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# Bis(tetraphenylarsonium) hexachloridozirconate(IV) acetonitrile tetrasolvate

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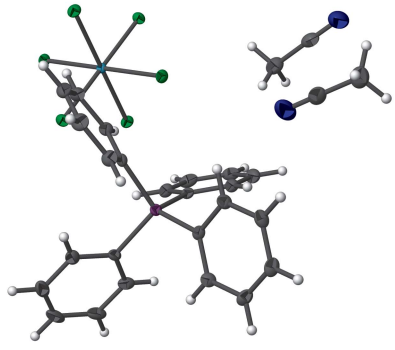
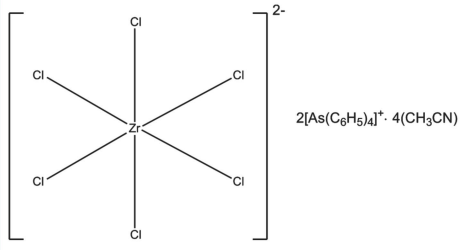
The bis(tetraphenylarsonium) hexachloridozirconate(IV) salt, $(AsPh_4)_2[ZrCl_6]$ (Ph = $C_6H_5$), was prepared more than 25 years ago [Esmadi & Sutcliffe (1991). *Indian J. Chem.* **30 A**, 99–101], but its crystal structure was never reported. By following a similar experimental procedure, the compound was synthesized and its crystal structure was investigated as a acetonitrile tetrasolvate, $(As(C_6H_5)_4)_2[ZrCl_6]\cdot 4CH_3CN$, by single-crystal *X*–ray diffraction. The $[ZrCl_6]^{2-}$ anion adopts a slightly distorted octahedral coordination sphere, with Zr—Cl bond lengths of 2.4586 (6), 2.4723 (6), and 2.4818 (5) Å, and Cl—Zr—Cl angles ranging from 89.602 (19) to 90.397 (19)°.

**3D view**



**Chemical scheme**




## Structure description

Zirconium tetrachloride is encountered in the nuclear fuel cycle for the recycling of zirconium from zirconium alloy cladding using a chloride volatility process (Bohe *et al.*, 1996; Collins *et al.*, 2012; Jeon *et al.*, 2013). The $ZrCl_4$ produced from these alloys at temperatures above 573 K contains several impurities that are difficult to separate. It has been considered that the impurities could be present due to the formation of intermediate ternary compounds, or by the co-crystallization of various chloride species. For these reasons, investigating the chemical behavior of $ZrCl_4$ in the presence of other chlorides is of importance. At least ten hexachloridozirconate(IV) salts have been prepared and their structures reported. The majority of these salts were prepared using $ZrCl_4$ and chloride salts as starting materials (Esmadi & Sutcliffe, 1991; Ohashi *et al.*, 1987). These $[ZrCl_6]^{2-}$ salts contain single-element cations (*e.g.* $Cs^+$, $Rb^+$, $Fe^{2+}$) or more complex cations {*e.g.* $[P(C_6H_5)_4]^+$, $[N(CH_3)_4]^+$}. On the other hand, crystal structures have not been reported for many of these hexachloridozirconates(IV) (*e.g.* $Na_2[ZrCl_6]$ and $K_2[ZrCl_6]$; Lister, 1964). One of these salts, bis(tetraphenylarsonium) hexachloridozirconate(IV), was synthesized (Esmadi & Sutcliffe, 1991) but its structure never

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zr1—Cl2 | 2.4586 (6) | As1—C1 | 1.911 (2) |
| Zr1—Cl3 | 2.4723 (6) | As1—C13 | 1.911 (2) |
| Zr1—Cl1 | 2.4818 (5) | As1—C19 | 1.916 (2) |
| As1—C7 | 1.906 (2) | | |
| | | | |
| Cl2—Zr1—Cl3 | 90.09 (2) | C7—As1—C1 | 110.95 (10) |
| Cl2$^{i}$—Zr1—Cl3 | 89.91 (2) | C7—As1—C13 | 110.73 (10) |
| Cl2—Zr1—Cl1$^{i}$ | 90.398 (19) | C1—As1—C13 | 107.65 (10) |
| Cl3—Zr1—Cl1$^{i}$ | 89.703 (19) | C7—As1—C19 | 107.83 (10) |
| Cl3$^{i}$—Zr1—Cl1$^{i}$ | 90.296 (19) | C1—As1—C19 | 111.76 (10) |
| Cl2—Zr1—Cl1 | 89.603 (19) | C13—As1—C19 | 107.89 (10) |

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

reported. Here, $(AsPh_4)_2[ZrCl_6]\cdot 4(CH_3CN)$ (Ph = $C_6H_5$) was crystallized as its acetonitrile tetrasolvate (Fig. 1) and its structure investigated by single-crystal X-ray diffraction.

The unit-cell packing of $(AsPh_4)_2[ZrCl_6]\cdot 4(CH_3CN)$ is shown in Fig. 2. The $(AsPh_4)^+$ cation adopts a distorted tetrahedral configuration in which the phenyl groups are asymmetrically attached (Fig. 1). The As—C bond lengths (Table 1) are similar to those reported for $(AsPh_4)_2[TcCl_6]$ (Baldas *et al.*, 1984) or $(AsPh_4)_2[ReBr_6]$ (Kochel, 2007). The asymmetric orientation of the phenyl groups is reflected by the deviation of the C—As—C angles from those of a perfect tetrahedron (Table 1).

The $[ZrCl_6]^{2-}$ anion, which is located on a position with site symmetry $\overline{1}$ (Wyckoff position 2*a*), adopts a slightly distorted octahedral coordination sphere (Fig. 1, Table 1), The shortest Zr ··· Zr distance in the structure is 9.6505 (7) Å that corresponds with the length of the *a* axis. The shortest As ··· As distance is 7.8562 (7) Å and corresponds to adjacent $(AsPh_4)^+$ cations within the same unit cell.

The isolated $(AsPh_4)^+$ cations and $[ZrCl_6]^{2-}$ anions pack in alternating rows extending parallel to [100]. The two unique solvent molecules are located in the voids of this arrangement (Fig. 2). The shortest distances observed between N or Cl atoms and H atoms range between 2.61 and 2.81 Å (Table 2). These distances suggest that the components interact only weakly through hydrogen bonding and that the structural cohesion is primarily accomplished by Coulombic attraction.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C3*S*—H3*SA*···Cl1$^{ii}$ | 0.98 | 2.81 | 3.674 (3) | 148 |
| C16—H16···Cl1$^{iii}$ | 0.95 | 2.73 | 3.646 (3) | 162 |
| C18—H18···N1*S*$^{iii}$ | 0.95 | 2.61 | 3.483 (4) | 154 |

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

## Synthesis and crystallization

All chemicals were purchased from Sigma Aldrich and used as received. The reaction used to prepare $(AsPh_4)_2[ZrCl_6]$ (Fig. 3) is similar to that described in the literature (Esmadi & Sutcliffe, 1991): A solution of $(AsPh_4)Cl$ (0.72 g, 1.7 mmol) in thionyl chloride (2 ml) was added dropwise to a stirring solution of $ZrCl_4$ (0.20 g, 0.86 mmol) in thionyl chloride (1 ml). After stirring the mixture for 20 h, ethyl acetate was added dropwise to induce precipitation. The white precipitate was washed with ethyl acetate (3 × 3 ml) and diethyl ether (3 × 3 ml), and then dried under vacuum over $CaCl_2$. Yield: 0.35 g (38%). Colorless block-shaped crystals were obtained by recrystallization from acetonitrile and slow evaporation at room temperature.

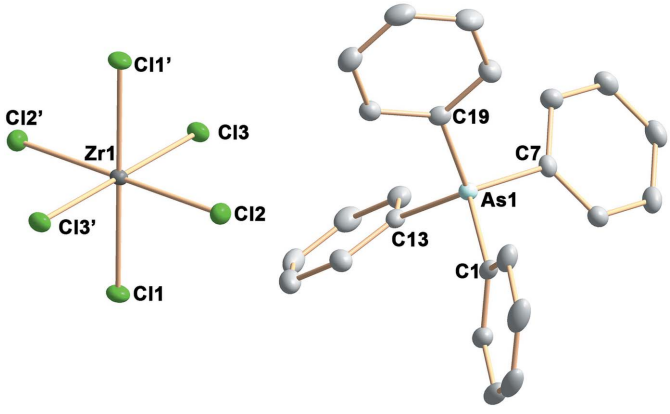



**Figure 1**
The molecular structures of the cation and anion in $(AsPh_4)_2[ZrCl_6]\cdot 4CH_3CN$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (') –x, 1 − *y*, 1 − *z*.]

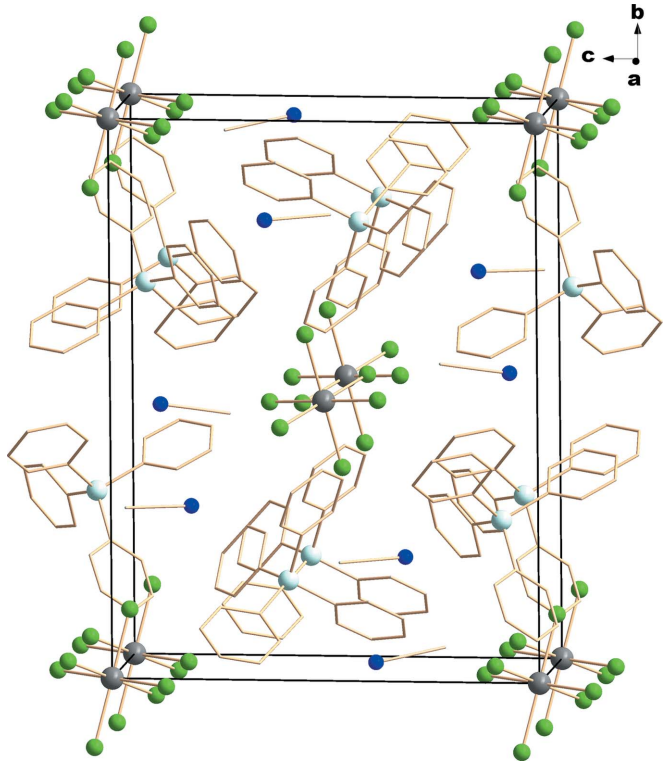



**Figure 2**
Representation of the expanded unit cell of $(AsPh_4)_2[ZrCl_6]\cdot 4CH_3CN$. Hydrogen atoms are omitted for clarity. Color of atoms: Zr in gray, Cl in green, N in blue, As in light turquoise, C in light brown.

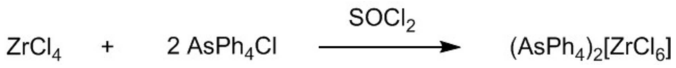



**Figure 3**
Reaction scheme.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.


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**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $(C_{24}H_{20}As)_2[ZrCl_6]\cdot 4C_2H_3N$ |
| $M_r$ | 1234.77 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 9.6505 (7), 19.3780 (13), 15.1026 (10) |
| $\beta$ (°) | 97.849 (1) |
| $V$ (Å$^3$) | 2797.8 (3) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.70 |
| Crystal size (mm) | 0.12 × 0.10 × 0.05 |
| Data collection | |
| Diffractometer | Bruker *SMART APEX* CCD area detector |
| Absorption correction | Multi-scan (*SADABS*; Bruker 2015) |
| $T_{min}$, $T_{max}$ | 0.80, 0.93 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 45888, 8589, 6236 |
| $R_{int}$ | 0.079 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.716 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.037, 0.082, 1.00 |
| No. of reflections | 8589 |
| No. of parameters | 315 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.59, −0.47 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2007) and *publCIF* (Westrip, 2010).


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# full crystallographic data

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## Bis(tetraphenylarsonium) hexachloridozirconate(IV) acetonitrile tetrasolvate

**Rosendo Borjas, Samundeeswari Mariappan Balasekaran and Frederic Poineau**

### Bis(tetraphenylarsonium) hexachloridozirconate(IV) acetonitrile tetrasolvate

*Crystal data*

$(C_{24}H_{20}As)_2[ZrCl_6]\cdot 4C_2H_3N$
$M_r$ = 1234.77
Monoclinic, $P2_1/c$
$a$ = 9.6505 (7) Å
$b$ = 19.3780 (13) Å
$c$ = 15.1026 (10) Å
$\beta$ = 97.849 (1)°
$V$ = 2797.8 (3) Å$^3$
$Z$ = 2
$F(000)$ = 1248
$D_x$ = 1.466 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9919 reflections
$\theta$ = 2.4–30.5°
$\mu$ = 1.70 mm$^{-1}$
$T$ = 100 K
Rectangular, translucent colourless
0.12 × 0.10 × 0.05 mm

*Data collection*

Bruker SMART APEX CCD area detector diffractometer
Radiation source: sealed tube
Curved graphite monochromator
Detector resolution: 8.3333 pixels mm$^{-1}$
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Bruker 2015)
$T_{min}$ = 0.80, $T_{max}$ = 0.93
45888 measured reflections
8589 independent reflections
6236 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.079
$\theta_{max}$ = 30.6°, $\theta_{min}$ = 1.7°
$h$ = −13→13
$k$ = −27→27
$l$ = −21→21

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.082
$S$ = 1.00
8589 reflections
315 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.8047P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.59 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.47 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 | 0.5 | 0.5 | 0.01200 (7) |
| Cl1 | −0.12452 (6) | 0.49192 (3) | 0.63295 (4) | 0.01817 (12) |
| Cl2 | 0.21611 (6) | 0.46095 (3) | 0.59151 (4) | 0.01759 (12) |
| Cl3 | −0.06208 (6) | 0.37896 (3) | 0.46088 (4) | 0.01820 (12) |
| As1 | 0.33890 (2) | 0.19416 (2) | 0.56737 (2) | 0.01347 (6) |
| C1 | 0.1981 (2) | 0.20864 (12) | 0.64294 (15) | 0.0158 (5) |
| C2 | 0.1159 (2) | 0.26745 (13) | 0.63054 (15) | 0.0183 (5) |
| H2 | 0.1348 | 0.3019 | 0.5891 | 0.022* |
| C3 | 0.0045 (3) | 0.27509 (14) | 0.68001 (17) | 0.0233 (5) |
| H3 | −0.053 | 0.315 | 0.6724 | 0.028* |
| C4 | −0.0218 (3) | 0.22430 (15) | 0.74010 (17) | 0.0261 (6) |
| H4 | −0.0977 | 0.2297 | 0.7735 | 0.031* |
| C5 | 0.0609 (3) | 0.16591 (14) | 0.75216 (17) | 0.0257 (6) |
| H5 | 0.0423 | 0.1317 | 0.794 | 0.031* |
| C6 | 0.1713 (3) | 0.15734 (13) | 0.70298 (16) | 0.0215 (5) |
| H6 | 0.2277 | 0.117 | 0.7102 | 0.026* |
| C7 | 0.4895 (2) | 0.14073 (12) | 0.62672 (15) | 0.0160 (5) |
| C8 | 0.5372 (3) | 0.15342 (13) | 0.71679 (16) | 0.0198 (5) |
| H8 | 0.489 | 0.1848 | 0.75 | 0.024* |
| C9 | 0.6563 (3) | 0.11940 (13) | 0.75712 (17) | 0.0223 (5) |
| H9 | 0.6901 | 0.1277 | 0.8182 | 0.027* |
| C10 | 0.7255 (3) | 0.07347 (13) | 0.70835 (17) | 0.0232 (5) |
| H10 | 0.8069 | 0.0505 | 0.7362 | 0.028* |
| C11 | 0.6772 (3) | 0.06076 (13) | 0.61916 (17) | 0.0226 (5) |
| H11 | 0.7253 | 0.029 | 0.5863 | 0.027* |
| C12 | 0.5584 (3) | 0.09436 (12) | 0.57771 (16) | 0.0192 (5) |
| H12 | 0.5247 | 0.0857 | 0.5166 | 0.023* |
| C13 | 0.2531 (2) | 0.14813 (12) | 0.46202 (15) | 0.0161 (5) |
| C14 | 0.1334 (3) | 0.10940 (13) | 0.46581 (18) | 0.0232 (5) |
| H14 | 0.0967 | 0.104 | 0.5207 | 0.028* |
| C15 | 0.0675 (3) | 0.07837 (14) | 0.3877 (2) | 0.0303 (6) |
| H15 | −0.0148 | 0.0517 | 0.3891 | 0.036* |
| C16 | 0.1224 (3) | 0.08663 (14) | 0.30838 (19) | 0.0319 (7) |
| H16 | 0.0763 | 0.0664 | 0.2551 | 0.038* |
| C17 | 0.2431 (3) | 0.12383 (14) | 0.30598 (18) | 0.0285 (6) |
| H17 | 0.2815 | 0.1277 | 0.2515 | 0.034* |
| C18 | 0.3090 (3) | 0.15558 (13) | 0.38228 (16) | 0.0220 (5) |
| H18 | 0.3913 | 0.1821 | 0.3804 | 0.026* |
| C19 | 0.4146 (2) | 0.27956 (12) | 0.53165 (15) | 0.0152 (5) |
| C20 | 0.3407 (3) | 0.31814 (13) | 0.46303 (16) | 0.0207 (5) |
| H20 | 0.2515 | 0.3033 | 0.4351 | 0.025* |
| C21 | 0.3994 (3) | 0.37853 (14) | 0.43617 (18) | 0.0264 (6) |
| H21 | 0.3498 | 0.4055 | 0.3897 | 0.032* |
| C22 | 0.5302 (3) | 0.40003 (13) | 0.47654 (18) | 0.0256 (6) |
| H22 | 0.5702 | 0.4412 | 0.4571 | 0.031* |

| | | | | |
|---|---|---|---|---|
| C23 | 0.6021 (3) | 0.36166 (14) | 0.54487 (18) | 0.0260 (6) |
| H23 | 0.6913 | 0.3767 | 0.5726 | 0.031* |
| C24 | 0.5446 (3) | 0.30097 (13) | 0.57344 (16) | 0.0203 (5) |
| H24 | 0.5936 | 0.2746 | 0.6208 | 0.024* |
| N1S | 0.6349 (3) | 0.29350 (14) | 0.8309 (2) | 0.0488 (8) |
| C1S | 0.8149 (3) | 0.29684 (15) | 0.9742 (2) | 0.0354 (7) |
| H1SA | 0.9092 | 0.2909 | 0.9581 | 0.053* |
| H1SB | 0.795 | 0.2595 | 1.0144 | 0.053* |
| H1SC | 0.809 | 0.3413 | 1.0043 | 0.053* |
| C2S | 0.7135 (3) | 0.29509 (14) | 0.8939 (2) | 0.0330 (7) |
| N2S | 0.7183 (3) | 0.47851 (14) | 0.89707 (18) | 0.0415 (7) |
| C3S | 0.5671 (3) | 0.45689 (15) | 0.74402 (18) | 0.0305 (6) |
| H3SA | 0.6178 | 0.4728 | 0.6959 | 0.046* |
| H3SB | 0.4785 | 0.4821 | 0.7413 | 0.046* |
| H3SC | 0.548 | 0.4074 | 0.737 | 0.046* |
| C4S | 0.6518 (3) | 0.46939 (14) | 0.8301 (2) | 0.0280 (6) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zr1 | 0.01241 (14) | 0.01349 (15) | 0.01014 (14) | −0.00022 (12) | 0.00168 (11) | 0.00088 (11) |
| Cl1 | 0.0181 (3) | 0.0237 (3) | 0.0137 (3) | 0.0007 (2) | 0.0057 (2) | 0.0023 (2) |
| Cl2 | 0.0159 (3) | 0.0219 (3) | 0.0144 (3) | 0.0019 (2) | 0.0001 (2) | 0.0022 (2) |
| Cl3 | 0.0206 (3) | 0.0155 (3) | 0.0184 (3) | −0.0018 (2) | 0.0024 (2) | −0.0012 (2) |
| As1 | 0.01339 (11) | 0.01436 (12) | 0.01258 (11) | −0.00053 (9) | 0.00148 (8) | −0.00037 (9) |
| C1 | 0.0124 (11) | 0.0194 (12) | 0.0154 (11) | −0.0027 (9) | 0.0017 (9) | −0.0023 (9) |
| C2 | 0.0197 (12) | 0.0192 (12) | 0.0162 (11) | 0.0001 (10) | 0.0027 (9) | 0.0001 (9) |
| C3 | 0.0200 (13) | 0.0240 (14) | 0.0261 (14) | 0.0018 (10) | 0.0033 (10) | −0.0049 (11) |
| C4 | 0.0204 (13) | 0.0368 (16) | 0.0222 (13) | −0.0031 (11) | 0.0073 (10) | −0.0072 (11) |
| C5 | 0.0269 (14) | 0.0305 (15) | 0.0215 (13) | −0.0052 (11) | 0.0099 (11) | 0.0016 (11) |
| C6 | 0.0220 (13) | 0.0214 (13) | 0.0216 (13) | −0.0004 (10) | 0.0045 (10) | 0.0028 (10) |
| C7 | 0.0148 (11) | 0.0139 (11) | 0.0192 (12) | 0.0002 (9) | 0.0020 (9) | 0.0029 (9) |
| C8 | 0.0212 (12) | 0.0210 (13) | 0.0165 (12) | 0.0000 (10) | 0.0007 (10) | −0.0006 (10) |
| C9 | 0.0225 (13) | 0.0231 (13) | 0.0196 (12) | −0.0028 (10) | −0.0037 (10) | 0.0026 (10) |
| C10 | 0.0187 (12) | 0.0236 (14) | 0.0266 (14) | 0.0025 (10) | 0.0001 (10) | 0.0078 (11) |
| C11 | 0.0199 (12) | 0.0193 (13) | 0.0291 (14) | 0.0055 (10) | 0.0058 (10) | 0.0041 (10) |
| C12 | 0.0225 (12) | 0.0183 (12) | 0.0167 (12) | 0.0011 (10) | 0.0017 (9) | 0.0015 (9) |
| C13 | 0.0170 (11) | 0.0161 (12) | 0.0144 (11) | 0.0038 (9) | −0.0014 (9) | −0.0030 (9) |
| C14 | 0.0195 (12) | 0.0190 (13) | 0.0298 (14) | 0.0039 (10) | −0.0008 (10) | −0.0040 (11) |
| C15 | 0.0224 (14) | 0.0228 (14) | 0.0421 (17) | 0.0045 (11) | −0.0087 (12) | −0.0096 (12) |
| C16 | 0.0381 (16) | 0.0250 (15) | 0.0280 (15) | 0.0125 (12) | −0.0122 (12) | −0.0131 (11) |
| C17 | 0.0375 (16) | 0.0278 (15) | 0.0186 (13) | 0.0133 (12) | −0.0018 (11) | −0.0057 (11) |
| C18 | 0.0273 (13) | 0.0207 (13) | 0.0179 (12) | 0.0070 (11) | 0.0030 (10) | −0.0008 (10) |
| C19 | 0.0160 (11) | 0.0144 (11) | 0.0165 (11) | −0.0006 (9) | 0.0066 (9) | −0.0001 (9) |
| C20 | 0.0192 (12) | 0.0228 (13) | 0.0208 (12) | 0.0021 (10) | 0.0050 (10) | 0.0022 (10) |
| C21 | 0.0321 (15) | 0.0228 (14) | 0.0271 (14) | 0.0069 (11) | 0.0136 (12) | 0.0049 (11) |
| C22 | 0.0325 (15) | 0.0152 (12) | 0.0328 (15) | −0.0029 (11) | 0.0179 (12) | −0.0002 (11) |
| C23 | 0.0238 (13) | 0.0256 (14) | 0.0309 (15) | −0.0070 (11) | 0.0123 (11) | −0.0045 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C24 | 0.0184 (12) | 0.0216 (13) | 0.0215 (12) | −0.0014 (10) | 0.0052 (10) | −0.0021 (10) |
| N1S | 0.0466 (17) | 0.0337 (16) | 0.061 (2) | 0.0065 (13) | −0.0098 (15) | −0.0145 (14) |
| C1S | 0.0304 (16) | 0.0303 (16) | 0.0450 (18) | −0.0015 (13) | 0.0039 (13) | 0.0032 (13) |
| C2S | 0.0276 (15) | 0.0175 (14) | 0.054 (2) | 0.0013 (11) | 0.0074 (14) | −0.0045 (13) |
| N2S | 0.0434 (16) | 0.0390 (16) | 0.0414 (16) | 0.0038 (13) | 0.0033 (13) | −0.0101 (13) |
| C3S | 0.0279 (15) | 0.0349 (16) | 0.0305 (15) | 0.0030 (12) | 0.0096 (12) | 0.0035 (12) |
| C4S | 0.0275 (15) | 0.0237 (14) | 0.0354 (16) | 0.0033 (11) | 0.0133 (13) | −0.0013 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zr1—Cl2 | 2.4586 (6) | C13—C14 | 1.385 (3) |
| Zr1—Cl2$^{i}$ | 2.4587 (6) | C13—C18 | 1.393 (3) |
| Zr1—Cl3 | 2.4723 (6) | C14—C15 | 1.397 (4) |
| Zr1—Cl3$^{i}$ | 2.4724 (6) | C14—H14 | 0.95 |
| Zr1—Cl1$^{i}$ | 2.4818 (6) | C15—C16 | 1.385 (4) |
| Zr1—Cl1 | 2.4818 (5) | C15—H15 | 0.95 |
| As1—C7 | 1.906 (2) | C16—C17 | 1.374 (4) |
| As1—C1 | 1.911 (2) | C16—H16 | 0.95 |
| As1—C13 | 1.911 (2) | C17—C18 | 1.382 (4) |
| As1—C19 | 1.916 (2) | C17—H17 | 0.95 |
| C1—C2 | 1.387 (3) | C18—H18 | 0.95 |
| C1—C6 | 1.393 (3) | C19—C24 | 1.389 (3) |
| C2—C3 | 1.398 (3) | C19—C20 | 1.393 (3) |
| C2—H2 | 0.95 | C20—C21 | 1.385 (3) |
| C3—C4 | 1.385 (4) | C20—H20 | 0.95 |
| C3—H3 | 0.95 | C21—C22 | 1.388 (4) |
| C4—C5 | 1.382 (4) | C21—H21 | 0.95 |
| C4—H4 | 0.95 | C22—C23 | 1.380 (4) |
| C5—C6 | 1.389 (3) | C22—H22 | 0.95 |
| C5—H5 | 0.95 | C23—C24 | 1.394 (3) |
| C6—H6 | 0.95 | C23—H23 | 0.95 |
| C7—C12 | 1.389 (3) | C24—H24 | 0.95 |
| C7—C8 | 1.397 (3) | N1S—C2S | 1.134 (4) |
| C8—C9 | 1.391 (3) | C1S—C2S | 1.451 (4) |
| C8—H8 | 0.95 | C1S—H1SA | 0.98 |
| C9—C10 | 1.384 (4) | C1S—H1SB | 0.98 |
| C9—H9 | 0.95 | C1S—H1SC | 0.98 |
| C10—C11 | 1.386 (4) | N2S—C4S | 1.135 (4) |
| C10—H10 | 0.95 | C3S—C4S | 1.459 (4) |
| C11—C12 | 1.391 (3) | C3S—H3SA | 0.98 |
| C11—H11 | 0.95 | C3S—H3SB | 0.98 |
| C12—H12 | 0.95 | C3S—H3SC | 0.98 |
| | | | |
| Cl2—Zr1—Cl2$^{i}$ | 180.0 | C7—C12—C11 | 119.2 (2) |
| Cl2—Zr1—Cl3 | 90.09 (2) | C7—C12—H12 | 120.4 |
| Cl2$^{i}$—Zr1—Cl3 | 89.91 (2) | C11—C12—H12 | 120.4 |
| Cl2—Zr1—Cl3$^{i}$ | 89.91 (2) | C14—C13—C18 | 121.1 (2) |
| Cl2$^{i}$—Zr1—Cl3$^{i}$ | 90.09 (2) | C14—C13—As1 | 119.17 (18) |

| | | | |
|---|---|---|---|
| Cl3—Zr1—Cl3$^{i}$ | 180.00 (3) | C18—C13—As1 | 119.75 (18) |
| Cl2—Zr1—Cl1$^{i}$ | 90.398 (19) | C13—C14—C15 | 119.0 (3) |
| Cl2$^{i}$—Zr1—Cl1$^{i}$ | 89.602 (19) | C13—C14—H14 | 120.5 |
| Cl3—Zr1—Cl1$^{i}$ | 89.703 (19) | C15—C14—H14 | 120.5 |
| Cl3$^{i}$—Zr1—Cl1$^{i}$ | 90.296 (19) | C16—C15—C14 | 119.8 (3) |
| Cl2—Zr1—Cl1 | 89.603 (19) | C16—C15—H15 | 120.1 |
| Cl2$^{i}$—Zr1—Cl1 | 90.397 (19) | C14—C15—H15 | 120.1 |
| Cl3—Zr1—Cl1 | 90.298 (19) | C17—C16—C15 | 120.6 (2) |
| Cl3$^{i}$—Zr1—Cl1 | 89.703 (19) | C17—C16—H16 | 119.7 |
| Cl1$^{i}$—Zr1—Cl1 | 180.0 | C15—C16—H16 | 119.7 |
| C7—As1—C1 | 110.95 (10) | C16—C17—C18 | 120.4 (3) |
| C7—As1—C13 | 110.73 (10) | C16—C17—H17 | 119.8 |
| C1—As1—C13 | 107.65 (10) | C18—C17—H17 | 119.8 |
| C7—As1—C19 | 107.83 (10) | C17—C18—C13 | 119.1 (3) |
| C1—As1—C19 | 111.76 (10) | C17—C18—H18 | 120.5 |
| C13—As1—C19 | 107.89 (10) | C13—C18—H18 | 120.5 |
| C2—C1—C6 | 121.3 (2) | C24—C19—C20 | 121.1 (2) |
| C2—C1—As1 | 118.72 (18) | C24—C19—As1 | 119.04 (18) |
| C6—C1—As1 | 119.64 (18) | C20—C19—As1 | 119.80 (18) |
| C1—C2—C3 | 118.9 (2) | C21—C20—C19 | 118.9 (2) |
| C1—C2—H2 | 120.6 | C21—C20—H20 | 120.6 |
| C3—C2—H2 | 120.6 | C19—C20—H20 | 120.6 |
| C4—C3—C2 | 119.8 (2) | C20—C21—C22 | 120.6 (2) |
| C4—C3—H3 | 120.1 | C20—C21—H21 | 119.7 |
| C2—C3—H3 | 120.1 | C22—C21—H21 | 119.7 |
| C5—C4—C3 | 120.9 (2) | C23—C22—C21 | 120.1 (2) |
| C5—C4—H4 | 119.5 | C23—C22—H22 | 120.0 |
| C3—C4—H4 | 119.5 | C21—C22—H22 | 120.0 |
| C4—C5—C6 | 119.9 (2) | C22—C23—C24 | 120.4 (2) |
| C4—C5—H5 | 120.1 | C22—C23—H23 | 119.8 |
| C6—C5—H5 | 120.1 | C24—C23—H23 | 119.8 |
| C5—C6—C1 | 119.1 (2) | C19—C24—C23 | 119.0 (2) |
| C5—C6—H6 | 120.4 | C19—C24—H24 | 120.5 |
| C1—C6—H6 | 120.4 | C23—C24—H24 | 120.5 |
| C12—C7—C8 | 121.0 (2) | C2S—C1S—H1SA | 109.5 |
| C12—C7—As1 | 119.35 (17) | C2S—C1S—H1SB | 109.5 |
| C8—C7—As1 | 119.40 (18) | H1SA—C1S—H1SB | 109.5 |
| C9—C8—C7 | 119.0 (2) | C2S—C1S—H1SC | 109.5 |
| C9—C8—H8 | 120.5 | H1SA—C1S—H1SC | 109.5 |
| C7—C8—H8 | 120.5 | H1SB—C1S—H1SC | 109.5 |
| C10—C9—C8 | 120.1 (2) | N1S—C2S—C1S | 179.5 (4) |
| C10—C9—H9 | 119.9 | C4S—C3S—H3SA | 109.5 |
| C8—C9—H9 | 119.9 | C4S—C3S—H3SB | 109.5 |
| C9—C10—C11 | 120.6 (2) | H3SA—C3S—H3SB | 109.5 |
| C9—C10—H10 | 119.7 | C4S—C3S—H3SC | 109.5 |
| C11—C10—H10 | 119.7 | H3SA—C3S—H3SC | 109.5 |
| C10—C11—C12 | 120.1 (2) | H3SB—C3S—H3SC | 109.5 |

| | | | |
|---|---|---|---|
| C10—C11—H11 | 119.9 | N2S—C4S—C3S | 179.3 (3) |
| C12—C11—H11 | 119.9 | | |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C3*S*—H3*SA*···Cl1$^{ii}$ | 0.98 | 2.81 | 3.674 (3) | 148 |
| C16—H16···Cl1$^{iii}$ | 0.95 | 2.73 | 3.646 (3) | 162 |
| C18—H18···N1*S*$^{iii}$ | 0.95 | 2.61 | 3.483 (4) | 154 |

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