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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 71020 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1022]

References

- Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Debaerdemaeker, T., Germain, G., Main, P., Refaat, L. S., Tate, C. & Woolfson, M. M. (1988). *MULTAN88. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Duchamp, D. J. (1964). *CRYM Crystallographic Computing System*. Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Larson, A. C. (1967). *Acta Cryst.* **23**, 644–665.
- Lyons, J. E., Ellis, P. E., Wagner, R. W., Thompson, P. E., Hughes, M. E., Hodge, J. A. & Gray, H. B. (1992). ACS Division of Petroleum Chemistry Symposium, ACS National Meeting, April 1992.

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Trimeric Bis(cyclopentadienyl)oxo-zirconium(IV) Benzene Solvate

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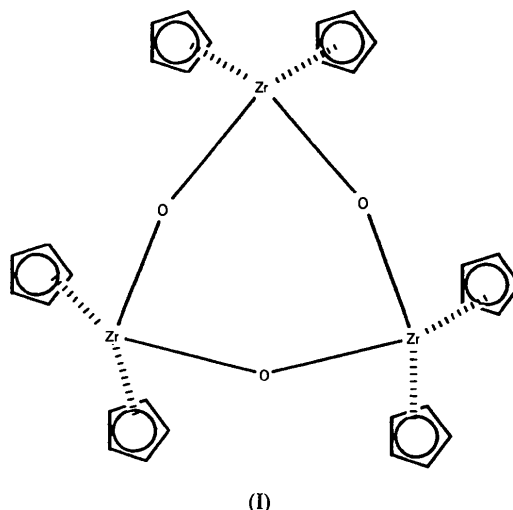
Abstract

The title compound, *cyclo-tri-μ-oxo-tris*[bis(η^5 -cyclopentadienyl)zirconium] benzene solvate, obtained from the reaction of zirconocene hydride with CO₂, is shown to contain planar Zr₃O₃ cycles with comparatively short

Zr—O distances [1.959 (5)–1.976 (5) Å] as a result of partial double bonding.

Comment

Oxo complexes of zirconocene are of interest as intermediates in carbon monoxide and carbon dioxide fixation processes. Cp₂ZrO units are often found to be associated in trimeric molecules where Zr₃O₃ six-membered cycles are planar owing to additional d_{π} - p_{π} interaction between O and Zr atoms. In previous studies, a toluene solvate of oxo-zirconocene trimer (I) was obtained via Cp₂Zr(CO)₂ reaction with CO₂ and characterized by means of X-ray structure analysis (Fachinetti, Floriani, Chiesi-Villa & Guastini, 1979).



Our investigations of carbon dioxide interaction with zirconocene and hafnocene hydrides have shown that [Cp₂ZrH₂]_n readily reacts with CO₂ at room temperature and atmospheric pressure yielding the benzene solvate of the oxo-zirconocene trimer, (II). Its crystal structure was determined and compared with that of (I) and that of (η^2 -formaldehyde)zirconocene trimer (III) (Kropp, Skibbe & Erker, 1983), which turns into (II) on thermolysis.

Crystals of (II) consist of trimeric bis(cyclopentadienyl)oxozirconium complexes [Cp₂ZrO]₃ and solvating benzene molecules. The Zr₃O₃ cycle is planar within 0.023 Å; the Zr—O bond lengths range from 1.959 (5) to 1.976 (5) Å, which is almost the same as in (I) (1.950–1.968 Å) and significantly shorter than in (III) (2.133–2.178 Å). Rather short Zr—O bond distances in (μ -oxo)-complexes (I) and (II) result from the partial double bonding which is absent in (η^2 -CH₂O)-complex (III) and (μ -hydroxo)(μ_3 -oxo)cyclopentadienylzirconium complexes reported in recent publications (Babcock, Day & Klemperer, 1989; Thewalt, Döppert & Lasser, 1986). The three Zr—O—Zr angles [142.6 (2), 142.4 (1) and 142.1 (2)°] are almost equal and close to those observed in (I) (average

142.5°). Note that Zr—(μ -OH)—Zr angles in the above-mentioned hydroxocomplexes are significantly smaller (103.6°).

Planar Cp rings are η^5 -bonded to Zr atoms and Zr—Cp distances [2.275 (3)–2.290 (3) Å] fall in the range given for other ZrCp complexes (Fachinetti, Floriani, Chiesi-Villa & Guastini, 1979; Babcock, Day & Klemperer, 1989). The Cp planes in the bent Cp₂Zr sandwiches in (II) form dihedral angles of 54.2 (3), 55.0 (3) and 55.6 (3)°, bisected by the Zr₃O₃-cycle mean plane.

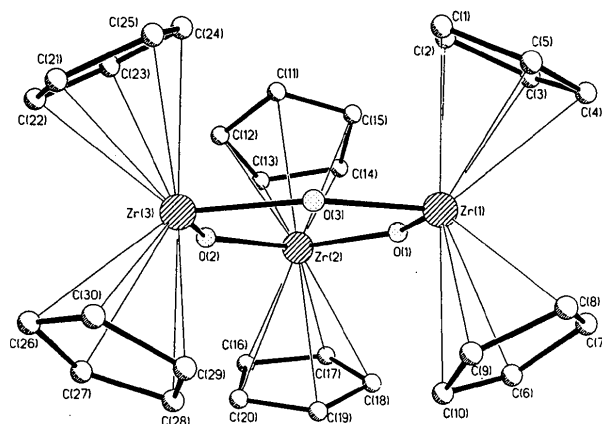


Fig. 1. View of the [Cp₂ZrO₃]₃ molecule showing the labelling of non-H atoms.

Experimental

Crystal data

[Zr₃O₃(C₅H₅)₆].C₆H₆

M_r = 790.30

Monoclinic

*P*2₁/*n*

a = 11.009 (5) Å

b = 10.236 (6) Å

c = 27.627 (12) Å

β = 97.02 (4)°

V = 3089.9 (27) Å³

Z = 4

D_x = 1.699 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 24

reflections

θ = 13–14°

μ = 1.012 mm⁻¹

T = 195.0 (10) K

0.4 × 0.3 × 0.2 mm

Colourless

Data collection

Syntex *P*2₁ diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

5520 measured reflections

5207 independent reflections

3685 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0430

θ_{\max} = 25.04°

h = 0 → 12

k = 0 → 12

l = -32 → 32

2 standard reflections

monitored every 98

reflections

intensity variation: 2%

Refinement

Refinement on *F*²

Final *R* = 0.0438

wR = 0.0926

(Δ/σ)_{max} = 0.685

$\Delta\rho_{\max}$ = 0.755 e Å⁻³

$\Delta\rho_{\min}$ = -0.824 e Å⁻³

S = 1.020

5178 reflections

523 parameters

H-atom parameters refined isotropically

Calculated weights

$$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 10.2145P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Refinement on *F*² for all reflections except those flagged for possible systematic errors; the observed threshold *I* > 2σ(*I*) is used only for calculating *R*(obs.) etc., given here for comparison with refinements on *F*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992).

Atomic scattering factors

from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for (II)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Zr1	0.85461 (6)	0.23029 (6)	0.08699 (2)	0.0174 (3)
Zr2	0.64921 (6)	0.45146 (6)	0.14636 (2)	0.0179 (3)
Zr3	0.98676 (6)	0.47057 (6)	0.18041 (2)	0.0172 (3)
O1	0.7064 (4)	0.3163 (4)	0.10382 (15)	0.020 (2)
O2	0.8097 (4)	0.5038 (4)	0.1793 (2)	0.021 (2)
O3	0.9746 (4)	0.3317 (4)	0.13042 (15)	0.020 (2)
C1	0.9641 (8)	0.3509 (8)	0.0239 (3)	0.032 (5)
C2	0.8415 (8)	0.3940 (8)	0.0159 (3)	0.031 (5)
C3	0.7696 (8)	0.2858 (9)	-0.0021 (2)	0.031 (5)
C4	0.8461 (8)	0.1788 (9)	-0.0054 (3)	0.032 (5)
C5	0.9677 (7)	0.2195 (9)	0.0111 (3)	0.031 (4)
C6	0.7498 (7)	0.0331 (7)	0.1226 (3)	0.032 (4)
C7	0.7937 (9)	-0.0127 (8)	0.0805 (3)	0.036 (6)
C8	0.9219 (8)	-0.0116 (7)	0.0877 (3)	0.034 (5)
C9	0.9588 (7)	0.0349 (7)	0.1347 (3)	0.027 (4)
C10	0.8526 (7)	0.0618 (7)	0.1555 (3)	0.028 (5)
C11	0.6721 (7)	0.6405 (7)	0.0866 (3)	0.029 (4)
C12	0.6224 (8)	0.6974 (7)	0.1263 (3)	0.036 (5)
C13	0.5046 (7)	0.6482 (8)	0.1271 (3)	0.036 (4)
C14	0.4811 (7)	0.5611 (8)	0.0878 (3)	0.034 (4)
C15	0.5833 (7)	0.5558 (8)	0.0628 (3)	0.031 (4)
C16	0.5181 (7)	0.4515 (8)	0.2173 (3)	0.030 (4)
C17	0.4520 (6)	0.3772 (7)	0.1799 (3)	0.025 (4)
C18	0.5156 (7)	0.2632 (8)	0.1732 (3)	0.029 (4)
C19	0.6225 (7)	0.2647 (7)	0.2072 (2)	0.026 (4)
C20	0.6226 (7)	0.3790 (7)	0.2340 (2)	0.025 (4)
C21	1.1679 (7)	0.6283 (8)	0.1743 (3)	0.031 (4)
C22	1.0711 (8)	0.7031 (8)	0.1875 (3)	0.032 (5)
C23	0.9779 (7)	0.7055 (7)	0.1480 (3)	0.029 (4)
C24	1.0154 (7)	0.6287 (7)	0.1105 (3)	0.030 (5)
C25	1.1324 (7)	0.5812 (8)	0.1273 (3)	0.034 (4)
C26	1.0992 (7)	0.4752 (9)	0.2686 (3)	0.035 (5)
C27	0.9803 (7)	0.4340 (8)	0.2726 (2)	0.031 (4)
C28	0.9643 (7)	0.3098 (7)	0.2511 (3)	0.028 (4)
C29	1.0732 (8)	0.2768 (8)	0.2328 (3)	0.031 (5)
C30	1.1560 (7)	0.3779 (9)	0.2430 (3)	0.038 (4)
C1B	0.2462 (8)	0.1628 (10)	0.0907 (4)	0.051 (5)
C2B	0.3019 (9)	0.2287 (11)	0.0574 (4)	0.056 (6)
C3B	0.4010 (10)	0.1799 (15)	0.0389 (4)	0.066 (6)
C4B	0.4428 (12)	0.0596 (20)	0.0550 (5)	0.085 (7)
C5B	0.3859 (12)	-0.0105 (12)	0.0886 (4)	0.068 (8)
C6B	0.2870 (9)	0.0441 (11)	0.1057 (4)	0.054 (6)

Table 2. Geometric parameters (Å, °) for (II)

Zr1—O1	1.959 (5)	C1—C5	1.393 (12)
Zr1—O3	1.968 (5)	C1—C2	1.412 (11)
Zr1—C1	2.555 (7)	C2—C3	1.415 (12)
Zr1—C10	2.563 (7)	C3—C4	1.391 (12)
Zr1—C5	2.569 (7)	C4—C5	1.423 (11)
Zr1—C2	2.573 (7)	C6—C10	1.394 (11)

Zr1—C7	2.577 (8)	C6—C7	1.395 (11)
Zr1—C6	2.579 (7)	C7—C8	1.401 (12)
Zr1—C8	2.584 (8)	C8—C9	1.397 (11)
Zr1—C9	2.585 (7)	C9—C10	1.392 (10)
Zr1—C3	2.587 (8)	C11—C12	1.409 (11)
Zr1—C4	2.596 (7)	C11—C15	1.409 (11)
Zr2—O2	1.960 (5)	C12—C13	1.394 (11)
Zr2—O1	1.968 (5)	C13—C14	1.404 (12)
Zr2—C14	2.563 (8)	C14—C15	1.392 (11)
Zr2—C15	2.567 (8)	C16—C20	1.399 (11)
Zr2—C16	2.571 (7)	C16—C17	1.411 (10)
Zr2—C11	2.576 (7)	C17—C18	1.385 (11)
Zr2—C20	2.583 (7)	C18—C19	1.413 (11)
Zr2—C17	2.577 (7)	C19—C20	1.384 (10)
Zr2—C13	2.582 (8)	C21—C22	1.396 (11)
Zr2—C18	2.587 (7)	C21—C25	1.395 (11)
Zr2—C19	2.586 (7)	C22—C23	1.404 (11)
Zr2—C12	2.587 (8)	C23—C24	1.402 (11)
Zr3—O2	1.976 (5)	C24—C25	1.401 (11)
Zr3—O3	1.975 (5)	C26—C27	1.392 (11)
Zr3—C22	2.554 (8)	C26—C30	1.411 (12)
Zr3—C30	2.564 (8)	C27—C28	1.406 (11)
Zr3—C29	2.569 (8)	C28—C29	1.398 (11)
Zr3—C23	2.563 (7)	C29—C30	1.385 (12)
Zr3—C25	2.566 (7)	C1B—C6B	1.343 (14)
Zr3—C24	2.569 (7)	C1B—C2B	1.347 (14)
Zr3—C27	2.584 (7)	C2B—C3B	1.356 (15)
Zr3—C21	2.587 (8)	C3B—C4B	1.370 (21)
Zr3—C28	2.588 (7)	C4B—C5B	1.381 (22)
Zr3—C26	2.596 (7)	C5B—C6B	1.360 (16)
O1—Zr1—O3	97.75 (13)	C18—C17—C16	109.1 (7)
O2—Zr2—O1	97.6 (2)	C17—C18—C19	107.2 (7)
O2—Zr3—O3	97.47 (14)	C20—C19—C18	108.1 (7)
Zr1—O1—Zr2	142.6 (2)	C19—C20—C16	109.0 (7)
Zr2—O2—Zr3	142.4 (1)	C22—C21—C25	107.3 (7)
Zr1—O3—Zr3	142.1 (2)	C21—C22—C23	108.3 (7)
C3—C2—C1	107.1 (8)	C24—C23—C22	108.1 (7)
C4—C3—C2	108.8 (8)	C25—C24—C23	107.0 (7)
C3—C4—C5	107.6 (8)	C21—C25—C24	109.2 (7)
C1—C5—C4	108.0 (8)	C27—C26—C30	107.8 (8)
C10—C6—C7	106.3 (7)	C26—C27—C28	108.1 (7)
C6—C7—C8	108.9 (8)	C29—C28—C27	107.6 (7)
C9—C8—C7	108.0 (7)	C30—C29—C28	108.6 (7)
C10—C9—C8	106.8 (7)	C29—C30—C26	108.0 (7)
C6—C10—C9	110.1 (7)	C6B—C1B—C2B	120.0 (10)
C12—C11—C15	107.7 (7)	C1B—C2B—C3B	121.9 (11)
C13—C12—C11	108.3 (8)	C2B—C3B—C4B	117.5 (11)
C12—C13—C14	107.5 (7)	C3B—C4B—C5B	121.6 (12)
C15—C14—C13	109.0 (7)	C6B—C5B—C4B	117.9 (12)
C14—C15—C11	107.5 (7)	C1B—C6B—C5B	121.1 (11)
C20—C16—C17	106.6 (7)		

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55975 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1023]

References

- Babcock, L. M., Day, V. W. & Klempner, W. G. (1989). *Inorg. Chem.* **28**, 806–810.
- Fachinetti, G., Floriani, C., Chiesi-Villa, A. & Guastini, C. (1979). *J. Am. Chem. Soc.* **101**, 1767–1775.
- Kropp, K., Skibbe, V. & Erker, G. (1983). *J. Am. Chem. Soc.* **105**, 3353–3354.
- Sheldrick, G. M. (1989). *SHELXTL-Plus*. PC version. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1992). *SHELXL92*. Program for the refinement of crystal structures. Beta test version. Univ. of Göttingen, Germany.
- Thewalt, U., Döppert, K. & Lasser, W. (1986). *J. Organomet. Chem.* **308**, 303–309.

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Cobaltocenium Bis[(4,5-dimercapto-*S*⁴,*S*⁵)-1,3-dithiole-2-thionato]nickelate

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Abstract

The coordination anions of the title compound [Co(C₅H₅)₂][Ni(dmit)₂] are planar with a shuttle-shaped *D*_{2h} configuration. The cobaltocenium cations take an eclipsed *D*_{5h} conformation with an average Co—C distance of 2.037 (16) Å. The crystal consists of sheets of S··S connected anionic stacks with pairs of cations between them.

Comment

Since Steimecke, Sieler, Kirmse & Hoyer (1979) first prepared (Bu₄N)_n[Ni(dmit)₂] (*n* = 1, 2), a great deal of attention has been directed to Z_x[M(dmit)₂] type complexes (*M* = Ni, Pd, Pt, Cu; H₂dmit = H₂C₃S₅ = 4,5-dimercapto-1,3-dithiole-2-thione; *Z* = various cations; 0 ≤ *x* ≤ 1 or *x* = 2 because they are known to possess molecular electrical conductivity. [M(dmit)₂]^{δ-} has a planar structure with a delocalized electronic state; these anions may adhere together by means of intermolecular S··S interactions forming anionic stacks, sheets or even networks. They combine with various closed-shell counter ions or open-shell organic radicals to form conducting complexes such as superconductors [(CH₃)₄N]_{0.5}[Ni(dmit)₂] (Kim, Kobayashi, Sasaki, Kato & Kobayashi, 1987) and TTF_{0.5}[Ni(dmit)₂] (Bousseau, Valade, Legros, Cassoux, Garbaskas & Interrante, 1986). Metalloceniums have different tendencies to accept electrons and when they interact with [Ni(dmit)₂]⁻ quite different compounds can be produced. The reaction of (Bu₄N)[Ni(dmit)₂] and [Fe(C₅H₅)₂]BF₄ produces a completed charge-transfer semiconductor [Ni(dmit)₂] (Fang, Li, Qu & You, 1992). However, the reaction of

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