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# Crystal structures of di-$\mu$-bromido-bis{dibromido-[$\eta^5$-2-(dimethylamino)indenyl]zirconium(IV)} and dibromidobis[$\eta^5$-2-(dimethylamino)indenyl]-zirconium(IV)

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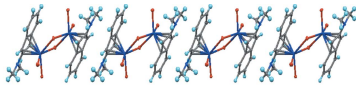
In the title compounds, $[Zr_2Br_6(C_{11}H_{12}N)_2]$, (I) and $[ZrBr_2(C_{11}H_{12}N)_2]$, (II), the positions of the $\eta^5$-binding 2-dimethylaminoindenyl units are fixed by intramolecular C—H···Br interactions involving aromatic or dimethylamino H atoms. The binuclear molecule of (I) is located on a general position, while the mononuclear molecule of (II) is situated on a twofold rotation axis. Both $Zr^{IV}$ atoms in (I) are ligated by one cyclopentadienyl (CP) ring and four Br ligands (two bridging, two terminal), while in (II) the $Zr^{IV}$ atom is ligated by two CP rings and two terminal Br ligands. The crystal structures of both (I) and (II) comprise of strands of $\pi$–$\pi$- and N–$\pi$-bonded molecules, which in turn are linked by C—H···Br interactions.

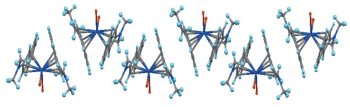
## 1. Chemical context

In the course of a systematic study of the molecular and crystal structures of cyclopentadienyl-halogenide complexes of zirconium(IV) and hafnium(IV) bearing oxygen- and nitrogen-containing substituents at the cyclopentadienyl-type ligand(s) to understand possible intra- and intermolecular interactions between the ligands resulting in specific conformational properties of the complexes as well as to explain influences of the electronic properties of the involved fragments, we have determined several new crystal structures. These results are of importance for the understanding of possible intermolecular interactions in solutions of the compounds under investigation for their further use in catalysis. Here we report on synthesis and crystal structures of two $Zr^{IV}$ complexes with substituted indenyl ligands, $[Zr_2(C_{11}H_{12}N)_2Br_6]$, (I) and $[Zr(C_{11}H_{12}N)_2Br_2]$, (II). Other zirconium(IV) complexes with indenyl ligands have been reported by Chirik (2010) and Pinkas & Lamač (2015).

(I)



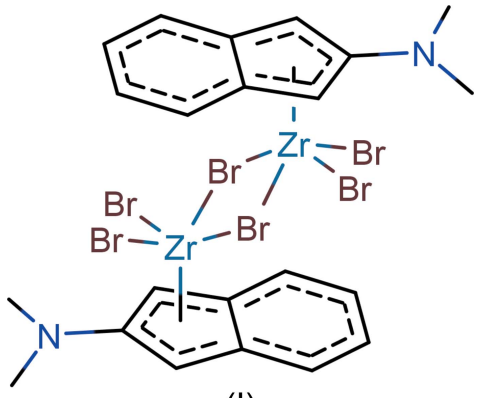
(II)



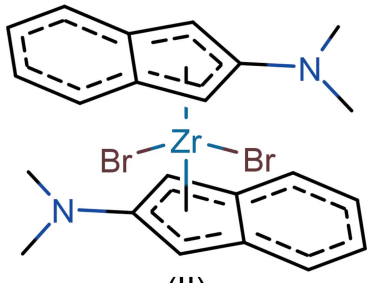
## 2. Structural commentary

Structure determination revealed that both title compounds are monomeric in the solid state, with the dimethylaminoindenyl anions acting as $\eta^5$-ligands and the $Zr^{IV}$ atoms being above the centres of cyclopentadienyl (CP) rings. The 2-dimethylaminoindenyl units deviate from planarity, the highest deviations involving the N atoms in (I) [0.165 (3) Å for N1 in the first anion and 0.171 (3) Å for N2 in the second

anion] and one C atom [0.187 (1) Å for C9] in (II). The Zr···centroid(CP) distances are 2.1815 (15) Å and 2.1823 (15) Å in (I) and 2.2278 (6) Å in (II). The dihedral angles between the planes of the indenyl units which belong to the same molecule are 3.70 (8)° in (I) and 44.25 (5)° in (II).




(I)




(II)

Compound (I) (Fig. 1) crystallizes with one binuclear complex molecule in the asymmetric unit. Each of the $Zr^{IV}$ atoms is coordinated by one CP and four Br ligands, with two Br ligands in a bridging and two in a terminal coordination mode. The Zr···Zr distance is 4.3359 (5) Å, a little longer than in a related complex with 2-(9*H*-carbazol-9-yl)indenyl ligands [4.3212 (7) Å; Lebedev *et al.*, 2009]. The Zr—centroid(CP) distances found in (I) are virtually identical to those of the related complex [2.1812 (15) and 2.1845 (15) Å; Lebedev *et al.*, 2009] and close to those of other similar complexes with Cl and Cp* ligands [2.176 (2) Å; Martín *et al.*, 1994] or Cl and 1-[*n*-butyl(dimethyl)silyl]-2,3,4,5,6,7-hexamethylindenyl ligands [2.1896 (8) Å; Buffet *et al.*, 2015]. In (I), the range of centroid(CP)—Zr—Br angles is 103–104° and 108–111° for bridging and terminal Br ligands, respectively. The Br—Zr—Br angles are 75.823 (13) and 76.248 (13)° for bridging Br ligands and 92.208 (16) and 90.069 (16)° for terminal Br ligands.

Compound (II) (Fig. 2) crystallizes with one half of the complex molecule in the asymmetric unit, the other half being completed by application of twofold rotation symmetry. Here the $Zr^{IV}$ atom is coordinated by two symmetry-related CP ligands and two symmetry-related terminal Br ligands. The Br—Zr—Br angle is 93.390 (7)°, smaller than in related structures with Cl ligands [95.04 (8) or 94.90 (8)°; Barsties *et al.*, 1996; Luttikhedde *et al.*, 1996]. Correspondingly, the

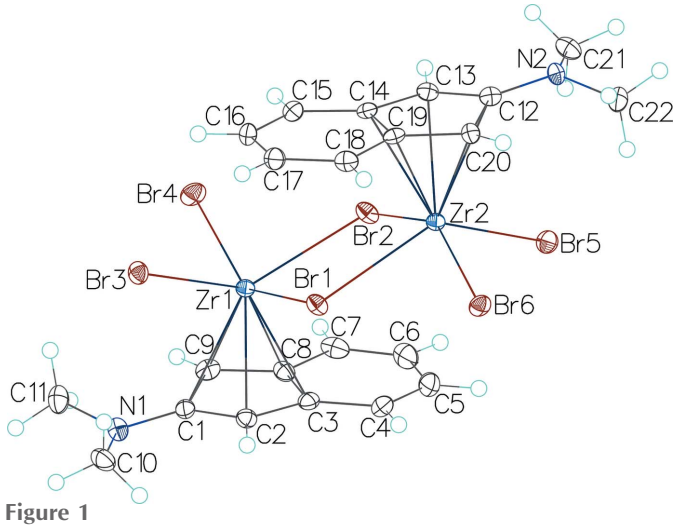



**Figure 1**
The molecular structure of compound (I) with displacement ellipsoids drawn at the 50% probability level.

centroid(CP)—Zr—centroid(CP) angle is a little bit larger at 133.42 (3)° *versus* 133.07 (12) and 132.77 (14)° in the related structures.

The positions of the 2-dimethylaminoindenyl units in the two structures are fixed by intramolecular C—H···Br interactions involving aromatic or dimethylamino H atoms (Tables 1 and 2).

## 3. Supramolecular features

The crystal structures of both (I) and (II) (Figs. 3 and 4) comprise of infinite strands (along [100] for (I) and along [001]

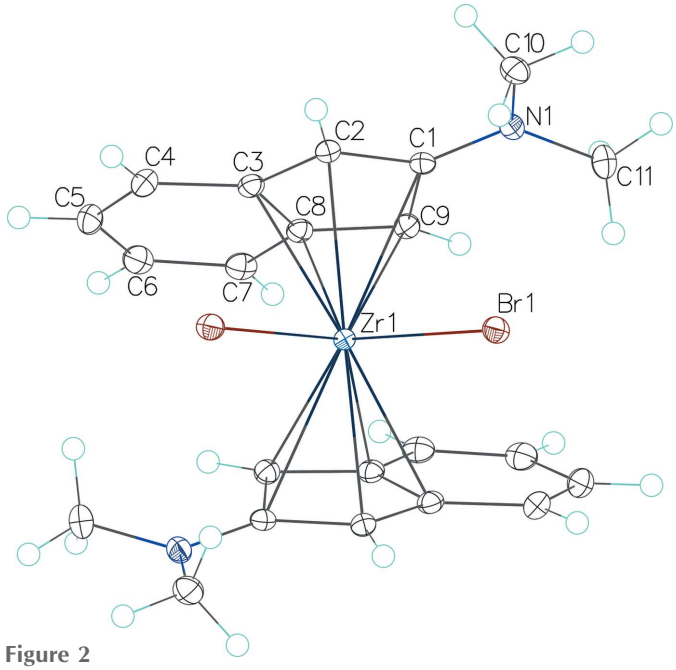



**Figure 2**
The molecular structure of compound (II) with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are generated by symmetry code $-x+1, y, -z+\frac{3}{2}$.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2···Br4$^{i}$ | 1.00 | 2.96 | 3.694 (4) | 131 |
| C4—H4···Br4$^{i}$ | 0.95 | 3.35 | 3.944 (4) | 123 |
| C4—H4···Br5$^{ii}$ | 0.95 | 3.42 | 4.123 (4) | 132 |
| C5—H5···Br5 | 0.95 | 3.53 | 3.998 (4) | 113 |
| C5—H5···Br5$^{ii}$ | 0.95 | 3.52 | 4.182 (4) | 129 |
| C5—H5···Br6$^{ii}$ | 0.95 | 2.93 | 3.840 (4) | 162 |
| C10—H10*C*···Br3 | 0.98 | 2.88 | 3.613 (4) | 133 |
| C11—H11*A*···Br6$^{iii}$ | 0.98 | 2.91 | 3.817 (4) | 154 |
| C11—H11*B*···Br3 | 0.98 | 3.21 | 3.843 (4) | 124 |
| C11—H11*B*···Br5$^{iv}$ | 0.98 | 3.44 | 3.919 (4) | 113 |
| C13—H13···Br6$^{v}$ | 1.00 | 3.04 | 3.690 (4) | 124 |
| C15—H15···Br6$^{v}$ | 0.95 | 3.04 | 3.655 (4) | 124 |
| C16—H16···Br3 | 0.95 | 3.27 | 3.763 (4) | 114 |
| C16—H16···Br3$^{vi}$ | 0.95 | 3.15 | 3.754 (4) | 123 |
| C17—H17···Br3$^{vi}$ | 0.95 | 2.97 | 3.665 (4) | 131 |
| C18—H18···Br2$^{vii}$ | 0.95 | 3.01 | 3.897 (4) | 155 |
| C20—H20···Br4$^{vii}$ | 1.00 | 3.17 | 4.115 (4) | 158 |
| C21—H21*B*···Br5 | 0.98 | 2.94 | 3.660 (4) | 131 |
| C21—H21*C*···Br3$^{viii}$ | 0.98 | 3.20 | 3.811 (4) | 122 |
| C22—H22*A*···Br4$^{vii}$ | 0.98 | 3.02 | 3.986 (4) | 167 |
| C22—H22*B*···Br4$^{viii}$ | 0.98 | 3.36 | 3.974 (4) | 122 |
| C22—H22*C*···Br5 | 0.98 | 3.06 | 3.738 (4) | 128 |

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

for (II)), of $\pi$–$\pi$- and N–$\pi$-bonded molecules, which in turn are linked by C—H···Br interactions. The plane-to-plane distances of the stacked dimethylaminoindenyl moieties are 3.656 (4) and 3.481 (3) Å for (I) and 3.6533 (10) Å for (II), with angles between the planes of 3.70 (8)° for (I) and 0° for (II). C—H···Br interactions are in the range 2.86–3.53 Å for both structures (Tables 1 and 2). The presence of the ternary amino function in the two structures plays a crucial role in the supramolecular architecture since dichlorido-bis($\eta^5$-2-dimethylaminoindenyl)zirconium(IV) (Barsties *et al.*, 1996; Luttikhedde *et al.*, 1996) also exhibits stacking interactions, but dichlorido-bis($\eta^5$-indenyl)zirconium(IV) (Repo *et al.*, 1996) does not.

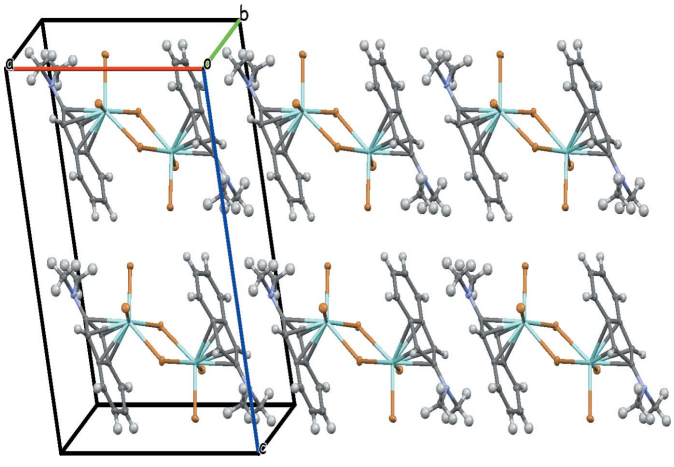



**Figure 3**
The crystal packing of compound (I) with displacement ellipsoids drawn at the 50% probability level.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C5—H5···Br1$^{i}$ | 0.95 | 2.98 | 3.8960 (13) | 163 |
| C6—H6···Br1$^{ii}$ | 0.95 | 3.10 | 3.7621 (13) | 128 |
| C7—H7···Br1$^{ii}$ | 0.95 | 3.09 | 3.7493 (12) | 128 |
| C10—H10*A*···Br1$^{iii}$ | 0.98 | 3.11 | 3.9381 (13) | 143 |
| C10—H10*C*···Br1 | 0.98 | 2.86 | 3.5178 (13) | 125 |
| C11—H11*A*···Br1$^{iv}$ | 0.98 | 3.41 | 3.9170 (13) | 115 |
| C11—H11*B*···Br1 | 0.98 | 3.04 | 3.6325 (13) | 120 |

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

## 4. Synthesis and crystallization

Di[($\mu$-bromido)($\eta^5$-2-dimethylaminoindenyl)dibromidozirconium(IV)], (I), was obtained by reaction of $Zr(NMe_2)_4$ with one equivalent of 2-dimethylamino-1*H*-indene in toluene, followed by treatment of an excess of $Me_3SiBr$. The crude product was recrystallized from toluene.

Bis($\eta^5$-2-dimethylaminoindenyl)dibromidozirconium(IV), (II), was obtained from the reaction of (I) with one equivalent (per Zr) of 2-dimethylaminoindenyllithium in tetrahydrofuran. The crude product was recrystallized from toluene.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were fixed geometrically and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic hydrogen atoms and $U_{iso}(H) = 1.5U_{eq}(C)$ for hydrogen atoms associated with methyl groups.

## Acknowledgements

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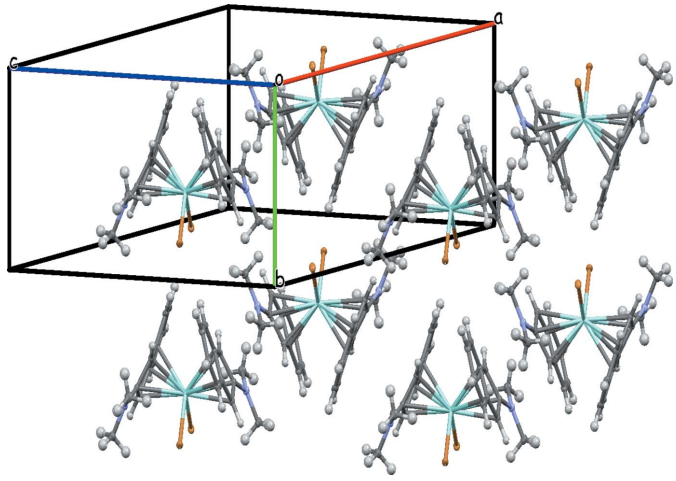


**Figure 4**
The crystal packing of compound (II) with displacement ellipsoids drawn at the 50% probability level.

**Table 3**
Experimental details.

| | (I) | (II) |
|---|---|---|
| Crystal data | | |
| Chemical formula | $[Zr_2Br_6(C_{11}H_{12}N)_2]$ | $[ZrBr_2(C_{11}H_{12}N)_2]$ |
| $M_r$ | 978.33 | 567.47 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $C2/c$ |
| Temperature (K) | 100 | 100 |
| $a, b, c$ (Å) | 11.3275 (6), 13.9365 (7), 17.6082 (9) | 18.4476 (5), 8.3497 (2), 14.3737 (4) |
| $\beta$ (°) | 99.028 (1) | 111.854 (1) |
| $V$ (Å$^3$) | 2745.3 (2) | 2054.90 (9) |
| $Z$ | 4 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 9.51 | 4.43 |
| Crystal size (mm) | 0.34 × 0.14 × 0.04 | 0.26 × 0.24 × 0.15 |
| Data collection | | |
| Diffractometer | Bruker APEXII CCD | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2008) | Multi-scan (*SADABS*; Bruker, 2008) |
| $T_{min}$, $T_{max}$ | 0.052, 0.165 | 0.552, 0.747 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 35046, 7921, 6465 | 13152, 3003, 2876 |
| $R_{int}$ | 0.050 | 0.017 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.703 | 0.703 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.033, 0.075, 1.04 | 0.015, 0.039, 1.07 |
| No. of reflections | 7921 | 3003 |
| No. of parameters | 293 | 125 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.23, −0.80 | 0.45, −0.42 |

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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# supporting information

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# Crystal structures of di-$\mu$-bromido-bis{dibromido[$\eta^5$-2-(dimethylamino)-indenyl]zirconium(IV)} and dibromidobis[$\eta^5$-2-(dimethylamino)-indenyl]zirconium(IV)

**Michael G. Medvedev, Ilya S. Borisov, Pavel S. Kulyabin, Vyatcheslav V. Izmer, Dmitry S. Kononovich, Dmitry V. Uborsky and Alexander Z. Voskoboynikov**

## Computing details

For both compounds, data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### (I) Di-$\mu$-bromido-bis{dibromido[$\eta^5$-2-(dimethylamino)indenyl]zirconium(IV)}

*Crystal data*

$[Zr_2Br_6(C_{11}H_{12}N)_2]$
$M_r$ = 978.33
Monoclinic, $P2_1/n$
$a$ = 11.3275 (6) Å
$b$ = 13.9365 (7) Å
$c$ = 17.6082 (9) Å
$\beta$ = 99.028 (1)°
$V$ = 2745.3 (2) Å$^3$
$Z$ = 4
$F(000)$ = 1840
$D_x$ = 2.367 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9986 reflections
$\theta$ = 2.3–35.3°
$\mu$ = 9.51 mm$^{-1}$
$T$ = 100 K
Plate, clear light yellow
0.34 × 0.14 × 0.04 mm

*Data collection*

Bruker APEXII CCD diffractometer
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.052, $T_{max}$ = 0.165
35046 measured reflections
7921 independent reflections
6465 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.050
$\theta_{max}$ = 30.0°, $\theta_{min}$ = 1.9°
$h$ = −15→15
$k$ = −19→19
$l$ = −24→24

*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
7921 reflections
293 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 4.7762P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.80 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zr1 | 0.36393 (3) | 0.65228 (2) | 0.29842 (2) | 0.01182 (7) |
| Zr2 | 0.64736 (3) | 0.55177 (2) | 0.17911 (2) | 0.01153 (7) |
| Br1 | 0.48396 (3) | 0.48720 (2) | 0.26602 (2) | 0.01492 (7) |
| Br2 | 0.51643 (3) | 0.71490 (2) | 0.20438 (2) | 0.01584 (8) |
| Br3 | 0.39515 (3) | 0.58155 (3) | 0.43385 (2) | 0.01707 (8) |
| Br4 | 0.39478 (4) | 0.82303 (3) | 0.35560 (2) | 0.02100 (8) |
| Br5 | 0.61893 (3) | 0.60910 (3) | 0.04056 (2) | 0.01838 (8) |
| Br6 | 0.63720 (3) | 0.37380 (2) | 0.13784 (2) | 0.01671 (8) |
| N1 | 0.0895 (3) | 0.5840 (2) | 0.36083 (18) | 0.0173 (6) |
| N2 | 0.9189 (3) | 0.6378 (2) | 0.12242 (17) | 0.0140 (6) |
| C1 | 0.1401 (3) | 0.6093 (3) | 0.2990 (2) | 0.0147 (7) |
| C2 | 0.1957 (3) | 0.5458 (3) | 0.2516 (2) | 0.0146 (7) |
| H2 | 0.1972 | 0.4743 | 0.2561 | 0.018* |
| C3 | 0.2185 (3) | 0.5991 (3) | 0.1849 (2) | 0.0155 (7) |
| C4 | 0.2623 (3) | 0.5706 (3) | 0.1174 (2) | 0.0202 (8) |
| H4 | 0.2819 | 0.5055 | 0.1095 | 0.024* |
| C5 | 0.2755 (4) | 0.6392 (3) | 0.0640 (2) | 0.0244 (8) |
| H5 | 0.3036 | 0.6210 | 0.0181 | 0.029* |
| C6 | 0.2485 (4) | 0.7367 (3) | 0.0755 (2) | 0.0250 (9) |
| H6 | 0.2573 | 0.7821 | 0.0365 | 0.030* |
| C7 | 0.2100 (3) | 0.7672 (3) | 0.1412 (2) | 0.0210 (8) |
| H7 | 0.1950 | 0.8333 | 0.1490 | 0.025* |
| C8 | 0.1928 (3) | 0.6973 (3) | 0.1979 (2) | 0.0160 (7) |
| C9 | 0.1556 (3) | 0.7050 (3) | 0.2719 (2) | 0.0174 (7) |
| H9 | 0.1235 | 0.7644 | 0.2931 | 0.021* |
| C10 | 0.0968 (3) | 0.4848 (3) | 0.3864 (2) | 0.0219 (8) |
| H10A | 0.0764 | 0.4423 | 0.3419 | 0.033* |
| H10B | 0.0405 | 0.4743 | 0.4226 | 0.033* |
| H10C | 0.1782 | 0.4710 | 0.4119 | 0.033* |
| C11 | 0.0659 (4) | 0.6577 (3) | 0.4155 (2) | 0.0226 (8) |
| H11A | 0.0293 | 0.7137 | 0.3875 | 0.034* |
| H11B | 0.1411 | 0.6767 | 0.4473 | 0.034* |
| H11C | 0.0113 | 0.6321 | 0.4486 | 0.034* |
| C12 | 0.8679 (3) | 0.6084 (2) | 0.1826 (2) | 0.0141 (7) |
| C13 | 0.8056 (3) | 0.6676 (2) | 0.2300 (2) | 0.0144 (7) |
| H13 | 0.7982 | 0.7390 | 0.2261 | 0.017* |
| C14 | 0.7834 (3) | 0.6109 (2) | 0.2951 (2) | 0.0135 (6) |

| | | | | |
|---|---|---|---|---|
| C15 | 0.7322 (3) | 0.6339 (3) | 0.3611 (2) | 0.0165 (7) |
| H15 | 0.7070 | 0.6975 | 0.3695 | 0.020* |
| C16 | 0.7198 (3) | 0.5621 (3) | 0.4129 (2) | 0.0160 (7) |
| H16 | 0.6874 | 0.5768 | 0.4581 | 0.019* |
| C17 | 0.7545 (3) | 0.4664 (3) | 0.4001 (2) | 0.0171 (7) |
| H17 | 0.7458 | 0.4186 | 0.4372 | 0.021* |
| C18 | 0.8005 (3) | 0.4412 (3) | 0.3351 (2) | 0.0167 (7) |
| H18 | 0.8206 | 0.3764 | 0.3262 | 0.020* |
| C19 | 0.8171 (3) | 0.5144 (3) | 0.2818 (2) | 0.0139 (6) |
| C20 | 0.8588 (3) | 0.5112 (3) | 0.2085 (2) | 0.0144 (7) |
| H20 | 0.8970 | 0.4544 | 0.1877 | 0.017* |
| C21 | 0.9014 (3) | 0.7371 (3) | 0.0964 (2) | 0.0200 (8) |
| H21A | 0.9215 | 0.7805 | 0.1403 | 0.030* |
| H21B | 0.8177 | 0.7466 | 0.0733 | 0.030* |
| H21C | 0.9532 | 0.7507 | 0.0581 | 0.030* |
| C22 | 0.9489 (3) | 0.5679 (3) | 0.0667 (2) | 0.0192 (7) |
| H22A | 0.9910 | 0.5135 | 0.0940 | 0.029* |
| H22B | 1.0004 | 0.5981 | 0.0338 | 0.029* |
| H22C | 0.8754 | 0.5451 | 0.0350 | 0.029* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zr1 | 0.01160 (15) | 0.01065 (15) | 0.01307 (16) | −0.00015 (11) | 0.00149 (12) | 0.00016 (11) |
| Zr2 | 0.01121 (15) | 0.01036 (15) | 0.01283 (15) | −0.00005 (11) | 0.00130 (12) | 0.00005 (11) |
| Br1 | 0.01492 (16) | 0.01102 (16) | 0.01984 (17) | 0.00068 (12) | 0.00585 (13) | 0.00148 (12) |
| Br2 | 0.01443 (16) | 0.01133 (16) | 0.02277 (19) | 0.00114 (12) | 0.00607 (13) | 0.00317 (13) |
| Br3 | 0.01681 (17) | 0.02043 (18) | 0.01397 (16) | 0.00111 (13) | 0.00243 (13) | 0.00302 (13) |
| Br4 | 0.0270 (2) | 0.01313 (17) | 0.02242 (19) | −0.00230 (14) | 0.00246 (15) | −0.00387 (13) |
| Br5 | 0.01924 (18) | 0.02087 (18) | 0.01419 (17) | −0.00033 (13) | 0.00006 (13) | 0.00387 (13) |
| Br6 | 0.02123 (18) | 0.01188 (16) | 0.01692 (17) | −0.00105 (13) | 0.00267 (13) | −0.00233 (12) |
| N1 | 0.0170 (15) | 0.0188 (15) | 0.0169 (15) | 0.0014 (12) | 0.0047 (12) | 0.0013 (12) |
| N2 | 0.0154 (14) | 0.0147 (14) | 0.0127 (14) | 0.0011 (11) | 0.0047 (11) | 0.0026 (11) |
| C1 | 0.0122 (15) | 0.0188 (17) | 0.0128 (16) | 0.0002 (13) | 0.0010 (13) | −0.0004 (13) |
| C2 | 0.0142 (16) | 0.0130 (16) | 0.0166 (17) | −0.0005 (12) | 0.0027 (13) | −0.0005 (12) |
| C3 | 0.0126 (16) | 0.0187 (17) | 0.0141 (17) | −0.0021 (13) | −0.0013 (13) | 0.0005 (13) |
| C4 | 0.0189 (18) | 0.025 (2) | 0.0162 (18) | −0.0028 (15) | 0.0012 (14) | −0.0048 (14) |
| C5 | 0.0210 (19) | 0.037 (2) | 0.0150 (18) | −0.0037 (16) | 0.0025 (15) | 0.0000 (16) |
| C6 | 0.0216 (19) | 0.033 (2) | 0.0192 (19) | −0.0021 (16) | 0.0001 (15) | 0.0117 (16) |
| C7 | 0.0161 (18) | 0.0198 (19) | 0.026 (2) | −0.0018 (14) | −0.0017 (15) | 0.0083 (15) |
| C8 | 0.0119 (16) | 0.0196 (18) | 0.0161 (17) | 0.0005 (13) | 0.0011 (13) | 0.0046 (13) |
| C9 | 0.0162 (17) | 0.0152 (17) | 0.0194 (18) | 0.0022 (13) | −0.0011 (14) | −0.0006 (13) |
| C10 | 0.0192 (18) | 0.024 (2) | 0.0224 (19) | −0.0052 (15) | 0.0041 (15) | 0.0063 (15) |
| C11 | 0.0234 (19) | 0.027 (2) | 0.0189 (19) | 0.0055 (16) | 0.0072 (15) | −0.0007 (15) |
| C12 | 0.0128 (16) | 0.0123 (16) | 0.0167 (17) | 0.0013 (12) | 0.0004 (13) | 0.0000 (12) |
| C13 | 0.0130 (15) | 0.0125 (16) | 0.0175 (17) | −0.0011 (12) | 0.0018 (13) | 0.0000 (13) |
| C14 | 0.0124 (15) | 0.0136 (16) | 0.0135 (16) | −0.0027 (12) | −0.0007 (12) | −0.0019 (12) |
| C15 | 0.0172 (17) | 0.0165 (17) | 0.0161 (17) | −0.0014 (13) | 0.0031 (13) | −0.0028 (13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 0.0176 (17) | 0.0182 (18) | 0.0130 (16) | 0.0004 (13) | 0.0046 (13) | −0.0020 (13) |
| C17 | 0.0185 (17) | 0.0179 (18) | 0.0146 (17) | −0.0010 (13) | 0.0013 (14) | 0.0039 (13) |
| C18 | 0.0172 (17) | 0.0139 (17) | 0.0183 (18) | −0.0005 (13) | 0.0003 (14) | 0.0026 (13) |
| C19 | 0.0112 (15) | 0.0145 (16) | 0.0145 (16) | −0.0009 (12) | −0.0025 (12) | −0.0016 (12) |
| C20 | 0.0142 (16) | 0.0154 (16) | 0.0141 (16) | 0.0005 (13) | 0.0037 (13) | −0.0001 (13) |
| C21 | 0.0165 (17) | 0.0186 (18) | 0.025 (2) | −0.0011 (14) | 0.0040 (15) | 0.0059 (15) |
| C22 | 0.0208 (18) | 0.0223 (19) | 0.0150 (17) | 0.0024 (14) | 0.0045 (14) | −0.0013 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zr1—Br1 | 2.7767 (5) | C6—H6 | 0.9500 |
| Zr1—Br2 | 2.7176 (5) | C6—C7 | 1.367 (6) |
| Zr1—Br3 | 2.5531 (5) | C7—H7 | 0.9500 |
| Zr1—Br4 | 2.5862 (5) | C7—C8 | 1.430 (5) |
| Zr1—C1 | 2.607 (3) | C8—C9 | 1.435 (5) |
| Zr1—C2 | 2.453 (3) | C9—H9 | 1.0000 |
| Zr1—C3 | 2.495 (4) | C10—H10A | 0.9800 |
| Zr1—C8 | 2.491 (4) | C10—H10B | 0.9800 |
| Zr1—C9 | 2.445 (4) | C10—H10C | 0.9800 |
| Zr2—Br1 | 2.7325 (5) | C11—H11A | 0.9800 |
| Zr2—Br2 | 2.7881 (5) | C11—H11B | 0.9800 |
| Zr2—Br5 | 2.5391 (5) | C11—H11C | 0.9800 |
| Zr2—Br6 | 2.5820 (5) | C12—C13 | 1.435 (5) |
| Zr2—C12 | 2.611 (3) | C12—C20 | 1.437 (5) |
| Zr2—C13 | 2.474 (3) | C13—H13 | 1.0000 |
| Zr2—C14 | 2.497 (3) | C13—C14 | 1.445 (5) |
| Zr2—C19 | 2.479 (3) | C14—C15 | 1.415 (5) |
| Zr2—C20 | 2.436 (3) | C14—C19 | 1.427 (5) |
| N1—C1 | 1.355 (5) | C15—H15 | 0.9500 |
| N1—C10 | 1.452 (5) | C15—C16 | 1.376 (5) |
| N1—C11 | 1.461 (5) | C16—H16 | 0.9500 |
| N2—C12 | 1.348 (5) | C16—C17 | 1.418 (5) |
| N2—C21 | 1.460 (5) | C17—H17 | 0.9500 |
| N2—C22 | 1.460 (5) | C17—C18 | 1.374 (5) |
| C1—C2 | 1.429 (5) | C18—H18 | 0.9500 |
| C1—C9 | 1.436 (5) | C18—C19 | 1.420 (5) |
| C2—H2 | 1.0000 | C19—C20 | 1.443 (5) |
| C2—C3 | 1.446 (5) | C20—H20 | 1.0000 |
| C3—C4 | 1.414 (5) | C21—H21A | 0.9800 |
| C3—C8 | 1.426 (5) | C21—H21B | 0.9800 |
| C4—H4 | 0.9500 | C21—H21C | 0.9800 |
| C4—C5 | 1.366 (6) | C22—H22A | 0.9800 |
| C5—H5 | 0.9500 | C22—H22B | 0.9800 |
| C5—C6 | 1.414 (6) | C22—H22C | 0.9800 |
| | | | |
| Br2—Zr1—Br1 | 76.248 (13) | C4—C3—C2 | 132.0 (3) |
| Br3—Zr1—Br1 | 82.618 (15) | C4—C3—C8 | 120.8 (3) |
| Br3—Zr1—Br2 | 133.232 (17) | C8—C3—Zr1 | 73.2 (2) |

| | | | |
|---|---|---|---|
| Br3—Zr1—Br4 | 90.069 (16) | C8—C3—C2 | 107.2 (3) |
| Br3—Zr1—C1 | 84.27 (8) | C3—C4—H4 | 120.9 |
| Br4—Zr1—Br1 | 143.296 (17) | C5—C4—C3 | 118.2 (4) |
| Br4—Zr1—Br2 | 83.207 (15) | C5—C4—H4 | 120.9 |
| Br4—Zr1—C1 | 106.38 (8) | C4—C5—H5 | 119.1 |
| C1—Zr1—Br1 | 108.57 (8) | C4—C5—C6 | 121.7 (4) |
| C1—Zr1—Br2 | 141.97 (8) | C6—C5—H5 | 119.1 |
| C2—Zr1—Br1 | 79.02 (8) | C5—C6—H6 | 119.2 |
| C2—Zr1—Br2 | 121.59 (9) | C7—C6—C5 | 121.6 (4) |
| C2—Zr1—Br3 | 93.84 (9) | C7—C6—H6 | 119.2 |
| C2—Zr1—Br4 | 137.53 (8) | C6—C7—H7 | 120.8 |
| C2—Zr1—C1 | 32.62 (11) | C6—C7—C8 | 118.4 (4) |
| C2—Zr1—C3 | 33.97 (12) | C8—C7—H7 | 120.8 |
| C2—Zr1—C8 | 55.74 (12) | C3—C8—Zr1 | 73.5 (2) |
| C3—Zr1—Br1 | 82.66 (9) | C3—C8—C7 | 119.2 (3) |
| C3—Zr1—Br2 | 90.58 (8) | C3—C8—C9 | 108.3 (3) |
| C3—Zr1—Br3 | 127.65 (8) | C7—C8—Zr1 | 119.5 (2) |
| C3—Zr1—Br4 | 128.11 (9) | C7—C8—C9 | 132.5 (4) |
| C3—Zr1—C1 | 54.16 (11) | C9—C8—Zr1 | 71.3 (2) |
| C8—Zr1—Br1 | 114.48 (9) | Zr1—C9—H9 | 125.1 |
| C8—Zr1—Br2 | 89.10 (8) | C1—C9—Zr1 | 79.8 (2) |
| C8—Zr1—Br3 | 137.66 (8) | C1—C9—H9 | 125.1 |
| C8—Zr1—Br4 | 95.00 (9) | C8—C9—Zr1 | 74.9 (2) |
| C8—Zr1—C1 | 53.97 (11) | C8—C9—C1 | 107.5 (3) |
| C8—Zr1—C3 | 33.24 (12) | C8—C9—H9 | 125.1 |
| C9—Zr1—Br1 | 134.33 (9) | N1—C10—H10A | 109.5 |
| C9—Zr1—Br2 | 118.29 (9) | N1—C10—H10B | 109.5 |
| C9—Zr1—Br3 | 106.39 (9) | N1—C10—H10C | 109.5 |
| C9—Zr1—Br4 | 82.25 (9) | H10A—C10—H10B | 109.5 |
| C9—Zr1—C1 | 32.83 (11) | H10A—C10—H10C | 109.5 |
| C9—Zr1—C2 | 56.10 (12) | H10B—C10—H10C | 109.5 |
| C9—Zr1—C3 | 55.98 (12) | N1—C11—H11A | 109.5 |
| C9—Zr1—C8 | 33.79 (12) | N1—C11—H11B | 109.5 |
| Br1—Zr2—Br2 | 75.823 (13) | N1—C11—H11C | 109.5 |
| Br5—Zr2—Br1 | 130.298 (17) | H11A—C11—H11B | 109.5 |
| Br5—Zr2—Br2 | 84.624 (15) | H11A—C11—H11C | 109.5 |
| Br5—Zr2—Br6 | 92.208 (16) | H11B—C11—H11C | 109.5 |
| Br5—Zr2—C12 | 84.51 (8) | N2—C12—Zr2 | 126.9 (2) |
| Br6—Zr2—Br1 | 80.623 (14) | N2—C12—C13 | 126.3 (3) |
| Br6—Zr2—Br2 | 145.776 (17) | N2—C12—C20 | 126.6 (3) |
| Br6—Zr2—C12 | 107.29 (8) | C13—C12—Zr2 | 68.41 (19) |
| C12—Zr2—Br1 | 144.67 (8) | C13—C12—C20 | 106.9 (3) |
| C12—Zr2—Br2 | 106.31 (8) | C20—C12—Zr2 | 66.86 (19) |
| C13—Zr2—Br1 | 121.87 (8) | Zr2—C13—H13 | 125.1 |
| C13—Zr2—Br2 | 77.50 (8) | C12—C13—Zr2 | 79.0 (2) |
| C13—Zr2—Br5 | 96.80 (8) | C12—C13—H13 | 125.1 |
| C13—Zr2—Br6 | 136.60 (8) | C12—C13—C14 | 108.0 (3) |
| C13—Zr2—C12 | 32.64 (11) | C14—C13—Zr2 | 74.00 (19) |

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|---|---|---|---|
| C13—Zr2—C14 | 33.80 (11) | C14—C13—H13 | 125.1 |
| C13—Zr2—C19 | 55.77 (11) | C13—C14—Zr2 | 72.21 (19) |
| C14—Zr2—Br1 | 92.08 (8) | C15—C14—Zr2 | 117.8 (2) |
| C14—Zr2—Br2 | 82.87 (8) | C15—C14—C13 | 132.2 (3) |
| C14—Zr2—Br5 | 130.59 (8) | C15—C14—C19 | 120.2 (3) |
| C14—Zr2—Br6 | 122.81 (8) | C19—C14—Zr2 | 72.64 (19) |
| C14—Zr2—C12 | 54.23 (12) | C19—C14—C13 | 107.5 (3) |
| C19—Zr2—Br1 | 92.21 (8) | C14—C15—H15 | 120.7 |
| C19—Zr2—Br2 | 115.21 (8) | C16—C15—C14 | 118.5 (3) |
| C19—Zr2—Br5 | 137.19 (8) | C16—C15—H15 | 120.7 |
| C19—Zr2—Br6 | 89.93 (8) | C15—C16—H16 | 119.4 |
| C19—Zr2—C12 | 54.30 (11) | C15—C16—C17 | 121.3 (3) |
| C19—Zr2—C14 | 33.33 (11) | C17—C16—H16 | 119.4 |
| C20—Zr2—Br1 | 122.31 (8) | C16—C17—H17 | 119.2 |
| C20—Zr2—Br2 | 133.25 (8) | C18—C17—C16 | 121.5 (3) |
| C20—Zr2—Br5 | 104.43 (8) | C18—C17—H17 | 119.2 |
| C20—Zr2—Br6 | 80.56 (8) | C17—C18—H18 | 120.9 |
| C20—Zr2—C12 | 32.86 (11) | C17—C18—C19 | 118.3 (3) |
| C20—Zr2—C13 | 56.07 (12) | C19—C18—H18 | 120.9 |
| C20—Zr2—C14 | 56.14 (12) | C14—C19—Zr2 | 74.03 (19) |
| C20—Zr2—C19 | 34.12 (12) | C14—C19—C20 | 108.0 (3) |
| Zr2—Br1—Zr1 | 103.816 (15) | C18—C19—Zr2 | 117.7 (2) |
| Zr1—Br2—Zr2 | 103.905 (15) | C18—C19—C14 | 120.2 (3) |
| C1—N1—C10 | 119.1 (3) | C18—C19—C20 | 131.7 (3) |
| C1—N1—C11 | 119.5 (3) | C20—C19—Zr2 | 71.29 (19) |
| C10—N1—C11 | 118.2 (3) | Zr2—C20—H20 | 125.0 |
| C12—N2—C21 | 118.8 (3) | C12—C20—Zr2 | 80.3 (2) |
| C12—N2—C22 | 119.9 (3) | C12—C20—C19 | 107.7 (3) |
| C22—N2—C21 | 117.1 (3) | C12—C20—H20 | 125.0 |
| N1—C1—Zr1 | 126.7 (2) | C19—C20—Zr2 | 74.6 (2) |
| N1—C1—C2 | 126.1 (3) | C19—C20—H20 | 125.0 |
| N1—C1—C9 | 126.7 (3) | N2—C21—H21A | 109.5 |
| C2—C1—Zr1 | 67.75 (19) | N2—C21—H21B | 109.5 |
| C2—C1—C9 | 107.0 (3) | N2—C21—H21C | 109.5 |
| C9—C1—Zr1 | 67.4 (2) | H21A—C21—H21B | 109.5 |
| Zr1—C2—H2 | 125.0 | H21A—C21—H21C | 109.5 |
| C1—C2—Zr1 | 79.6 (2) | H21B—C21—H21C | 109.5 |
| C1—C2—H2 | 125.0 | N2—C22—H22A | 109.5 |
| C1—C2—C3 | 107.9 (3) | N2—C22—H22B | 109.5 |
| C3—C2—Zr1 | 74.6 (2) | N2—C22—H22C | 109.5 |
| C3—C2—H2 | 125.0 | H22A—C22—H22B | 109.5 |
| C2—C3—Zr1 | 71.4 (2) | H22A—C22—H22C | 109.5 |
| C4—C3—Zr1 | 118.8 (2) | H22B—C22—H22C | 109.5 |
| | | | |
| Zr1—C1—C2—C3 | −70.0 (2) | C6—C7—C8—C9 | 179.1 (4) |
| Zr1—C1—C9—C8 | 70.4 (2) | C7—C8—C9—Zr1 | −113.2 (4) |
| Zr1—C2—C3—C4 | 112.4 (4) | C7—C8—C9—C1 | 172.9 (4) |
| Zr1—C2—C3—C8 | −65.0 (2) | C8—C3—C4—C5 | −2.1 (5) |

| | | | |
|---|---|---|---|
| Zr1—C3—C4—C5 | −88.9 (4) | C9—C1—C2—Zr1 | 55.9 (2) |
| Zr1—C3—C8—C7 | 115.0 (3) | C9—C1—C2—C3 | −14.0 (4) |
| Zr1—C3—C8—C9 | −63.3 (2) | C10—N1—C1—Zr1 | −83.6 (4) |
| Zr1—C8—C9—C1 | −73.9 (2) | C10—N1—C1—C2 | 4.1 (5) |
| Zr2—C12—C13—C14 | 69.0 (2) | C10—N1—C1—C9 | −171.1 (3) |
| Zr2—C12—C20—C19 | −70.3 (2) | C11—N1—C1—Zr1 | 75.6 (4) |
| Zr2—C13—C14—C15 | −111.7 (4) | C11—N1—C1—C2 | 163.3 (3) |
| Zr2—C13—C14—C19 | 64.5 (2) | C11—N1—C1—C9 | −11.9 (6) |
| Zr2—C14—C15—C16 | 87.4 (4) | C12—C13—C14—Zr2 | −72.4 (2) |
| Zr2—C14—C19—C18 | −113.1 (3) | C12—C13—C14—C15 | 175.9 (4) |
| Zr2—C14—C19—C20 | 63.7 (2) | C12—C13—C14—C19 | −7.8 (4) |
| Zr2—C19—C20—C12 | 74.2 (2) | C13—C12—C20—Zr2 | 56.7 (2) |
| N1—C1—C2—Zr1 | −120.0 (4) | C13—C12—C20—C19 | −13.5 (4) |
| N1—C1—C2—C3 | 170.0 (3) | C13—C14—C15—C16 | 178.1 (4) |
| N1—C1—C9—Zr1 | 119.8 (4) | C13—C14—C19—Zr2 | −64.3 (2) |
| N1—C1—C9—C8 | −169.8 (3) | C13—C14—C19—C18 | −177.4 (3) |
| N2—C12—C13—Zr2 | 120.6 (4) | C13—C14—C19—C20 | −0.6 (4) |
| N2—C12—C13—C14 | −170.4 (3) | C14—C15—C16—C17 | −1.5 (5) |
| N2—C12—C20—Zr2 | −119.7 (4) | C14—C19—C20—Zr2 | −65.5 (2) |
| N2—C12—C20—C19 | 170.1 (3) | C14—C19—C20—C12 | 8.8 (4) |
| C1—C2—C3—Zr1 | 73.4 (2) | C15—C14—C19—Zr2 | 112.6 (3) |
| C1—C2—C3—C4 | −174.1 (4) | C15—C14—C19—C18 | −0.6 (5) |
| C1—C2—C3—C8 | 8.4 (4) | C15—C14—C19—C20 | 176.2 (3) |
| C2—C1—C9—Zr1 | −56.2 (2) | C15—C16—C17—C18 | −0.8 (6) |
| C2—C1—C9—C8 | 14.3 (4) | C16—C17—C18—C19 | 2.4 (5) |
| C2—C3—C4—C5 | −179.2 (4) | C17—C18—C19—Zr2 | −88.6 (4) |
| C2—C3—C8—Zr1 | 63.8 (2) | C17—C18—C19—C14 | −1.7 (5) |
| C2—C3—C8—C7 | 178.8 (3) | C17—C18—C19—C20 | −177.6 (4) |
| C2—C3—C8—C9 | 0.5 (4) | C18—C19—C20—Zr2 | 110.8 (4) |
| C3—C4—C5—C6 | 1.0 (6) | C18—C19—C20—C12 | −174.9 (4) |
| C3—C8—C9—Zr1 | 64.7 (2) | C19—C14—C15—C16 | 2.2 (5) |
| C3—C8—C9—C1 | −9.1 (4) | C20—C12—C13—Zr2 | −55.8 (2) |
| C4—C3—C8—Zr1 | −114.0 (3) | C20—C12—C13—C14 | 13.2 (4) |
| C4—C3—C8—C7 | 1.0 (5) | C21—N2—C12—Zr2 | 82.5 (4) |
| C4—C3—C8—C9 | −177.3 (3) | C21—N2—C12—C13 | −6.4 (5) |
| C4—C5—C6—C7 | 1.3 (6) | C21—N2—C12—C20 | 169.3 (3) |
| C5—C6—C7—C8 | −2.4 (6) | C22—N2—C12—Zr2 | −73.8 (4) |
| C6—C7—C8—Zr1 | 88.0 (4) | C22—N2—C12—C13 | −162.6 (3) |
| C6—C7—C8—C3 | 1.3 (5) | C22—N2—C12—C20 | 13.1 (5) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2···Br4$^{i}$ | 1.00 | 2.96 | 3.694 (4) | 131 |
| C4—H4···Br4$^{i}$ | 0.95 | 3.35 | 3.944 (4) | 123 |
| C4—H4···Br5$^{ii}$ | 0.95 | 3.42 | 4.123 (4) | 132 |
| C5—H5···Br5 | 0.95 | 3.53 | 3.998 (4) | 113 |
| C5—H5···Br5$^{ii}$ | 0.95 | 3.52 | 4.182 (4) | 129 |

| | | | | |
|---|---|---|---|---|
| C5—H5···Br6$^{ii}$ | 0.95 | 2.93 | 3.840 (4) | 162 |
| C10—H10*C*···Br3 | 0.98 | 2.88 | 3.613 (4) | 133 |
| C11—H11*A*···Br6$^{iii}$ | 0.98 | 2.91 | 3.817 (4) | 154 |
| C11—H11*B*···Br3 | 0.98 | 3.21 | 3.843 (4) | 124 |
| C11—H11*B*···Br5$^{iv}$ | 0.98 | 3.44 | 3.919 (4) | 113 |
| C13—H13···Br6$^{v}$ | 1.00 | 3.04 | 3.690 (4) | 124 |
| C15—H15···Br6$^{v}$ | 0.95 | 3.04 | 3.655 (4) | 124 |
| C16—H16···Br3 | 0.95 | 3.27 | 3.763 (4) | 114 |
| C16—H16···Br3$^{vi}$ | 0.95 | 3.15 | 3.754 (4) | 123 |
| C17—H17···Br3$^{vi}$ | 0.95 | 2.97 | 3.665 (4) | 131 |
| C18—H18···Br2$^{vii}$ | 0.95 | 3.01 | 3.897 (4) | 155 |
| C20—H20···Br4$^{vii}$ | 1.00 | 3.17 | 4.115 (4) | 158 |
| C21—H21*B*···Br5 | 0.98 | 2.94 | 3.660 (4) | 131 |
| C21—H21*C*···Br3$^{viii}$ | 0.98 | 3.20 | 3.811 (4) | 122 |
| C22—H22*A*···Br4$^{vii}$ | 0.98 | 3.02 | 3.986 (4) | 167 |
| C22—H22*B*···Br4$^{viii}$ | 0.98 | 3.36 | 3.974 (4) | 122 |
| C22—H22*C*···Br5 | 0.98 | 3.06 | 3.738 (4) | 128 |

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

### (II) Dibromidobis[$\eta^5$-2-(dimethylamino)indenyl]zirconium(IV)

*Crystal data*

$[ZrBr_2(C_{11}H_{12}N)_2]$
$M_r$ = 567.47
Monoclinic, *C*2/*c*
*a* = 18.4476 (5) Å
*b* = 8.3497 (2) Å
*c* = 14.3737 (4) Å
*β* = 111.854 (1)°
*V* = 2054.90 (9) Å$^3$
*Z* = 4
*F*(000) = 1120
$D_x$ = 1.834 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9893 reflections
*θ* = 2.7–35.7°
*μ* = 4.43 mm$^{-1}$
*T* = 100 K
Prism, yellow
0.26 × 0.24 × 0.15 mm

*Data collection*

Bruker APEXII CCD diffractometer
Graphite monochromator
*φ* and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.552, $T_{max}$ = 0.747
13152 measured reflections
3003 independent reflections
2876 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017
$\theta_{max}$ = 30.0°, $\theta_{min}$ = 2.4°
*h* = −25→25
*k* = −11→11
*l* = −20→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.015
$wR(F^2)$ = 0.039
*S* = 1.07
3003 reflections
125 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 2.1368P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.45 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zr1 | 0.5000 | 0.74647 (2) | 0.7500 | 0.00832 (4) |
| Br1 | 0.38964 (2) | 0.96156 (2) | 0.68020 (2) | 0.01412 (4) |
| N1 | 0.35083 (6) | 0.76823 (12) | 0.85552 (8) | 0.01326 (19) |
| C1 | 0.42107 (7) | 0.70340 (14) | 0.86778 (8) | 0.0114 (2) |
| C2 | 0.49565 (7) | 0.77305 (14) | 0.92202 (9) | 0.0116 (2) |
| H2 | 0.5045 | 0.8746 | 0.9616 | 0.014* |
| C3 | 0.55415 (7) | 0.65358 (14) | 0.93154 (8) | 0.0120 (2) |
| C4 | 0.63626 (7) | 0.65095 (16) | 0.98526 (9) | 0.0156 (2) |
| H4 | 0.6625 | 0.7421 | 1.0221 | 0.019* |
| C5 | 0.67705 (7) | 0.51419 (17) | 0.98303 (10) | 0.0175 (2) |
| H5 | 0.7319 | 0.5112 | 1.0190 | 0.021* |
| C6 | 0.63885 (7) | 0.37755 (16) | 0.92804 (9) | 0.0167 (2) |
| H6 | 0.6684 | 0.2839 | 0.9293 | 0.020* |
| C7 | 0.55973 (7) | 0.37769 (14) | 0.87287 (9) | 0.0148 (2) |
| H7 | 0.5348 | 0.2857 | 0.8358 | 0.018* |
| C8 | 0.51605 (7) | 0.51796 (14) | 0.87243 (9) | 0.0116 (2) |
| C9 | 0.43396 (7) | 0.55692 (14) | 0.82397 (9) | 0.0119 (2) |
| H9 | 0.3922 | 0.4798 | 0.7851 | 0.014* |
| C10 | 0.34843 (7) | 0.92403 (15) | 0.89929 (10) | 0.0166 (2) |
| H10A | 0.3813 | 0.9222 | 0.9708 | 0.025* |
| H10B | 0.2945 | 0.9492 | 0.8911 | 0.025* |
| H10C | 0.3678 | 1.0058 | 0.8655 | 0.025* |
| C11 | 0.28038 (7) | 0.69950 (17) | 0.78212 (10) | 0.0184 (2) |
| H11A | 0.2784 | 0.5848 | 0.7953 | 0.028* |
| H11B | 0.2807 | 0.7148 | 0.7147 | 0.028* |
| H11C | 0.2345 | 0.7526 | 0.7868 | 0.028* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zr1 | 0.00882 (7) | 0.00802 (7) | 0.00796 (7) | 0.000 | 0.00294 (5) | 0.000 |
| Br1 | 0.01459 (6) | 0.01476 (6) | 0.01381 (6) | 0.00574 (4) | 0.00618 (4) | 0.00414 (4) |
| N1 | 0.0113 (4) | 0.0155 (5) | 0.0137 (4) | −0.0001 (4) | 0.0054 (4) | −0.0013 (4) |
| C1 | 0.0125 (5) | 0.0128 (5) | 0.0098 (5) | −0.0001 (4) | 0.0054 (4) | 0.0011 (4) |
| C2 | 0.0119 (5) | 0.0130 (5) | 0.0097 (5) | −0.0002 (4) | 0.0041 (4) | −0.0013 (4) |
| C3 | 0.0134 (5) | 0.0132 (5) | 0.0095 (5) | 0.0007 (4) | 0.0043 (4) | 0.0015 (4) |
| C4 | 0.0139 (5) | 0.0193 (6) | 0.0119 (5) | 0.0001 (4) | 0.0028 (4) | 0.0008 (4) |
| C5 | 0.0132 (5) | 0.0230 (6) | 0.0150 (5) | 0.0037 (5) | 0.0037 (4) | 0.0046 (5) |
| C6 | 0.0190 (6) | 0.0163 (6) | 0.0163 (5) | 0.0067 (4) | 0.0082 (5) | 0.0058 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7 | 0.0192 (5) | 0.0120 (5) | 0.0142 (5) | 0.0025 (4) | 0.0076 (4) | 0.0029 (4) |
| C8 | 0.0133 (5) | 0.0115 (5) | 0.0103 (5) | 0.0007 (4) | 0.0048 (4) | 0.0022 (4) |
| C9 | 0.0125 (5) | 0.0115 (5) | 0.0115 (5) | −0.0011 (4) | 0.0045 (4) | 0.0003 (4) |
| C10 | 0.0169 (5) | 0.0177 (6) | 0.0168 (5) | 0.0035 (4) | 0.0081 (4) | −0.0015 (4) |
| C11 | 0.0112 (5) | 0.0225 (6) | 0.0200 (6) | −0.0021 (5) | 0.0042 (4) | −0.0007 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zr1—Br1 | 2.6183 (2) | C3—C4 | 1.4215 (16) |
| Zr1—Br1$^{i}$ | 2.6183 (2) | C3—C8 | 1.4330 (16) |
| Zr1—C1 | 2.6365 (11) | C4—H4 | 0.9500 |
| Zr1—C1$^{i}$ | 2.6365 (11) | C4—C5 | 1.3745 (18) |
| Zr1—C2 | 2.5134 (11) | C5—H5 | 0.9500 |
| Zr1—C2$^{i}$ | 2.5134 (11) | C5—C6 | 1.4171 (19) |
| Zr1—C3$^{i}$ | 2.5432 (11) | C6—H6 | 0.9500 |
| Zr1—C3 | 2.5432 (11) | C6—C7 | 1.3775 (17) |
| Zr1—C8 | 2.5371 (11) | C7—H7 | 0.9500 |
| Zr1—C8$^{i}$ | 2.5371 (11) | C7—C8 | 1.4203 (16) |
| Zr1—C9 | 2.4666 (12) | C8—C9 | 1.4488 (16) |
| Zr1—C9$^{i}$ | 2.4665 (12) | C9—H9 | 1.0000 |
| N1—C1 | 1.3538 (15) | C10—H10A | 0.9800 |
| N1—C10 | 1.4529 (16) | C10—H10B | 0.9800 |
| N1—C11 | 1.4528 (16) | C10—H10C | 0.9800 |
| C1—C2 | 1.4284 (16) | C11—H11A | 0.9800 |
| C1—C9 | 1.4355 (16) | C11—H11B | 0.9800 |
| C2—H2 | 1.0000 | C11—H11C | 0.9800 |
| C2—C3 | 1.4382 (16) | | |

| | | | |
|---|---|---|---|
| Br1$^{i}$—Zr1—Br1 | 93.390 (7) | C9—Zr1—C8$^{i}$ | 82.39 (4) |
| Br1$^{i}$—Zr1—C1 | 112.58 (3) | C9$^{i}$—Zr1—C8 | 82.39 (4) |
| Br1$^{i}$—Zr1—C1$^{i}$ | 78.64 (3) | C9$^{i}$—Zr1—C8$^{i}$ | 33.62 (4) |
| Br1—Zr1—C1 | 78.64 (3) | C9$^{i}$—Zr1—C9 | 100.17 (6) |
| Br1—Zr1—C1$^{i}$ | 112.58 (3) | C1—N1—C10 | 118.92 (10) |
| C1—Zr1—C1$^{i}$ | 164.32 (5) | C1—N1—C11 | 119.38 (10) |
| C2$^{i}$—Zr1—Br1$^{i}$ | 90.65 (3) | C11—N1—C10 | 120.33 (10) |
| C2—Zr1—Br1$^{i}$ | 82.39 (3) | N1—C1—Zr1 | 126.33 (8) |
| C2—Zr1—Br1 | 90.65 (3) | N1—C1—C2 | 126.08 (11) |
| C2$^{i}$—Zr1—Br1 | 82.39 (3) | N1—C1—C9 | 126.19 (11) |
| C2—Zr1—C1 | 32.09 (4) | C2—C1—Zr1 | 69.20 (6) |
| C2$^{i}$—Zr1—C1$^{i}$ | 32.09 (4) | C2—C1—C9 | 107.64 (10) |
| C2—Zr1—C1$^{i}$ | 150.61 (4) | C9—C1—Zr1 | 67.25 (6) |
| C2$^{i}$—Zr1—C1 | 150.61 (4) | Zr1—C2—H2 | 125.2 |
| C2—Zr1—C2$^{i}$ | 169.87 (5) | C1—C2—Zr1 | 78.70 (6) |
| C2—Zr1—C3$^{i}$ | 153.14 (4) | C1—C2—H2 | 125.2 |
| C2$^{i}$—Zr1—C3 | 153.14 (4) | C1—C2—C3 | 107.80 (10) |
| C2—Zr1—C3 | 33.04 (4) | C3—C2—Zr1 | 74.62 (6) |
| C2$^{i}$—Zr1—C3$^{i}$ | 33.04 (4) | C3—C2—H2 | 125.2 |
| C2—Zr1—C8$^{i}$ | 135.28 (4) | C2—C3—Zr1 | 72.34 (6) |

| | | | |
|---|---|---|---|
| C2—Zr1—C8 | 54.71 (4) | C4—C3—Zr1 | 119.62 (8) |
| C2$^{i}$—Zr1—C8 | 135.28 (4) | C4—C3—C2 | 132.26 (11) |
| C2$^{i}$—Zr1—C8$^{i}$ | 54.71 (4) | C4—C3—C8 | 119.88 (11) |
| C3—Zr1—Br1$^{i}$ | 82.16 (3) | C8—C3—Zr1 | 73.38 (6) |
| C3$^{i}$—Zr1—Br1 | 82.16 (3) | C8—C3—C2 | 107.86 (10) |
| C3—Zr1—Br1 | 123.69 (3) | C3—C4—H4 | 120.6 |
| C3$^{i}$—Zr1—Br1$^{i}$ | 123.69 (3) | C5—C4—C3 | 118.83 (12) |
| C3—Zr1—C1 | 53.09 (4) | C5—C4—H4 | 120.6 |
| C3$^{i}$—Zr1—C1$^{i}$ | 53.09 (4) | C4—C5—H5 | 119.4 |
| C3$^{i}$—Zr1—C1 | 121.15 (4) | C4—C5—C6 | 121.26 (11) |
| C3—Zr1—C1$^{i}$ | 121.16 (4) | C6—C5—H5 | 119.4 |
| C3—Zr1—C3$^{i}$ | 144.49 (5) | C5—C6—H6 | 119.3 |
| C8$^{i}$—Zr1—Br1 | 112.13 (3) | C7—C6—C5 | 121.39 (11) |
| C8$^{i}$—Zr1—Br1$^{i}$ | 130.91 (3) | C7—C6—H6 | 119.3 |
| C8—Zr1—Br1$^{i}$ | 112.13 (3) | C6—C7—H7 | 120.6 |
| C8—Zr1—Br1 | 130.91 (3) | C6—C7—C8 | 118.75 (11) |
| C8$^{i}$—Zr1—C1$^{i}$ | 53.26 (4) | C8—C7—H7 | 120.6 |
| C8—Zr1—C1 | 53.26 (4) | C3—C8—Zr1 | 73.85 (6) |
| C8—Zr1—C1$^{i}$ | 113.14 (4) | C3—C8—C9 | 107.57 (10) |
| C8$^{i}$—Zr1—C1 | 113.14 (4) | C7—C8—Zr1 | 122.88 (8) |
| C8$^{i}$—Zr1—C3 | 112.47 (4) | C7—C8—C3 | 119.78 (11) |
| C8—Zr1—C3$^{i}$ | 112.47 (4) | C7—C8—C9 | 132.61 (11) |
| C8—Zr1—C3 | 32.77 (4) | C9—C8—Zr1 | 70.52 (6) |
| C8$^{i}$—Zr1—C3$^{i}$ | 32.77 (4) | Zr1—C9—H9 | 125.1 |
| C8$^{i}$—Zr1—C8 | 82.46 (5) | C1—C9—Zr1 | 80.30 (7) |
| C9$^{i}$—Zr1—Br1$^{i}$ | 99.61 (3) | C1—C9—C8 | 107.14 (10) |
| C9—Zr1—Br1 | 99.61 (3) | C1—C9—H9 | 125.1 |
| C9—Zr1—Br1$^{i}$ | 135.50 (3) | C8—C9—Zr1 | 75.86 (7) |
| C9$^{i}$—Zr1—Br1 | 135.50 (3) | C8—C9—H9 | 125.1 |
| C9—Zr1—C1$^{i}$ | 131.97 (4) | N1—C10—H10A | 109.5 |
| C9—Zr1—C1 | 32.46 (4) | N1—C10—H10B | 109.5 |
| C9$^{i}$—Zr1—C1 | 131.97 (4) | N1—C10—H10C | 109.5 |
| C9$^{i}$—Zr1—C1$^{i}$ | 32.46 (4) | H10A—C10—H10B | 109.5 |
| C9—Zr1—C2$^{i}$ | 133.04 (4) | H10A—C10—H10C | 109.5 |
| C9$^{i}$—Zr1—C2 | 133.04 (4) | H10B—C10—H10C | 109.5 |
| C9—Zr1—C2 | 55.31 (4) | N1—C11—H11A | 109.5 |
| C9$^{i}$—Zr1—C2$^{i}$ | 55.31 (4) | N1—C11—H11B | 109.5 |
| C9—Zr1—C3 | 55.28 (4) | N1—C11—H11C | 109.5 |
| C9$^{i}$—Zr1—C3 | 100.26 (4) | H11A—C11—H11B | 109.5 |
| C9$^{i}$—Zr1—C3$^{i}$ | 55.28 (4) | H11A—C11—H11C | 109.5 |
| C9—Zr1—C3$^{i}$ | 100.26 (4) | H11B—C11—H11C | 109.5 |
| C9—Zr1—C8 | 33.62 (4) | | |

| | | | |
|---|---|---|---|
| Zr1—C1—C2—C3 | −69.62 (8) | C3—C8—C9—Zr1 | 65.07 (8) |
| Zr1—C1—C9—C8 | 71.81 (8) | C3—C8—C9—C1 | −9.88 (13) |
| Zr1—C2—C3—C4 | 114.30 (13) | C4—C3—C8—Zr1 | −115.04 (10) |
| Zr1—C2—C3—C8 | −65.30 (8) | C4—C3—C8—C7 | 3.99 (17) |
| Zr1—C3—C4—C5 | −90.04 (13) | C4—C3—C8—C9 | −177.92 (10) |

| | | | |
|---|---|---|---|
| Zr1—C3—C8—C7 | 119.04 (11) | C4—C5—C6—C7 | 1.52 (19) |
| Zr1—C3—C8—C9 | −62.88 (8) | C5—C6—C7—C8 | −0.58 (18) |
| Zr1—C8—C9—C1 | −74.95 (8) | C6—C7—C8—Zr1 | 87.19 (13) |
| N1—C1—C2—Zr1 | −120.49 (11) | C6—C7—C8—C3 | −2.14 (17) |
| N1—C1—C2—C3 | 169.89 (11) | C6—C7—C8—C9 | −179.66 (12) |
| N1—C1—C9—Zr1 | 119.29 (11) | C7—C8—C9—Zr1 | −117.19 (13) |
| N1—C1—C9—C8 | −168.89 (11) | C7—C8—C9—C1 | 167.86 (12) |
| C1—C2—C3—Zr1 | 72.44 (8) | C8—C3—C4—C5 | −3.07 (17) |
| C1—C2—C3—C4 | −173.26 (12) | C9—C1—C2—Zr1 | 56.29 (8) |
| C1—C2—C3—C8 | 7.14 (13) | C9—C1—C2—C3 | −13.33 (13) |
| C2—C1—C9—Zr1 | −57.49 (8) | C10—N1—C1—Zr1 | −88.58 (12) |
| C2—C1—C9—C8 | 14.32 (12) | C10—N1—C1—C2 | 0.89 (17) |
| C2—C3—C4—C5 | 177.38 (12) | C10—N1—C1—C9 | −175.32 (11) |
| C2—C3—C8—Zr1 | 64.61 (8) | C11—N1—C1—Zr1 | 78.11 (13) |
| C2—C3—C8—C7 | −176.35 (10) | C11—N1—C1—C2 | 167.58 (11) |
| C2—C3—C8—C9 | 1.73 (13) | C11—N1—C1—C9 | −8.63 (18) |
| C3—C4—C5—C6 | 0.36 (18) | | |

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C5—H5···Br1$^{ii}$ | 0.95 | 2.98 | 3.8960 (13) | 163 |
| C6—H6···Br1$^{iii}$ | 0.95 | 3.10 | 3.7621 (13) | 128 |
| C7—H7···Br1$^{iii}$ | 0.95 | 3.09 | 3.7493 (12) | 128 |
| C10—H10*A*···Br1$^{iv}$ | 0.98 | 3.11 | 3.9381 (13) | 143 |
| C10—H10*C*···Br1 | 0.98 | 2.86 | 3.5178 (13) | 125 |
| C11—H11*A*···Br1$^{v}$ | 0.98 | 3.41 | 3.9170 (13) | 115 |
| C11—H11*B*···Br1 | 0.98 | 3.04 | 3.6325 (13) | 120 |

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