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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1256). Services for accessing these data are described at the back of the journal.

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Diphenylzirconocene

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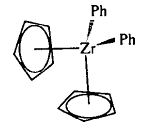
Abstract

The title compound, $[Zr(C_5H_5)_2(C_6H_5)_2]$, has two cyclopentadienyl and two phenyl ligands arranged in a distorted tetrahedral geometry around the Zr atom. Steric interactions produce an opening of the Cp—Zr—Cp angle to 131.7 (1)° and a tilting of both phenyl rings in their own planes about the Zr—C bonds by several degrees.

Comment

Since the discovery by Sinn *et al.* (1980) that the zirconocene dichloride/methylaluminoxane system was effective as a homogeneous Ziegler–Natta catalyst, there has been considerable research into zirconocene derivatives as polymerization catalysts. Structural analysis of these zirconocenes may provide important clues to the mechanism of polymerization, as well as increasing our knowledge of the structural chemistry of organozirconium compounds.

One of the aims of our current research is to synthesize a mixed lithium–zirconium cluster. Diphenylzirconocene, (I), was chosen as one of the starting materials in the attempted preparation of such a cluster. It was first prepared by Samuel & Rausch (1973) as a white solid, which is stable in air for short periods of time, but is unstable at elevated temperatures, decomposing at 413 K. We report here the previously unknown crystal structure of diphenylzirconocene.



(I)

Considering the two cyclopentadienyl (Cp) ligands as occupying one coordination site each, the coordination geometry of zirconium is a rather distorted tetrahedron, with the angle enclosed by the two Cp ligands opened up to 131.7 (1)° and all the other angles reduced from the ideal value of 109.5°. A search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals a large number of Cp_2ZrX_2 molecular structures, including those with substituted Cp ligands. Of these, 16 have monodentate carbon ligands X (alkyl, alkenyl, alkynyl, aryl or carbonyl) and no constraint on coordination geometry from linking of the Cp ligands through their substituents. The X—Zr—X angle varies widely, between 86.8 [for dicarbonylbis(indenyl)zirconium; Rausch *et al.*, 1987] and 131.3° (for a mixed alkyl–alkenyl complex; Hey-Hawkins & Lindenberg, 1992), while the range of Cp—Zr—Cp angles is much smaller, 126.9–145.0°. These variations appear to have mainly steric origins. The Zr—Cp and Zr—C(Ph) distances in diphenylzirconocene lie well within the ranges observed for these other complexes.

The dihedral angle between the two Cp rings is 52.1 (2)°, and that between the two phenyl rings is also 52.1 (2)°. Both phenyl substituents show a distortion from regular hexagonal geometry, with a reduced C—C—C angle at the *ipso*-C atom, and each is tilted within its own plane relative to the Zr—C bond, so that one Zr—C—C angle is markedly larger than the other, probably also to reduce steric interactions. There are no notably short intermolecular contacts. Highly

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anisotropic displacement parameters of the Cp ring atoms are consistent with marked rotational freedom of these groups, but may also be a consequence of static disorder, which it was not possible to resolve.

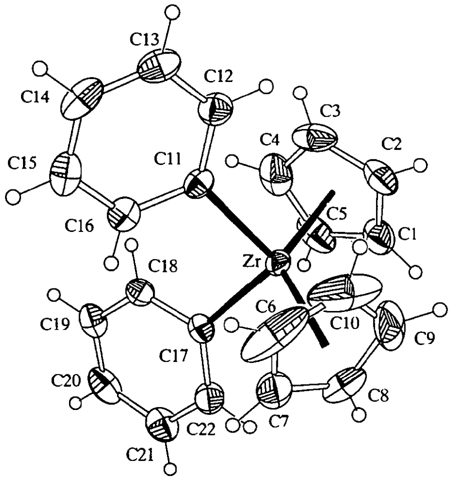

Fig. 1. The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.

Experimental

The compound was prepared according to the method of Samuel & Rausch (1973), and was added to a hexane–toluene solution of lithium *tert*-butylamine (Barnett *et al.*, 1996) with the intention of preparing a mixed lithium–zirconium amide derivative. However, a few single crystals of the title compound were recovered on cooling the solution to 249 K overnight.

Crystal data

$[Zr(C_5H_5)_2(C_6H_5)_2]$
$M_r = 375.60$
Orthorhombic
$Pna2_1$
$a = 16.5090\,(15)$ Å
$b = 8.2204\,(8)$ Å
$c = 12.7283\,(12)$ Å
$V = 1727.4\,(3)$ Å^3
$Z = 4$
$D_x = 1.444$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8889 reflections
$\theta = 2.47$–$28.53°$
$\mu = 0.633$ mm^{-1}
$T = 160\,(2)$ K
Block
0.54 × 0.49 × 0.40 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: multiscan (*SHELXTL*; Sheldrick, 1994)
$T_{min} = 0.695$, $T_{max} = 0.797$
10 277 measured reflections

2144 independent reflections, with 1807 Friedel opposites
2097 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.55°$
$h = -17 \rightarrow 22$
$k = -10 \rightarrow 9$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.059$
$S = 1.088$
3951 reflections
209 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 0.9569P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.359$ e Å^{-3}
$\Delta\rho_{min} = -0.300$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0021 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (4)

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

Zr—C11	2.304 (2)	Zr—*Cp*1†	2.218 (2)
Zr—C17	2.297 (2)	Zr—*Cp*2†	2.222 (2)
C11—Zr—C17	105.7 (1)	C16—C11—C12	115.6 (2)
*Cp*1—Zr—*Cp*2	131.7 (1)	C16—C11—Zr	115.4 (2)
C11—Zr—*Cp*1	107.9 (1)	C12—C11—Zr	128.7 (2)
C17—Zr—*Cp*1	102.4 (1)	C18—C17—C22	115.1 (2)
C11—Zr—*Cp*2	101.2 (1)	C18—C17—Zr	114.7 (2)
C17—Zr—*Cp*2	105.9 (1)	C22—C17—Zr	130.1 (2)

† *Cp*1 and *Cp*2 are the centroids of the two Cp rings, C1–C5 and C6–C10, respectively.

The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. H atoms were placed geometrically and refined with a riding model, and with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. Each member of a Friedel pair was treated as an independent observation in the least-squares refinement.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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$H_2N(CH_2)_2NH_3^+.[Mn\{H_2N(CH_2)_2NH_2\}_3]^{2+}.-[SbSe_4]^{3-}$

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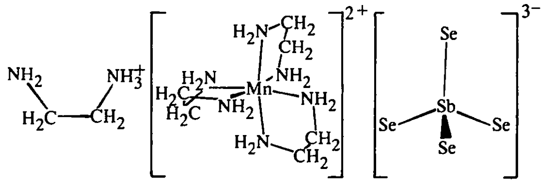
Abstract

The reaction of elemental manganese, antimony and selenium with 1,2-ethanediamine (en) in an aqueous ethaneamine solution under hydrothermal conditions yields orange crystals of 2-aminoethylammonium tris(1,2-ethanediamine)manganese tetraselenoantimonate, enH.Mn(en)$_3$.SbSe$_4$. The structure contains tetrahedral $SbSe_4^{3-}$ anions and octahedral $Mn(en)_3^{2+}$ cations, as well as monoprotonated ethanediamine molecules.

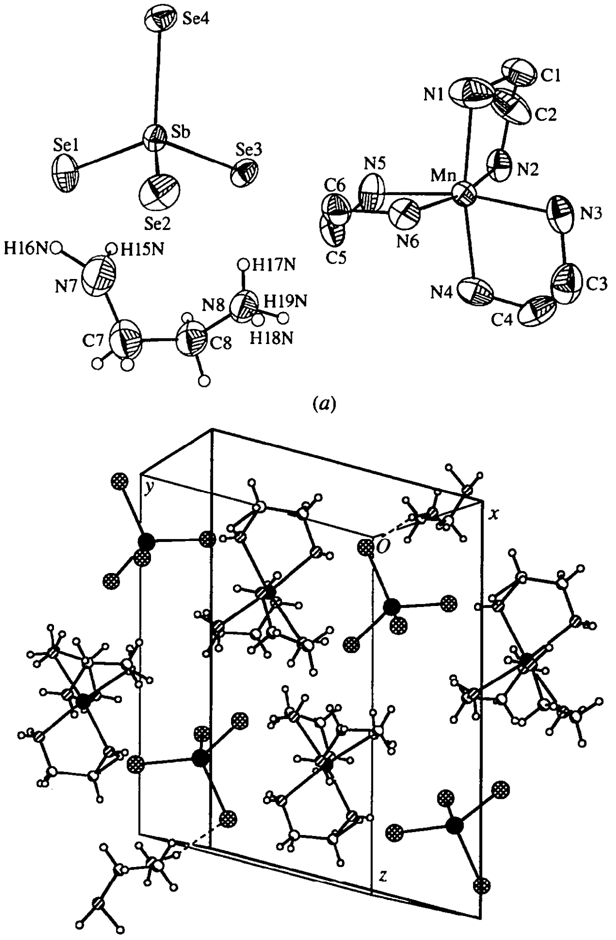
Comment

Applications of mild solvothermal processes have led to a wealth of novel chalcogenides, ranging from unique thiometallate clusters to three-dimensional frameworks (Sheldrick & Kaub, 1986; Sheldrick & Wachhold, 1997; Krebs, 1983). Despite expectations of new and unusual electronic properties, the chemistry of the heavier chalcogenides is less developed. This might be in part due to the ease of hydrolysis of seleno- and tellurometallates. Consequently, non-aqueous reaction media are preferred for their syntheses. In our recent investigations, we have isolated the novel transition metal complex $[Mn(en)_3]_2[Mn_4(en)_9(SbSe_4)_4].2H_2O$ by reacting elemental manganese, antimony and selenium in an aqueous amine solution using high amine concentrations (Bensch *et al.*, 1997). Since it is well known that temperature has an enormous effect on product formation (Sheldrick & Wachhold, 1997), we have investigated the aforementioned system under different synthesis conditions. By using higher temperatures, we have obtained enH.Mn(en)$_3$.SbSe$_4$, (I), as a pure phase forming orange needles.



(I)

The crystal structure of the title compound contains isolated $Mn(en)_3^{2+}$ cations and $SbSe_4^{3-}$ anions. Monoprotonated ethanediamine solvent molecules complete the crystal structure and balance the charge of the $SbSe_4^{3-}$ anions. Each Mn cation is sixfold coordinated by the six N atoms of the chelating en ligands within a distorted octahedron. The Mn—N distances are between 2.235 (6) and 2.286 (5) Å. The Sb—Se distances of the tetrahedral $SbSe_4^{3-}$ anion are between 2.470 (1) and 2.478 (1) Å,



(*a*)

(*b*)

Fig. 1. The crystal structure of the title compound. (*a*) View of the SbSe$_4$ anion, the Mn(en)$_3$ cation and the enH cation with labelling and displacement ellipsoids drawn at the 50% probability level (disorder has been omitted for clarity). (*b*) Packing diagram viewed along [100] with the shortest intermolecular Se—H distances (2.35 Å) indicated by dotted lines.