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*Acta Cryst.* (1995). **C51**, 565–567

## Zirconocene Dichloride

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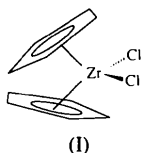
(Received 4 February 1994; accepted 11 October 1994)

### Abstract

The  $\alpha$  form of dichlorobis( $\eta^5$ -cyclopentadienyl)zircononium,  $[\text{ZrCl}_2(\text{C}_5\text{H}_5)_2]$ , crystallizes in space group  $P\bar{1}$  and is isomorphous with  $\alpha\text{-Cp}_2\text{TiCl}_2$  and  $\alpha\text{-Cp}_2\text{HfCl}_2$ . The two Cl ligands and the centroids of the Cp rings adopt an irregular tetrahedral arrangement about the Zr center. The angle between the Cl–Zr–Cl plane and the  $\text{Cp}_{\text{centroid}}\text{-Zr-Cp}_{\text{centroid}}$  plane is  $89.4^\circ$  for molecule (1) and  $89.7^\circ$  for molecule (2) of the asymmetric unit. The average bond distances are C–C =  $1.384(5)$  and Zr–Cl =  $2.447(3)$  Å in molecule (1), and C–C =  $1.359(7)$  and Zr–Cl =  $2.447(1)$  Å in molecule (2).

### Comment

A commercial sample of the title compound, (I), was recrystallized from chloroform over a two month period at 278 K to provide the  $\alpha$  crystalline form. A  $\beta$  form of zirconocene dichloride (space group  $P2_1/a$ ,  $Z = 8$ ) has been obtained by recrystallization from tetrahydrofuran and the structural parameters have been described briefly (Soloveichik, Arkhireeva, Bel'skii & Bulychev, 1988).



The structure determination of the  $\alpha$  form, which was first reported in 1974 (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974), indicated that the atoms of the cyclopentadienyl rings exhibited large displacement parameters in the ring planes, consistent with either static or dynamic disorder. This disorder was modeled using rigid bodies with isotropic atomic displacement parameters to describe two orientations of partial occupancy for the rings associated with one molecule and large anisotropic atomic displacement parameters to describe a single-ring orientation for the other independent molecule. The model converged at  $R = 0.095$ . A later attempt to refine the structure of  $\alpha\text{-Cp}_2\text{ZrCl}_2$  was abandoned when the same disorder was observed (Clearfield, Warner, Saldarriaga-Molina, Ropal & Bernal, 1975). In the present redetermination, Mo  $K\alpha$  radiation rather than Cu  $K\alpha$  radiation has been used, thus reducing the effects of absorption considerably. Furthermore, refinement of each of the cyclopentadienyl rings using unconstrained single orientations with anisotropic atomic displacement parameters has led to convergence at  $R = 0.032$  and  $S = 1.08$ , and also permitted the direct location and refinement of the cyclopentadienyl H atoms. Large anisotropic displacement parameters of the ring C atoms are again indicative of either static or dynamic disorder. The short mean C–C distances,  $1.384(5)$  Å in molecule (1) and  $1.359(7)$  Å in molecule (2) (*cf.* typical C–C distance of  $1.397$  Å; Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989), are also consistent with this assertion. The structures of  $\alpha\text{-Cp}_2\text{TiCl}_2$  (recrystallized from  $\text{C}_6\text{H}_6$ ) (Clearfield, Warner, Saldarriaga-Molina, Ropal & Bernal, 1975) and  $\alpha\text{-Cp}_2\text{HfCl}_2$  (recrystallized from  $\text{CH}_2\text{Cl}_2$ ) (Soloveichik, Arkhireeva, Bel'skii & Bulychev, 1988) are isomorphous with the  $\text{Cp}_2\text{ZrCl}_2$  structure reported here. All three metallocene dihalides exhibit a similar disorder problem in the Cp rings. A comparison of selected parameters for the three metallocene dihalides is given in Table 3.

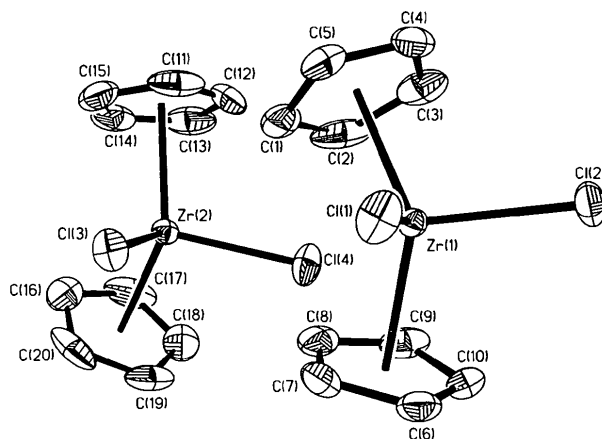


Fig. 1. Displacement ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1991) of the title compound. Ellipsoids are scaled to enclose 50% probability and H atoms are omitted for clarity.

The metallocene dihalides and related derivatives of titanium and zirconium are utilized as homogeneous Ziegler–Natta catalyst precursors for the polymerization of olefins (Collman, Hegedus, Norton & Finke, 1987).

## Experimental

### Crystal data

[ZrCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] $M_r = 292.3$ 

Triclinic

 $P\bar{1}$  $a = 8.109(3) \text{ \AA}$  $b = 11.845(5) \text{ \AA}$  $c = 12.364(5) \text{ \AA}$  $\alpha = 71.08(3)^\circ$  $\beta = 76.82(3)^\circ$  $\gamma = 87.62(3)^\circ$  $V = 1093.1(7) \text{ \AA}^3$  $Z = 4$  $D_x = 1.776 \text{ Mg m}^{-3}$ 

### Data collection

Siemens R3m/V diffractometer

 $\omega/2\theta$  scansAbsorption correction: empirical ( $\psi$  scan) $T_{\min} = 0.735$ ,  $T_{\max} = 1.000$ 

6835 measured reflections

6418 independent reflections

4450 observed reflections

 $[F > 4.0\sigma(F)]$ 

### Refinement

Refinement on  $F^2$  $R = 0.0320$  $wR = 0.0379$  $S = 1.08$ 

4450 reflections

316 parameters

All H-atom parameters refined

 $w = 1/[\sigma^2(F) + 0.0004F^2]$   
 $(\Delta/\sigma)_{\max} = 0.159$ Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 14 reflections

 $\theta = 10\text{--}13^\circ$  $\mu = 1.435 \text{ mm}^{-1}$  $T = 298 \text{ K}$ 

Rectangular

 $0.6 \times 0.3 \times 0.2 \text{ mm}$ 

Colorless

 $R_{\text{int}} = 0.0178$  $\theta_{\max} = 30^\circ$  $h = 0 \rightarrow 11$  $k = -16 \rightarrow 16$  $l = -16 \rightarrow 17$ 

3 standard reflections monitored every 50 reflections

intensity decay: 3%

 $\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = 0.39 \text{ e \AA}^{-3}$ 

Extinction correction: Larson (1970)

Extinction coefficient:

 $\chi = 0.0003(2)$ Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

C(6)	0.3694 (5)	0.3521 (4)	0.1014 (4)	0.063 (2)
C(7)	0.2271 (7)	0.4139 (4)	0.1385 (6)	0.079 (3)
C(8)	0.1400 (6)	0.3398 (6)	0.2480 (5)	0.083 (3)
C(9)	0.2261 (6)	0.2354 (5)	0.2772 (4)	0.074 (2)
C(10)	0.3677 (5)	0.2451 (4)	0.1884 (4)	0.064 (2)
C(11)	−0.5282 (8)	0.1781 (8)	0.5284 (6)	0.097 (3)
C(12)	−0.4821 (7)	0.0860 (5)	0.6125 (8)	0.100 (3)
C(13)	−0.5403 (8)	0.0989 (6)	0.7169 (6)	0.099 (3)
C(14)	−0.6306 (6)	0.2002 (7)	0.7003 (6)	0.093 (3)
C(15)	−0.6241 (6)	0.2528 (5)	0.5842 (7)	0.091 (3)
C(16)	−0.4037 (7)	0.3769 (7)	0.7527 (7)	0.096 (3)
C(17)	−0.3490 (9)	0.2706 (6)	0.8122 (4)	0.093 (3)
C(18)	−0.1797 (8)	0.2660 (6)	0.7680 (5)	0.085 (3)
C(19)	−0.1281 (7)	0.3674 (6)	0.6807 (5)	0.085 (3)
C(20)	−0.2642 (12)	0.4389 (5)	0.6699 (5)	0.102 (4)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Zr(1)—Cl(1)	2.444 (1)	Zr(1)—Cp1 †	2.200
Zr(1)—Cl(2)	2.450 (1)	Zr(1)—Cp2 †	2.201
Zr(2)—Cl(3)	2.448 (1)	Zr(2)—Cp3 †	2.208
Zr(2)—Cl(4)	2.446 (2)	Zr(2)—Cp4 †	2.202
C—C [C(1)—C(5)]	1.382 (7) ‡	C—C [C(11)—C(15)]	1.382 (7) ‡
C—C [C(6)—C(10)]	1.385 (7) ‡	C—C [C(16)—C(20)]	1.360 (9) ‡
Cl(1)—Zr(1)—Cl(2)	97.0 (1)	Cp1—Zr(1)—Cp2	129.5
Cl(3)—Zr(2)—Cl(4)	97.1 (1)	Cp3—Zr(2)—Cp4	129.1
C—C—C [C(1)—C(5)]	108.0 (4) ‡	C—C—C [C(11)—C(15)]	108.0 (8) ‡
C—C—C [C(6)—C(10)]	108.0 (4) ‡	C—C—C [C(16)—C(20)]	108.0 (3) ‡

† Cp1, Cp2, Cp3 and Cp4 are the centroids of the cyclopentadienyl rings.

‡ E.s.d.'s for averaged dimensions were calculated according to  $\sigma = [\sum(d_i - d)^2/n(n-1)]^{1/2}$ .

Table 3. Comparison of structural parameters ( $\text{\AA}$ ,  $^\circ$ ) in  $\text{Cp}_2\text{MCl}_2$  ( $M = \text{Ti, Zr, Hf}$ )

	$\text{Cp}_2\text{TiCl}_2^a$	$\text{Cp}_2\text{ZrCl}_2^b$	$\text{Cp}_2\text{HfCl}_2^c$
$M\text{—Cl}^d$	2.364 (2)	2.447 (1)	2.423 (2)
$Cp\text{—}M$	2.059	2.203	2.18
C—C range	1.339–1.419	1.325–1.408	1.299–1.448
Average C—C <sup>e</sup>	1.370 (4)	1.371 (5)	1.383 (10)
Cl—M—Cl	94.5 (1)	97.0 (1)	96.2
$Cp\text{—}M\text{—}Cp$	131.0	129.3	127.1

Notes: (a) Clearfield, Warner, Saldarriago–Molina, Ropal & Bernal (1975); (b) this work; (c) Soloveichik, Arkhireeva, Bel'skii & Bulychev (1988); (d) average e.s.d.'s calculated as in footnote † to Table 2; (e) calculated for all C—C distances from published data.

As some disorder was indicated from the larger  $U_{\text{eq}}$  values for the C atoms, attempts were made to resolve the disorder. However, due to the closeness of the C atoms in the disorder model ( $<0.3 \text{ \AA}$ ), a split-atom model could not be refined.

Refinement was also attempted using  $F_o^2$  (SHELXL93; Sheldrick, 1993), but no improvement was observed. Two types of empirical absorption correction were tried: (i)  $\psi$  scan (SHELXL93 XEMP), and (ii) using equivalent reflections, the former resulting in a better quality structure.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation (CHE-9213688), to the Research Board of the University of Missouri and to a Research Incentive Award from the University of Missouri – St Louis, for support of this work.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
Zr(1)	0.1120 (1)	0.2380 (1)	0.1066 (1)	0.035 (1)
Zr(2)	−0.3301 (1)	0.2654 (1)	0.6126 (1)	0.037 (1)
Cl(1)	0.1383 (1)	0.3758 (1)	−0.0929 (1)	0.068 (1)
Cl(2)	0.2779 (1)	0.0785 (1)	0.0536 (1)	0.063 (1)
Cl(3)	−0.2801 (1)	0.4223 (1)	0.4211 (1)	0.063 (1)
Cl(4)	−0.0906 (1)	0.1437 (1)	0.5656 (1)	0.069 (1)
C(1)	−0.1921 (5)	0.2648 (5)	0.1823 (5)	0.074 (2)
C(2)	−0.1455 (6)	0.1651 (7)	0.2637 (4)	0.093 (3)
C(3)	−0.1090 (6)	0.0757 (5)	0.2114 (5)	0.079 (2)
C(4)	−0.1361 (5)	0.1233 (4)	0.0985 (4)	0.062 (2)
C(5)	−0.1877 (5)	0.2372 (4)	0.0820 (4)	0.065 (2)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 567–569

## An Oxovanadium(IV) Complex Chelated by Dipyrindyl Sulfide

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(Received 14 February 1994; accepted 11 July 1994)

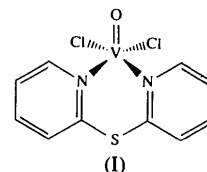
### Abstract

The complex (di-2-pyridyl sulfide-*N,N'*)dichlorooxovanadium(IV),  $[\text{VOCl}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})]$ , was prepared by the reaction of  $\text{VCl}_3$  and sodium 2-mercaptopyridine *N*-oxide in ethanol solution under an atmosphere of argon. The N atoms of the dipyrindyl sulfide ligand and the two chloride ligands coordinate to the oxovanadium(IV) ion, to give a complex with square-pyramidal geometry. The

dipyrindyl sulfide ligand forms a folded six-membered chelate ring with a larger N—V—N bite angle than that formed by 2,2'-bipyridyl.

### Comment

Pyridines have been utilized widely in the synthesis of transition metal complexes because of their  $\sigma/\pi$ -bonding capability. An additional and significant effect on the geometry of the complex formed is expected when multidentate polypyridines are used. 2,2'-Bipyridine (bpy) is one such ligand (Holloway & Melnik, 1985), and gives rise to a five-membered chelate ring. Ligands of the type py—X—py (bpyX; X = O or S) give six-membered chelate rings, modifying the metal–nitrogen bonding. Many vanadium complexes of bpy have been synthesized and characterized by X-ray crystallography (Boas & Pessoa, 1987), whereas vanadium complexes of bpyX are few. Here we report the structure of the title complex, (I).



The structure of the the title complex, (I), is shown in Fig. 1. The mononuclear vanadium(IV) center is ligated by an O, two Cl and two N atoms. The V—O bond distance [1.573 (2) Å] is typical for vanadium complexes having a terminal oxo group (Nugent & Mayer, 1988). The N—V—N, O—V—Cl, O—V—N and Cl—V—N bond angles indicate a typical square-pyramidal  $\text{VOCl}_2\text{N}_2$  core with the oxo ligand occupying the apical site. The V atom lies 0.52 Å above the plane formed by the two Cl and two N atoms. The O atom of the sodium 2-mercaptopyridine *N*-oxide used in the synthesis of (I) is a likely source of the terminal oxo ligand, while the presence of vanadium may promote the ligand-coupling reaction which results in the formation of the bpyS ligand, an unexpected product of the reaction. The bpyS ligand is not planar, and the six-membered chelate ring has a folded boat-like conformation. In the chelate ring the N—V—N, V—N—C, N—C—S and C—S—C bond angles, and the V—N, N—C and C—S bond lengths all fall within the range of usual values; hence the six-membered ring is not strained. The N(1)—V(1)—N(2) bond angle is larger than that found for the rigid five-membered chelate ring formed by bpy in the oxovanadium(IV) complex  $[\text{VO}(\text{bpy})(\text{N-methoxyiminodiacetate})]$  [77.4 (2)°] (de C. T. Carrondo, Duarte, Silva & da Silva, 1991). The V—N bond lengths in the title complex are longer than those in  $[\text{VO}(\text{bpy})(\text{N-methoxyiminodiacetate})]$  [2.088 (4), 2.094 (4) Å]. These results show that the