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Acta Cryst. (1994). C**50**, 1000–1002

μ-[1,2-Bis(diethylphosphino)ethane]-*P*:*P′*-bis[bis(diethyldithiocarbamato-*S*,*S′*)zinc(II)] Ditoluene Solvate

D. Zeng and M. J. Hampden-Smith

Department of Chemistry and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131, USA

E. M. Larson

Department of Geology, University of New Mexico, Albuquerque, NM 87131, USA

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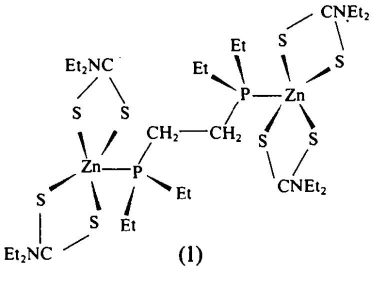
Abstract

The title complex, [$Zn_2(C_5H_{10}NS_2)_4(C_{10}H_{24}P_2)$], is positioned symmetrically about an inversion center at the cell origin, which is situated at the center of the bridging diphosphine ligand. Toluene is disordered in this structure such that the rotation between the two positions of the methyl C atom is 36°. The geometry about Zn can be described as a distorted trigonal bipyramid. The Zn—P distance is 2.388 (2) Å and the Zn—S distances range from 2.320 (2) to 2.653 (2) Å.

Comment

The structure of the title complex (1), shown in Fig. 1, shows some similarity to that of the parent dimer bis(diethyldithiocarbamato)zinc(II), (2) (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). In the latter, one dithiocarbamate ligand bridges both Zn atoms of this dimeric complex, while the other type chelates to each Zn. A five-coordinate distorted trigonal-bipyramidal environment for Zn results from the long (2.81 Å) sulfur bridge. The inversion center of the monoclinic cell lies at the center of the zinc dimer (2) between the bridging dithiocarbamate ligands. Upon introducing the diphosphine ligand, an expansion of the monoclinic cell is observed with a contraction of β. However, the symmetry of the cell, $P2_1/c$, remains the same. Both dithiocarbamate ligands become chelating, whereupon the diphosphine bridges the Zn atoms and the inversion center lies between the P atoms. In the title complex (1), the Zn coordination geometry remains similar to that of the parent compound and can also be represented by a distorted trigonal bipyramid.



(1)

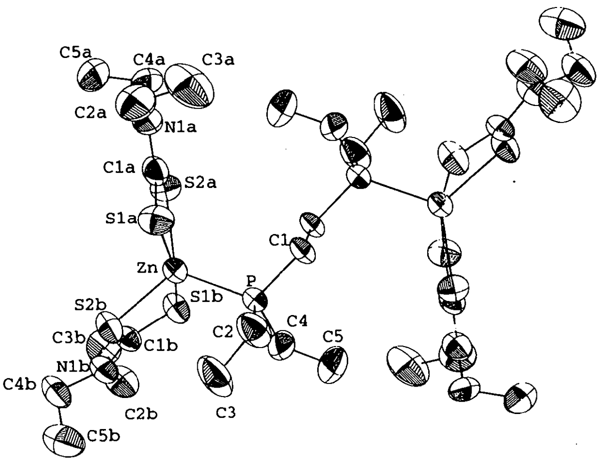


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the zinc dimer. Each half of the molecule is related to the other by the inversion center. The disordered toluene rings are not shown for the purpose of clarity.

Experimental

The synthesis of this compound is described elsewhere (Zeng & Hampden-Smith, 1994). The crystal used for data collection was recrystallized from toluene and mounted in a 0.2 mm diameter sealed capillary tube containing the mother liquor in order to prevent decomposition, as the loss of solvated toluene is rapid in the open atmosphere. (However, the large decrease in intensity of the standard reflections revealed that degradation of the crystal still occurred.)

Crystal data

[$Zn_2(C_5H_{10}NS_2)_4(C_{10}H_{24}P_2)$].-$2C_7H_8$
$M_r = 1114.4$
Monoclinic
$P2_1/c$
$a = 12.960\ (1)$ Å
$b = 11.311\ (2)$ Å
$c = 20.129\ (5)$ Å
$\beta = 96.46\ (1)°$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 45 reflections
$\theta = 5.5–13.5°$
$\mu = 1.189\ mm^{-1}$
$T = 298$ K
Needle
0.4 × 0.2 × 0.2 mm

$V = 2932\ (9)$ Å^3
$Z = 2$
$D_x = 1.254$ Mg m^{-3}

Colorless

Data collection

Kuma KM-4 diffractometer
θ-2θ scans
Absorption correction: spherical
$T_{\min} = 0.8375$, $T_{\max} = 0.8380$
4306 measured reflections
3857 independent reflections
2705 observed reflections $[F > \sigma(F)]$

$R_{\rm int} = 0.026$
$\theta_{\max} = 45°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = -21 \rightarrow 21$
2 standard reflections monitored every 50 reflections intensity variation: 40%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.072$
$S = 4.18$
2531 reflections $[I > 3\sigma(I)]$
232 parameters
H atoms not placed

$w = (2F_o/\sigma F_o^2)^2$
$\Delta\rho_{\max} = 0.768$ e Å^{-3}
$\Delta\rho_{\min} = -0.732$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for solvent C atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_i U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Zn	0.22228 (8)	0.00208 (10)	0.13061 (5)	0.0551
P	0.17153 (17)	0.02645 (21)	0.01365 (11)	0.0502
C1	0.0435 (6)	−0.0315 (8)	−0.0161 (4)	0.0509
C2	0.2550 (7)	−0.0581 (11)	−0.0388 (5)	0.0824
C3	0.3684 (8)	−0.0224 (14)	−0.0233 (6)	0.1161
C4	0.1716 (8)	0.1807 (9)	−0.0133 (5)	0.0802
C5	0.1379 (10)	0.2026 (11)	−0.0867 (6)	0.1108
S1*a*	0.23159 (21)	−0.23105 (22)	0.11772 (14)	0.0711
S2*a*	0.10560 (20)	−0.08128 (21)	0.19647 (12)	0.0614
N1*a*	0.0920 (6)	−0.3153 (7)	0.1942 (4)	0.0716
C1*a*	0.1387 (7)	−0.2208 (8)	0.1716 (4)	0.0585
C2*a*	0.1226 (10)	−0.4379 (10)	0.1746 (6)	0.0995
C3*a*	0.0514 (11)	−0.4788 (10)	0.1117 (8)	0.1298
C4*a*	0.0120 (8)	−0.3035 (10)	0.2408 (5)	0.0785
C5*a*	0.0646 (9)	−0.3083 (12)	0.3132 (5)	0.1021
S1*b*	0.22282 (20)	0.22095 (22)	0.16682 (14)	0.0653
S2*b*	0.39220 (18)	0.04896 (22)	0.17197 (13)	0.0622
N1*b*	0.4174 (6)	0.2693 (7)	0.2147 (4)	0.0644
C1*b*	0.3506 (7)	0.1890 (8)	0.1871 (4)	0.0522
C2*b*	0.3853 (8)	0.3953 (8)	0.2228 (6)	0.0795
C3*b*	0.3409 (9)	0.4126 (10)	0.2896 (6)	0.0937
C4*b*	0.5267 (7)	0.2399 (9)	0.2422 (6)	0.0801
C5*b*	0.5968 (9)	0.2621 (10)	0.1909 (7)	0.1088
C1*t*	0.2399 (7)	−0.0356 (9)	0.4203 (10)	0.151 (14)
C1′*t*	0.2560 (9)	−0.0097 (11)	0.3823 (6)	0.127 (10)
C2*t*	0.3621 (10)	0.0704 (12)	0.4995 (5)	0.103 (10)
C2′*t*	0.3124 (9)	0.0192 (10)	0.5006 (5)	0.113 (9)
C3*t*	0.2801 (11)	−0.0105 (11)	0.4865 (7)	0.154 (15)
C3′*t*	0.2465 (7)	−0.0358 (9)	0.4495 (7)	0.122 (10)
C4*t*	0.2817 (11)	0.0202 (13)	0.3670 (6)	0.128 (12)
C4′*t*	0.3313 (10)	0.0714 (11)	0.3660 (4)	0.111 (9)
C5*t*	0.4039 (7)	0.1262 (7)	0.4462 (8)	0.138 (13)
C5′*t*	0.3877 (7)	0.1004 (8)	0.4843 (5)	0.096 (8)
C6*t*	0.4831 (15)	0.2043 (16)	0.4587 (17)	0.177 (20)
C6′*t*	0.4512 (15)	0.1535 (16)	0.5335 (11)	0.134 (13)
C7*t*	0.3637 (11)	0.1011 (12)	0.3800 (6)	0.126 (12)
C7′*t*	0.3972 (8)	0.1264 (8)	0.4170 (6)	0.108 (9)

Table 2. *Selected geometric parameters* (Å, °)

Zn—P	2.388 (2)		
P—C1	1.822 (8)	C2—C3	1.522 (14)
C1—C1$^{\rm i}$	1.537 (16)	P—C4	1.827 (10)
P—C2	1.859 (10)	C4—C5	1.514 (14)
Zn—S1*a*	2.653 (2)	Zn—S1*b*	2.580 (2)
Zn—S2*a*	2.320 (2)	Zn—S2*b*	2.326 (2)
S1*a*—C1*a*	1.712 (9)	S1*b*—C1*b*	1.699 (9)
S2*a*—C1*a*	1.724 (9)	S2*b*—C1*b*	1.712 (9)
C1*a*—N1*a*	1.334 (10)	C1*b*—N1*b*	1.332 (10)
S1*a*···S2*a*	2.937 (3)	S1*b*···S2*b*	2.926 (3)
N1*a*—C2*a*	1.506 (13)	N1*b*—C2*b*	1.498 (11)
C2*a*—C3*a*	1.551 (17)	C2*b*—C3*b*	1.533 (14)
N1*a*—C4*a*	1.480 (12)	N1*b*—C4*b*	1.499 (11)
C4*a*—C5*a*	1.538 (14)	C4*b*—C5*b*	1.472 (15)
Zn—P—C1	115.01 (27)	C1—P—C2	101.2 (4)
Zn—P—C2	112.77 (35)	C1—P—C4	106.1 (4)
Zn—P—C4	113.16 (33)	C2—P—C4	107.6 (5)
P—Zn—S1*a*	91.65 (9)	P—Zn—S1*b*	99.17 (9)
P—Zn—S2*a*	119.03 (9)	P—Zn—S2*b*	118.11 (9)
S1*a*—Zn—S2*a*	72.05 (8)	S1*b*—Zn—S2*b*	73.01 (9)
S1*a*—Zn—S1*b*	169.17 (10)	S2*a*—Zn—S1*b*	102.10 (9)
S1*a*—Zn—S2*b*	102.11 (9)	S2*a*—Zn—S2*b*	122.66 (10)
Zn—S1*a*—C1*a*	80.07 (33)	Zn—S1*b*—C1*b*	80.54 (31)
Zn—S2*a*—C1*a*	90.36 (31)	Zn—S2*b*—C1*b*	88.29 (30)
S1*a*—C1*a*—N1*a*	122.7 (7)	S1*b*—C1*b*—N1*b*	121.7 (7)
S2*a*—C1*a*—N1*a*	119.8 (8)	S2*b*—C1*b*—N1*b*	120.1 (7)
S1*a*—C1*a*—S2*a*	117.5 (5)	S1*b*—C1*b*—S2*b*	118.2 (5)
Toluene			
C(ring)—C(methyl)	1.35 (2)		
C(ring)—C(methyl)	1.404 (4)		

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

The Zn atom was located using standard Patterson methods and the remaining atoms were found through successive difference Fourier calculations. Iterative refinement of atomic positions and anisotropic displacement for all atoms except those of the disordered toluene, which was modeled with isotropic displacement parameters, was performed using *GSAS* (Larson & von Dreele, 1990). Two toluene rings were modeled as rigid bodies with two positions for each C atom. All ring angles were constrained to 120° and one methyl C—C and only one ring C—C distance were allowed to refine for both rigid bodies. The rotation angle between the two methyls refined to −35.98 (56)°. The sum of the occupancies for the rings was fixed at 1.0, with final values of 0.454 (24) and 0.546 (24) for each ring. The function minimized was $\chi = w(F_o - F_c)^2$. The sum of all ρ values in the final Fourier map was 0.292 e.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71761 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1040]

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Bis(η^5-methylcyclopentadienyl)chromium, $[Cr(C_6H_7)_2]$

FRANCO BENETOLLO, ANDREA CAMPORESE AND GILBERTO ROSSETTO

Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, Corso Stati Uniti 4, 35020 Padova, Italy

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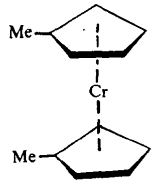
Abstract

Dimethylchromocene contains planar C_5H_4Me rings in an eclipsed sandwich structure. The Cr atom is 1.788 (2) Å from each MeCp plane. The two substituted MeCp ligands are almost parallel [dihedral angle 5.9 (1)° and $MeCp_{centroid}$—Cr—$MeCp_{centroid}$ 178.1 (1)°].

Comment

The structural investigation of the title compound, (I), was undertaken as part of our work on chromium-deposition thin films, MOCVD (metal-organic chemical vapor deposition). The whole structure consists of well separated $(MeCp)_2Cr$ units where the two Cp ligands are bound to a metal ion in an eclipsed sandwich orientation. The two Cp ligands are almost parallel. The metal–centroid distances of 1.788 (2) Å are short with respect to the value of 1.832 (5) Å found in bis(tetraphenylcyclopentadienyl)chromium, which has a staggered conformation (Castellani, Geib, Rheingold & Trogler, 1987). The structure of Cp_2Cr^{II} has been reported by Weiss & Fischer (1956) to have an average Cr—Cp bond distance of 2.2 Å, comparable with the value of 2.158 (3) Å found in the title compound.



(I)

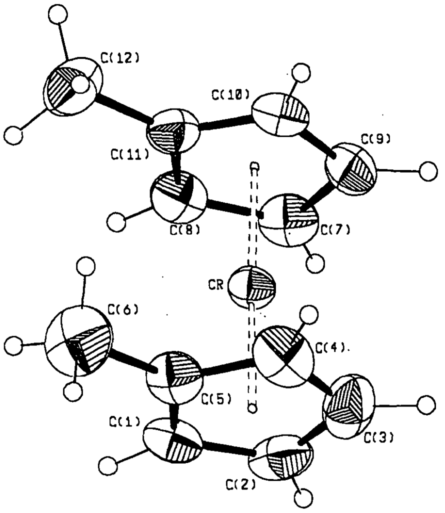


Fig. 1. A perspective view of the molecule, with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

Experimental

Bis(η^5-methylcyclopentadienyl)chromium was obtained following the previously reported procedure (Kohler, 1976) by reacting chromium(II) chloride with potassium methylcyclopentadienide in tetrahydrofuran. Crystals of $[Cr(C_5H_4CH_3)_2]$ suitable for X-ray determination were obtained by slow sublimation at 310 K and 8×10^{-3} mmHg (1.067 Pa).

Crystal data

$[Cr(C_6H_7)_2]$
M_r = 210.24
Monoclinic
$P2_1/c$
a = 12.281 (2) Å
b = 7.728 (2) Å
c = 11.159 (2) Å
β = 102.71 (3)°
V = 1033.1 (4) Å^3
Z = 4
D_x = 1.35 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 13–18°
μ = 1.03 mm^{-1}
T = 293 K
Prism
0.62 × 0.52 × 0.16 mm
Transparent red

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.78, T_{max} = 1.00
2891 measured reflections
2496 independent reflections
2010 observed reflections $[I \geq 3\sigma(I)]$

R_{int} = 0.013
θ_{max} = 28°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 14$
2 standard reflections
frequency: 180 min
intensity variation: none