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Crystal structures of di-μ-bromido-bis{dibromido-[η^5-2-(dimethylamino)indenyl]zirconium(IV)} and dibromidobis[η^5-2-(dimethylamino)indenyl]-zirconium(IV)

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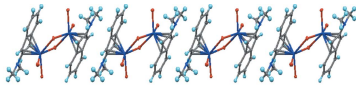
In the title compounds, $[Zr_2Br_6(C_{11}H_{12}N)_2]$, (I) and $[ZrBr_2(C_{11}H_{12}N)_2]$, (II), the positions of the η^5-binding 2-dimethylaminoindenyl units are fixed by intramolecular C—H···Br interactions involving aromatic or dimethylamino H atoms. The binuclear molecule of (I) is located on a 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 π–π- and N–π-bonded molecules, which in turn are linked by C—H···Br interactions.

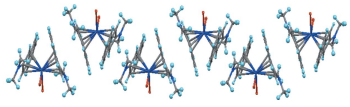
1. Chemical context

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)



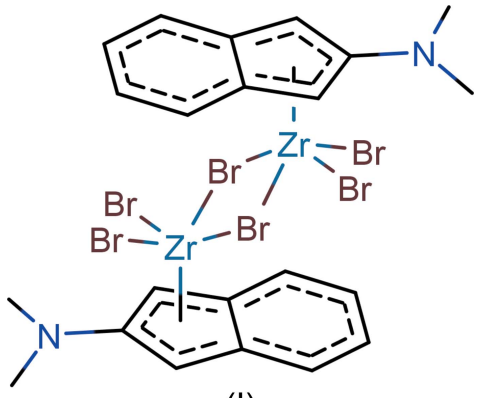
(II)



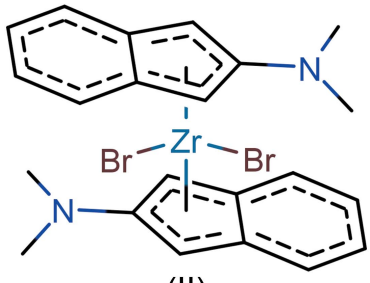
2. Structural commentary

Structure determination revealed that both title compounds are monomeric in the solid state, with the dimethylaminoindenyl anions acting as η^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

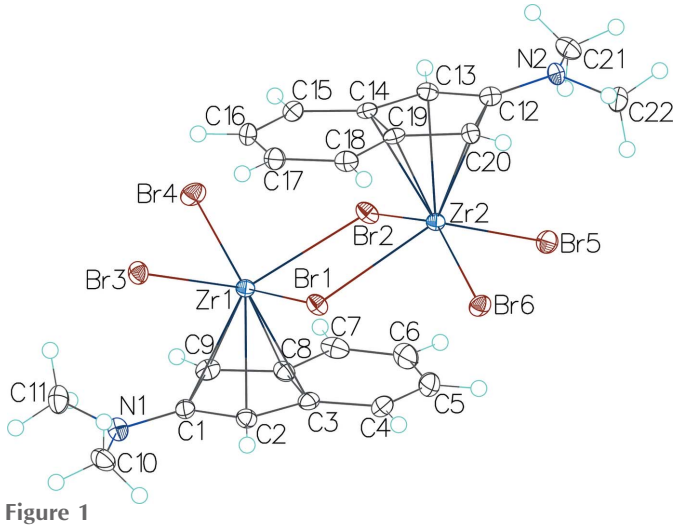


Figure 1
The molecular structure of compound (I) with displacement ellipsoids drawn at the 50% probability level.

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]

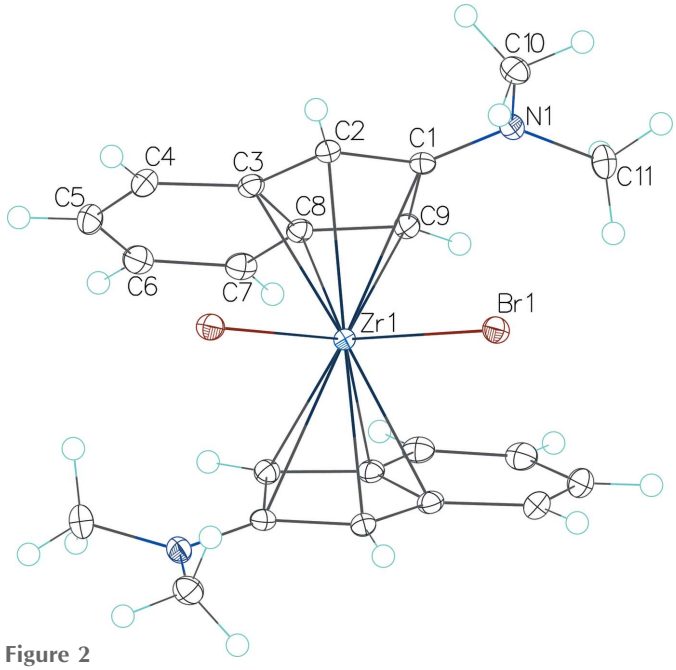


Figure 2
The molecular structure of compound (II) with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are generated by symmetry code $-x+1, y, -z+\frac{3}{2}$.

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 π–π- and N–π-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(η^5-2-dimethylaminoindenyl)zirconium(IV) (Barsties *et al.*, 1996; Luttikhedde *et al.*, 1996) also exhibits stacking interactions, but dichlorido-bis(η^5-indenyl)zirconium(IV) (Repo *et al.*, 1996) does not.

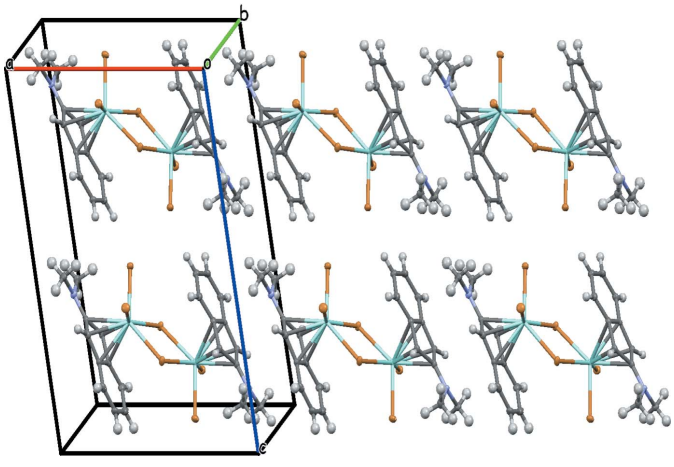


Figure 3
The crystal packing of compound (I) with displacement ellipsoids drawn at the 50% probability level.

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[(μ-bromido)(η^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(η^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

This work was supported by the Russian Ministry of Education and Science (project No. 2015–14-585–0002, unique identifier RFMEFI61315X0041).

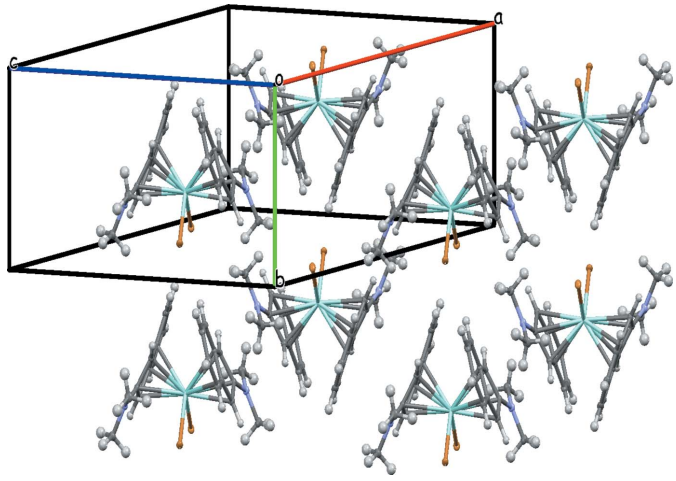


Figure 4
The crystal packing of compound (II) with displacement ellipsoids drawn at the 50% probability level.

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)
β (°)	99.028 (1)	111.854 (1)
V (Å^3)	2745.3 (2)	2054.90 (9)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (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-μ-bromido-bis{dibromido[η^5-2-(dimethylamino)-indenyl]zirconium(IV)} and dibromidobis[η^5-2-(dimethylamino)-indenyl]zirconium(IV)

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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-μ-bromido-bis{dibromido[η^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
β = 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, λ = 0.71073 Å
Cell parameters from 9986 reflections
θ = 2.3–35.3°
μ = 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
φ and ω 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
θ_{max} = 30.0°, θ_{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)

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[η^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
θ_{max} = 30.0°, θ_{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.