0.937375	0.496448	0.139*
H25C	0.181659	0.995074	0.435801	0.139*
C26	−0.0375 (5)	0.8324 (4)	0.2696 (3)	0.1022 (17)
H26A	−0.114192	0.871618	0.269622	0.123*
H26B	−0.019911	0.831970	0.220101	0.123*
C27	−0.0658 (5)	0.7353 (3)	0.2895 (3)	0.0954 (16)
H27A	−0.125867	0.706441	0.250202	0.143*
H27B	−0.103592	0.736367	0.332907	0.143*
H27C	0.013090	0.698463	0.298443	0.143*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0347 (2)	0.02971 (19)	0.0491 (2)	0.00194 (14)	−0.00099 (15)	−0.00165 (15)
Cl1	0.0515 (5)	0.0583 (5)	0.0652 (6)	−0.0095 (4)	0.0166 (4)	−0.0010 (4)
O1	0.0354 (12)	0.0274 (10)	0.0807 (16)	0.0054 (9)	−0.0048 (11)	−0.0021 (11)
N1	0.0323 (12)	0.0226 (11)	0.0377 (13)	0.0017 (9)	0.0053 (10)	−0.0002 (10)
C1	0.0342 (15)	0.0242 (13)	0.0347 (14)	0.0018 (11)	0.0077 (12)	0.0005 (11)
Cl2	0.0686 (6)	0.0675 (6)	0.0451 (5)	0.0157 (5)	−0.0061 (4)	0.0039 (4)
O2	0.094 (2)	0.0442 (15)	0.096 (2)	−0.0164 (14)	0.0075 (18)	−0.0254 (15)
N2	0.0536 (18)	0.0287 (14)	0.088 (2)	0.0003 (13)	0.0215 (17)	−0.0089 (16)
C2	0.0335 (15)	0.0281 (14)	0.0429 (16)	0.0045 (12)	0.0033 (13)	−0.0006 (12)
O3	0.127 (3)	0.0299 (13)	0.109 (3)	−0.0107 (15)	0.046 (2)	0.0033 (15)
C3	0.0312 (14)	0.0335 (14)	0.0362 (15)	0.0015 (12)	0.0052 (12)	−0.0037 (12)
C4	0.0320 (15)	0.0301 (14)	0.0417 (16)	0.0006 (12)	0.0065 (12)	−0.0014 (12)
C5	0.0398 (17)	0.0305 (15)	0.061 (2)	−0.0055 (13)	0.0049 (15)	−0.0029 (14)
C6	0.053 (2)	0.0232 (14)	0.072 (2)	−0.0038 (14)	0.0077 (17)	−0.0020 (15)
C7	0.0447 (18)	0.0264 (14)	0.071 (2)	0.0056 (13)	0.0039 (16)	0.0023 (15)
C8	0.0389 (17)	0.0286 (14)	0.0517 (18)	0.0040 (13)	0.0043 (14)	0.0002 (13)
C9	0.0363 (15)	0.0248 (13)	0.0374 (15)	0.0009 (11)	0.0064 (12)	−0.0014 (12)
C10	0.0290 (14)	0.0249 (13)	0.0422 (16)	0.0037 (11)	0.0066 (12)	−0.0028 (12)

C11	0.0439 (17)	0.0282 (14)	0.0419 (16)	0.0026 (13)	0.0031 (13)	0.0021 (13)
C12	0.0461 (18)	0.0354 (16)	0.0488 (18)	0.0018 (14)	0.0034 (15)	−0.0090 (14)
C13	0.0397 (17)	0.0232 (13)	0.061 (2)	0.0013 (12)	0.0142 (15)	−0.0068 (14)
C14	0.0517 (19)	0.0275 (14)	0.0531 (19)	0.0081 (13)	0.0158 (15)	0.0088 (14)
C15	0.0407 (16)	0.0334 (15)	0.0406 (16)	0.0045 (13)	0.0084 (13)	0.0018 (13)
C16	0.0361 (16)	0.0333 (15)	0.0410 (16)	−0.0030 (12)	0.0027 (13)	0.0000 (13)
C17	0.0395 (17)	0.0353 (15)	0.0506 (18)	0.0024 (13)	0.0015 (14)	−0.0052 (14)
C18	0.0375 (18)	0.0501 (19)	0.070 (2)	0.0072 (15)	−0.0023 (16)	−0.0028 (18)
C19	0.0406 (19)	0.055 (2)	0.067 (2)	−0.0060 (16)	−0.0117 (17)	−0.0032 (18)
C20	0.056 (2)	0.054 (2)	0.049 (2)	−0.0070 (17)	−0.0011 (16)	−0.0154 (17)
C21	0.0415 (18)	0.0480 (18)	0.0480 (18)	0.0014 (14)	0.0048 (15)	−0.0114 (15)
N3	0.0412 (15)	0.0396 (15)	0.0621 (18)	−0.0017 (12)	0.0112 (14)	0.0001 (13)
C22	0.060 (2)	0.048 (2)	0.076 (3)	0.0071 (17)	0.009 (2)	0.0089 (19)
C23	0.065 (2)	0.074 (3)	0.059 (2)	−0.008 (2)	0.010 (2)	0.010 (2)
C24	0.082 (3)	0.070 (3)	0.085 (3)	0.009 (2)	0.034 (3)	0.001 (2)
C25	0.126 (4)	0.091 (3)	0.064 (3)	−0.024 (3)	0.028 (3)	−0.016 (3)
C26	0.097 (4)	0.087 (4)	0.118 (4)	−0.032 (3)	0.007 (3)	−0.008 (3)
C27	0.104 (4)	0.079 (3)	0.100 (4)	−0.025 (3)	0.011 (3)	0.007 (3)

Geometric parameters (Å, º)

Zn1—Cl1	2.2140 (10)	C15—H15	0.9300
Zn1—O1	1.996 (2)	C16—C17	1.386 (4)
Zn1—N1	2.073 (2)	C16—C21	1.390 (4)
Zn1—Cl2	2.2289 (10)	C17—H17	0.9300
O1—C8	1.327 (4)	C17—C18	1.385 (4)
N1—C1	1.327 (3)	C18—H18	0.9300
N1—C9	1.373 (3)	C18—C19	1.372 (5)
C1—C2	1.396 (4)	C19—H19	0.9300
C1—C10	1.491 (4)	C19—C20	1.371 (5)
O2—N2	1.220 (4)	C20—H20	0.9300
N2—O3	1.216 (4)	C20—C21	1.381 (4)
N2—C13	1.472 (4)	C21—H21	0.9300
C2—H2	0.9300	N3—H3	0.89 (4)
C2—C3	1.376 (4)	N3—C22	1.493 (4)
C3—C4	1.432 (4)	N3—C24	1.509 (5)
C3—C16	1.482 (4)	N3—C26	1.519 (5)
C4—C5	1.415 (4)	C22—H22A	0.9700
C4—C9	1.416 (4)	C22—H22B	0.9700
C5—H5	0.9300	C22—C23	1.515 (5)
C5—C6	1.363 (4)	C23—H23A	0.9600
C6—H6	0.9300	C23—H23B	0.9600
C6—C7	1.391 (5)	C23—H23C	0.9600
C7—H7	0.9300	C24—H24A	0.9700
C7—C8	1.380 (4)	C24—H24B	0.9700
C8—C9	1.440 (4)	C24—C25	1.493 (6)
C10—C11	1.386 (4)	C25—H25A	0.9600
C10—C15	1.390 (4)	C25—H25B	0.9600

C11—H11	0.9300	C25—H25C	0.9600
C11—C12	1.376 (4)	C26—H26A	0.9700
C12—H12	0.9300	C26—H26B	0.9700
C12—C13	1.377 (4)	C26—C27	1.446 (6)
C13—C14	1.375 (4)	C27—H27A	0.9600
C14—H14	0.9300	C27—H27B	0.9600
C14—C15	1.387 (4)	C27—H27C	0.9600

Cl1—Zn1—Cl2	113.51 (4)	C17—C16—C21	118.3 (3)
O1—Zn1—Cl1	118.40 (8)	C21—C16—C3	121.7 (3)
O1—Zn1—N1	83.44 (8)	C16—C17—H17	119.7
O1—Zn1—Cl2	109.89 (8)	C18—C17—C16	120.7 (3)
N1—Zn1—Cl1	109.50 (7)	C18—C17—H17	119.7
N1—Zn1—Cl2	119.15 (7)	C17—C18—H18	119.9
C8—O1—Zn1	110.95 (17)	C19—C18—C17	120.2 (3)
C1—N1—Zn1	132.16 (18)	C19—C18—H18	119.9
C1—N1—C9	118.9 (2)	C18—C19—H19	120.1
C9—N1—Zn1	108.92 (17)	C20—C19—C18	119.9 (3)
N1—C1—C2	121.7 (2)	C20—C19—H19	120.1
N1—C1—C10	117.6 (2)	C19—C20—H20	119.9
C2—C1—C10	120.6 (2)	C19—C20—C21	120.3 (3)
O2—N2—C13	118.4 (3)	C21—C20—H20	119.9
O3—N2—O2	123.8 (3)	C16—C21—H21	119.7
O3—N2—C13	117.8 (3)	C20—C21—C16	120.7 (3)
C1—C2—H2	119.3	C20—C21—H21	119.7
C3—C2—C1	121.4 (3)	C22—N3—H3	109 (2)
C3—C2—H2	119.3	C22—N3—C24	111.0 (3)
C2—C3—C4	118.0 (2)	C22—N3—C26	108.2 (3)
C2—C3—C16	120.3 (3)	C24—N3—H3	110 (2)
C4—C3—C16	121.8 (2)	C24—N3—C26	110.2 (3)
C5—C4—C3	124.5 (3)	C26—N3—H3	109 (2)
C5—C4—C9	118.4 (3)	N3—C22—H22A	109.1
C9—C4—C3	117.1 (2)	N3—C22—H22B	109.1
C4—C5—H5	120.2	N3—C22—C23	112.7 (3)
C6—C5—C4	119.6 (3)	H22A—C22—H22B	107.8
C6—C5—H5	120.2	C23—C22—H22A	109.1
C5—C6—H6	119.1	C23—C22—H22B	109.1
C5—C6—C7	121.9 (3)	C22—C23—H23A	109.5
C7—C6—H6	119.1	C22—C23—H23B	109.5
C6—C7—H7	119.1	C22—C23—H23C	109.5
C8—C7—C6	121.7 (3)	H23A—C23—H23B	109.5
C8—C7—H7	119.1	H23A—C23—H23C	109.5
O1—C8—C7	123.4 (3)	H23B—C23—H23C	109.5
O1—C8—C9	119.8 (2)	N3—C24—H24A	108.7
C7—C8—C9	116.8 (3)	N3—C24—H24B	108.7
N1—C9—C4	122.6 (2)	H24A—C24—H24B	107.6
N1—C9—C8	116.2 (2)	C25—C24—N3	114.3 (4)
C4—C9—C8	121.2 (2)	C25—C24—H24A	108.7

C11—C10—C1	120.3 (3)	C25—C24—H24B	108.7
C11—C10—C15	119.7 (3)	C24—C25—H25A	109.5
C15—C10—C1	120.0 (3)	C24—C25—H25B	109.5
C10—C11—H11	119.6	C24—C25—H25C	109.5
C12—C11—C10	120.8 (3)	H25A—C25—H25B	109.5
C12—C11—H11	119.6	H25A—C25—H25C	109.5
C11—C12—H12	120.8	H25B—C25—H25C	109.5
C11—C12—C13	118.3 (3)	N3—C26—H26A	108.5
C13—C12—H12	120.8	N3—C26—H26B	108.5
C12—C13—N2	118.6 (3)	H26A—C26—H26B	107.5
C14—C13—N2	118.8 (3)	C27—C26—N3	115.0 (4)
C14—C13—C12	122.6 (3)	C27—C26—H26A	108.5
C13—C14—H14	120.8	C27—C26—H26B	108.5
C13—C14—C15	118.5 (3)	C26—C27—H27A	109.5
C15—C14—H14	120.8	C26—C27—H27B	109.5
C10—C15—H15	120.0	C26—C27—H27C	109.5
C14—C15—C10	120.1 (3)	H27A—C27—H27B	109.5
C14—C15—H15	120.0	H27A—C27—H27C	109.5
C17—C16—C3	120.0 (3)	H27B—C27—H27C	109.5

Zn1—O1—C8—C7	171.4 (3)	C4—C3—C16—C21	48.1 (4)
Zn1—O1—C8—C9	−8.9 (4)	C4—C5—C6—C7	1.2 (5)
Zn1—N1—C1—C2	−175.0 (2)	C5—C4—C9—N1	173.4 (3)
Zn1—N1—C1—C10	3.8 (4)	C5—C4—C9—C8	−6.9 (4)
Zn1—N1—C9—C4	−178.8 (2)	C5—C6—C7—C8	−3.1 (6)
Zn1—N1—C9—C8	1.5 (3)	C6—C7—C8—O1	179.7 (3)
O1—C8—C9—N1	5.0 (4)	C6—C7—C8—C9	−0.1 (5)
O1—C8—C9—C4	−174.7 (3)	C7—C8—C9—N1	−175.2 (3)
N1—C1—C2—C3	−3.7 (4)	C7—C8—C9—C4	5.1 (5)
N1—C1—C10—C11	48.7 (4)	C9—N1—C1—C2	1.6 (4)
N1—C1—C10—C15	−131.9 (3)	C9—N1—C1—C10	−179.5 (2)
C1—N1—C9—C4	3.9 (4)	C9—C4—C5—C6	3.7 (5)
C1—N1—C9—C8	−175.9 (3)	C10—C1—C2—C3	177.5 (3)
C1—C2—C3—C4	0.3 (4)	C10—C11—C12—C13	1.0 (5)
C1—C2—C3—C16	−179.5 (3)	C11—C10—C15—C14	−2.9 (4)
C1—C10—C11—C12	−179.1 (3)	C11—C12—C13—N2	176.2 (3)
C1—C10—C15—C14	177.7 (3)	C11—C12—C13—C14	−2.1 (5)
O2—N2—C13—C12	13.8 (5)	C12—C13—C14—C15	0.7 (5)
O2—N2—C13—C14	−167.8 (3)	C13—C14—C15—C10	1.8 (5)
N2—C13—C14—C15	−177.6 (3)	C15—C10—C11—C12	1.5 (4)
C2—C1—C10—C11	−132.4 (3)	C16—C3—C4—C5	4.1 (5)
C2—C1—C10—C15	47.0 (4)	C16—C3—C4—C9	−175.5 (3)
C2—C3—C4—C5	−175.7 (3)	C16—C17—C18—C19	1.1 (5)
C2—C3—C4—C9	4.7 (4)	C17—C16—C21—C20	1.7 (5)
C2—C3—C16—C17	47.5 (4)	C17—C18—C19—C20	0.6 (6)
C2—C3—C16—C21	−132.1 (3)	C18—C19—C20—C21	−1.1 (6)
O3—N2—C13—C12	−164.9 (3)	C19—C20—C21—C16	−0.1 (5)
O3—N2—C13—C14	13.5 (5)	C21—C16—C17—C18	−2.2 (5)

C3—C4—C5—C6	−175.9 (3)	C22—N3—C24—C25	−67.7 (5)
C3—C4—C9—N1	−7.0 (4)	C22—N3—C26—C27	169.5 (4)
C3—C4—C9—C8	172.7 (3)	C24—N3—C22—C23	169.8 (3)
C3—C16—C17—C18	178.2 (3)	C24—N3—C26—C27	−68.9 (6)
C3—C16—C21—C20	−178.7 (3)	C26—N3—C22—C23	−69.1 (4)
C4—C3—C16—C17	−132.3 (3)	C26—N3—C24—C25	172.4 (4)

Hydrogen-bond geometry (Å, º)

Cg3 and Cg5 are the centroids of C4-C9 and C16-C21, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1	0.88 (4)	1.92 (4)	2.807 (4)	178 (4)
C12—H12···*Cg*3^{i}	0.93	2.78	3.553 (4)	141
C14—H14···*Cg*3^{ii}	0.93	3.04	3.837 (4)	145
C24—H24*B*···*Cg*5^{iii}	0.97	2.94	3.809 (5)	149

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

Bis(triethylammonium) {2,2′-[1,4-phenylenebis(nitrilomethylidyne)]diphenolato}bis[dichloridozinc(II)] (ZnBS)

Crystal data

$(C_6H_{16}N)_2[Zn_2(C_{20}H_{14}N_2O_2)Cl_4]$
M_r = 791.24
Monoclinic, $P2_1/c$
a = 11.9843 (9) Å
b = 13.4570 (7) Å
c = 11.9944 (11) Å
β = 103.838 (9)°
V = 1878.2 (3) Å^3
Z = 2
$F(000)$ = 820
D_x = 1.399 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3646 reflections
θ = 3.0–27.7°
μ = 1.59 mm^{-1}
T = 293 K
Block, orangish brown
0.5 × 0.5 × 0.5 mm

Data collection

SuperNova, Single source at offset/far, Eos diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 15.9631 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
T_{min} = 0.473, T_{max} = 1.000
10514 measured reflections
3814 independent reflections
2836 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 26.4°, θ_{min} = 2.6°
h = −14→14
k = −16→15
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.158
S = 1.05
3814 reflections
206 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.7323P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.26755 (4)	0.45138 (3)	0.68426 (4)	0.0407 (2)
Cl1	0.37732 (10)	0.32105 (8)	0.66656 (10)	0.0572 (3)
O1	0.2337 (3)	0.5315 (2)	0.5445 (2)	0.0478 (7)
N1	0.3640 (3)	0.5558 (2)	0.7831 (3)	0.0356 (7)
C1	0.2399 (3)	0.6292 (3)	0.5442 (3)	0.0389 (9)
Cl2	0.11116 (10)	0.41690 (10)	0.74634 (14)	0.0734 (4)
C2	0.1859 (4)	0.6806 (3)	0.4441 (4)	0.0495 (10)
H2A	0.146066	0.645011	0.380496	0.059*
C3	0.1907 (4)	0.7823 (4)	0.4379 (4)	0.0577 (12)
H3	0.153834	0.814314	0.370471	0.069*
C4	0.2495 (4)	0.8379 (4)	0.5303 (4)	0.0619 (13)
H4	0.252095	0.906859	0.525949	0.074*
C5	0.3038 (4)	0.7891 (3)	0.6282 (4)	0.0600 (13)
H5	0.345075	0.826185	0.689899	0.072*
C6	0.3000 (3)	0.6862 (3)	0.6396 (3)	0.0399 (9)
C7	0.3605 (3)	0.6466 (3)	0.7493 (3)	0.0423 (9)
H7	0.401718	0.692082	0.801615	0.051*
C8	0.4335 (3)	0.5297 (3)	0.8932 (3)	0.0370 (8)
C9	0.5314 (3)	0.5822 (3)	0.9465 (3)	0.0421 (9)
H9	0.553630	0.637402	0.910344	0.051*
C10	0.5960 (4)	0.5531 (3)	1.0529 (4)	0.0422 (9)
H10	0.660230	0.589988	1.088557	0.051*
N2	0.2124 (3)	0.4098 (3)	0.3531 (3)	0.0542 (9)
C11	0.1537 (5)	0.4581 (4)	0.2419 (5)	0.0652 (14)
H11A	0.195358	0.518079	0.232368	0.078*
H11B	0.076908	0.477601	0.246096	0.078*
C12	0.1446 (6)	0.3922 (5)	0.1357 (5)	0.0908 (19)
H12A	0.106666	0.428237	0.068169	0.136*
H12B	0.101226	0.333556	0.142833	0.136*
H12C	0.220244	0.373539	0.129589	0.136*
C13	0.1557 (5)	0.3189 (4)	0.3848 (5)	0.0790 (16)
H13A	0.152196	0.269200	0.325422	0.095*
H13B	0.202858	0.292250	0.455665	0.095*
C14	0.0394 (5)	0.3356 (5)	0.3998 (6)	0.095 (2)
H14A	−0.009863	0.356026	0.328064	0.142*
H14B	0.041376	0.386598	0.456219	0.142*
H14C	0.010573	0.275206	0.424967	0.142*
C15	0.3399 (5)	0.3890 (4)	0.3623 (4)	0.0692 (14)
H15A	0.373086	0.358910	0.436289	0.083*

H15B	0.346897	0.341748	0.303305	0.083*
C16	0.4060 (6)	0.4798 (6)	0.3498 (6)	0.100 (2)
H16A	0.389363	0.499031	0.270413	0.150*
H16B	0.486673	0.466640	0.376430	0.150*
H16C	0.384566	0.532625	0.394328	0.150*
H2	0.217 (4)	0.461 (3)	0.410 (4)	0.054 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0438 (3)	0.0306 (3)	0.0447 (3)	−0.00034 (18)	0.0046 (2)	0.00142 (17)
Cl1	0.0699 (8)	0.0381 (6)	0.0628 (7)	0.0139 (5)	0.0142 (6)	0.0004 (5)
O1	0.0635 (19)	0.0363 (15)	0.0399 (16)	0.0023 (13)	0.0055 (13)	−0.0005 (11)
N1	0.0391 (17)	0.0307 (17)	0.0368 (17)	−0.0030 (13)	0.0089 (14)	0.0018 (12)
C1	0.040 (2)	0.037 (2)	0.040 (2)	0.0022 (16)	0.0120 (17)	0.0023 (16)
Cl2	0.0423 (6)	0.0692 (8)	0.1099 (11)	0.0044 (6)	0.0208 (6)	0.0289 (7)
C2	0.053 (3)	0.051 (3)	0.043 (2)	0.005 (2)	0.0069 (19)	0.0054 (18)
C3	0.062 (3)	0.056 (3)	0.056 (3)	0.013 (2)	0.015 (2)	0.021 (2)
C4	0.079 (3)	0.038 (2)	0.067 (3)	0.002 (2)	0.013 (3)	0.013 (2)
C5	0.073 (3)	0.036 (2)	0.068 (3)	−0.005 (2)	0.010 (3)	0.002 (2)
C6	0.042 (2)	0.035 (2)	0.045 (2)	−0.0018 (16)	0.0143 (18)	0.0015 (16)
C7	0.045 (2)	0.038 (2)	0.043 (2)	−0.0027 (17)	0.0067 (17)	−0.0054 (17)
C8	0.041 (2)	0.036 (2)	0.033 (2)	−0.0018 (16)	0.0085 (16)	−0.0004 (15)
C9	0.049 (2)	0.036 (2)	0.042 (2)	−0.0082 (17)	0.0109 (18)	0.0081 (16)
C10	0.045 (2)	0.040 (2)	0.040 (2)	−0.0126 (17)	0.0068 (17)	0.0005 (16)
N2	0.069 (3)	0.043 (2)	0.055 (2)	−0.0016 (18)	0.0244 (19)	−0.0083 (18)
C11	0.061 (3)	0.068 (3)	0.065 (3)	0.018 (2)	0.014 (2)	−0.002 (2)
C12	0.094 (4)	0.113 (5)	0.060 (4)	0.010 (4)	0.007 (3)	−0.013 (3)
C13	0.102 (4)	0.055 (3)	0.076 (4)	−0.014 (3)	0.013 (3)	−0.010 (3)
C14	0.063 (4)	0.103 (5)	0.123 (6)	−0.031 (3)	0.031 (4)	−0.008 (4)
C15	0.084 (4)	0.073 (4)	0.053 (3)	0.025 (3)	0.021 (3)	−0.006 (2)
C16	0.081 (4)	0.118 (6)	0.116 (6)	−0.003 (4)	0.050 (4)	−0.008 (4)

Geometric parameters (Å, º)

Zn1—Cl1	2.2327 (11)	C10—H10	0.9300
Zn1—O1	1.952 (3)	N2—C11	1.499 (6)
Zn1—N1	2.015 (3)	N2—C13	1.492 (7)
Zn1—Cl2	2.2248 (13)	N2—C15	1.531 (6)
O1—C1	1.316 (4)	N2—H2	0.96 (5)
N1—C7	1.284 (5)	C11—H11A	0.9700
N1—C8	1.427 (5)	C11—H11B	0.9700
C1—C2	1.403 (5)	C11—C12	1.534 (8)
C1—C6	1.422 (5)	C12—H12A	0.9600
C2—H2A	0.9300	C12—H12B	0.9600
C2—C3	1.372 (6)	C12—H12C	0.9600
C3—H3	0.9300	C13—H13A	0.9700
C3—C4	1.383 (7)	C13—H13B	0.9700

C4—H4	0.9300	C13—C14	1.465 (8)
C4—C5	1.367 (6)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C5—C6	1.394 (6)	C14—H14C	0.9600
C6—C7	1.444 (5)	C15—H15A	0.9700
C7—H7	0.9300	C15—H15B	0.9700
C8—C9	1.388 (5)	C15—C16	1.483 (9)
C8—C10^{i}	1.376 (5)	C16—H16A	0.9600
C9—H9	0.9300	C16—H16B	0.9600
C9—C10	1.382 (5)	C16—H16C	0.9600
C10—C8^{i}	1.376 (5)		

O1—Zn1—Cl1	111.00 (9)	C11—N2—H2	105 (3)
O1—Zn1—N1	95.27 (12)	C13—N2—C11	115.9 (4)
O1—Zn1—Cl2	112.58 (10)	C13—N2—C15	109.8 (4)
N1—Zn1—Cl1	109.60 (9)	C13—N2—H2	111 (3)
N1—Zn1—Cl2	111.06 (10)	C15—N2—H2	101 (3)
Cl2—Zn1—Cl1	115.51 (5)	N2—C11—H11A	108.7
C1—O1—Zn1	123.6 (2)	N2—C11—H11B	108.7
C7—N1—Zn1	120.5 (3)	N2—C11—C12	114.4 (4)
C7—N1—C8	119.6 (3)	H11A—C11—H11B	107.6
C8—N1—Zn1	119.9 (2)	C12—C11—H11A	108.7
O1—C1—C2	118.7 (3)	C12—C11—H11B	108.7
O1—C1—C6	123.6 (3)	C11—C12—H12A	109.5
C2—C1—C6	117.6 (4)	C11—C12—H12B	109.5
C1—C2—H2A	119.3	C11—C12—H12C	109.5
C3—C2—C1	121.4 (4)	H12A—C12—H12B	109.5
C3—C2—H2A	119.3	H12A—C12—H12C	109.5
C2—C3—H3	119.4	H12B—C12—H12C	109.5
C2—C3—C4	121.1 (4)	N2—C13—H13A	108.7
C4—C3—H3	119.4	N2—C13—H13B	108.7
C3—C4—H4	120.8	H13A—C13—H13B	107.6
C5—C4—C3	118.4 (4)	C14—C13—N2	114.2 (5)
C5—C4—H4	120.8	C14—C13—H13A	108.7
C4—C5—H5	118.6	C14—C13—H13B	108.7
C4—C5—C6	122.8 (4)	C13—C14—H14A	109.5
C6—C5—H5	118.6	C13—C14—H14B	109.5
C1—C6—C7	125.6 (3)	C13—C14—H14C	109.5
C5—C6—C1	118.7 (4)	H14A—C14—H14B	109.5
C5—C6—C7	115.8 (4)	H14A—C14—H14C	109.5
N1—C7—C6	127.6 (4)	H14B—C14—H14C	109.5
N1—C7—H7	116.2	N2—C15—H15A	109.0
C6—C7—H7	116.2	N2—C15—H15B	109.0
C9—C8—N1	122.9 (3)	H15A—C15—H15B	107.8
C10^{i}—C8—N1	118.4 (3)	C16—C15—N2	112.9 (5)
C10^{i}—C8—C9	118.7 (3)	C16—C15—H15A	109.0
C8—C9—H9	119.8	C16—C15—H15B	109.0
C10—C9—C8	120.4 (4)	C15—C16—H16A	109.5

C10—C9—H9	119.8	C15—C16—H16B	109.5
C8^{i}—C10—C9	120.9 (4)	C15—C16—H16C	109.5
C8^{i}—C10—H10	119.5	H16A—C16—H16B	109.5
C9—C10—H10	119.5	H16A—C16—H16C	109.5
C11—N2—C15	113.0 (4)	H16B—C16—H16C	109.5
Zn1—O1—C1—C2	−163.5 (3)	C4—C5—C6—C1	1.9 (7)
Zn1—O1—C1—C6	17.6 (5)	C4—C5—C6—C7	−179.1 (5)
Zn1—N1—C7—C6	−5.5 (6)	C5—C6—C7—N1	175.5 (4)
Zn1—N1—C8—C9	154.8 (3)	C6—C1—C2—C3	0.0 (6)
Zn1—N1—C8—C10^{i}	−23.2 (5)	C7—N1—C8—C9	−27.6 (6)
O1—C1—C2—C3	−179.0 (4)	C7—N1—C8—C10^{i}	154.5 (4)
O1—C1—C6—C5	178.0 (4)	C8—N1—C7—C6	176.9 (4)
O1—C1—C6—C7	−1.0 (6)	C8—C9—C10—C8^{i}	1.6 (7)
N1—C8—C9—C10	−179.5 (4)	C10^{i}—C8—C9—C10	−1.6 (7)
C1—C2—C3—C4	0.3 (7)	C11—N2—C13—C14	−61.3 (6)
C1—C6—C7—N1	−5.5 (7)	C11—N2—C15—C16	57.8 (6)
C2—C1—C6—C5	−1.0 (6)	C13—N2—C11—C12	−61.6 (6)
C2—C1—C6—C7	−180.0 (4)	C13—N2—C15—C16	−171.1 (5)
C2—C3—C4—C5	0.5 (7)	C15—N2—C11—C12	66.4 (6)
C3—C4—C5—C6	−1.6 (8)	C15—N2—C13—C14	169.1 (5)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.96 (4)	1.84 (4)	2.782 (4)	165 (4)
C9—H9···Cl1^{ii}	0.93	2.83	3.752 (4)	171
C11—H11···Cl2^{iii}	0.97	2.68	3.625 (6)	164
C13—H13···Cl2^{iv}	0.97	2.68	3.562 (6)	151
C15—H15*A*···Cl1	0.97	2.80	3.684 (5)	152
C15—H15*B*···Cl1^{iv}	0.97	2.81	3.769 (5)	169

Symmetry codes: (ii) −*x*+1, *y*+1/2, −*z*+3/2; (iii) −*x*, −*y*+1, −*z*+1; (iv) *x*, −*y*+1/2, *z*−1/2.