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Copper(II) Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

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Abstract

The title compound, {4,5,9,10,14,15,19,20-octachloro-2,7,12,17-tetrakis(pentafluorophenyl)-20,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1,3(21),4,6,8(22),9,11,13(23),14,16,18(24),19-dodecaene}copper(II) ($CuTFPPCl_8$) dichloromethane solvate, shows a large tetrahedral distortion or ruffling, with pairs of Cl atoms alternately averaging +1.20 and −1.18 Å out of the plane of the four N atoms; the Cu atom is 0.01 Å out of the plane and the N atoms show a slight (±0.12 Å) tetrahedral distortion. A Cl atom of the solvent, at 3.515 (6) Å in an approximately axial position, is the closest non-bonded neighbor of the Cu atom.

† Contribution No. 8623.

Comment

Derivatives of halogenated porphyrins are active catalysts for oxygenation of light alkanes, requiring no added co-reductants or sacrificial O-atom donors for their activity (Lyons, Ellis, Wagner, Thompson, Hughes, Hodge & Gray, 1992). The $CuTFPPCl_8$ derivative was synthesized from the metal-free porphyrin and copper acetate in methanol solution and purified by elution from silica gel with hexane/dichloromethane. Reddish prisms were grown by evaporation of CH_2Cl_2 solutions of the complex at room temperature over 7–10 d. The Cu atom has approximately square-planar coordination. The four N atoms show a slight tetrahedral distortion (±0.12 Å from their plane) and the nearest axial neighbor atom is a Cl of the solvent, 3.515 (5) Å on one side of the plane. On the other side, C13 of an adjacent molecule is 2.968 (4) Å distant. The molecule is shown in Fig. 1.

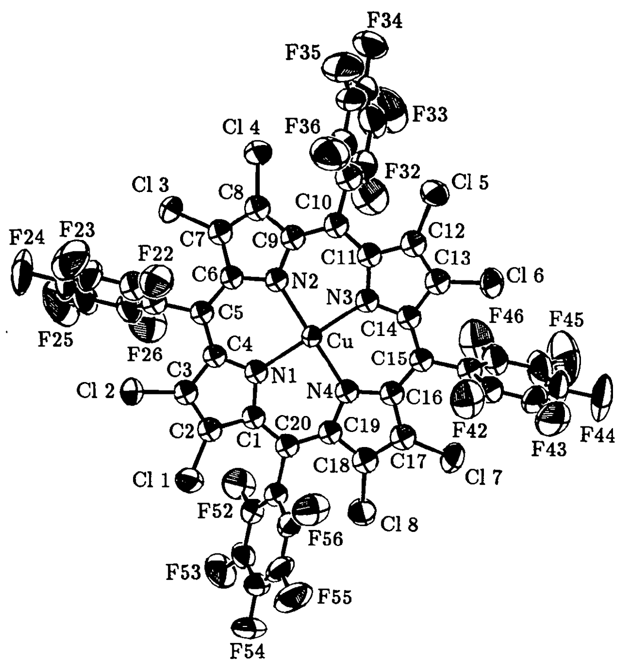

Fig. 1. An *ORTEP*II drawing of the porphyrin molecule with 75% probability ellipsoids showing the numbering system.

The porphyrin molecule shows a strong tetrahedral distortion, reaching ±0.7 Å for the pyrrole C atoms and ±1.19 Å for the Cl atoms (Fig. 2). This appears to be a steric effect caused by crowding between the pentafluorophenyl groups and the Cl atoms on the periphery of the porphyrin. The β C atoms have planar coordination, but the angles to Cl atoms at them are altered to move the Cl atoms away from the phenyl rings. The tetrahedral distortion accomplishes the same effect, but even the combination of the two leaves exceedingly close

Cl···apical-C contacts: the closest is 2.97 Å and the average of all eight is 3.00 (2) Å. A van der Waals contact would be 3.45 Å, so the crowding here is significant. The Cl···Cl contacts are similarly close – 3.20 (2) *vs* 3.60 Å for a van der Waals contact – so nothing can be gained by moving the Cl atoms in the plane; it must deform. The phenyl rings have turned so their planes are perpendicular to the Cl–Cl vector of their close neighbors, implying other contacts to *ortho* C atoms or F atoms. It appears that the Cl···C contacts are the more important; they average 3.28 (9) Å, still 0.17 Å or more shorter than a van der Waals distance (3.45 Å expected; one found at 3.13, two 3.18 and all others at greater than 3.23 Å). Thus the distortion from planarity appears to arise not primarily from the influence of the metal atom, but more from the crowding of the β Cl atoms and the *meso* phenyl groups.

The packing drawing (Fig. 3) shows the solvent CH_2Cl_2 molecule with one Cl atom in an approximately axial position with respect to the Cu, but 3.515 (5) Å from it. Other intermolecular contacts are at van der Waals distances or greater.

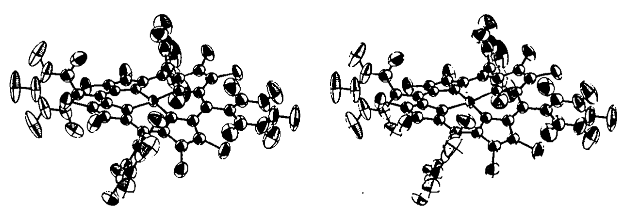

Fig. 2. A stereoview of the porphyrin molecule showing the pronounced smooth tetrahedral distortion. Note that the phenyl rings are approximately perpendicular to the vector between their close Cl neighbors.

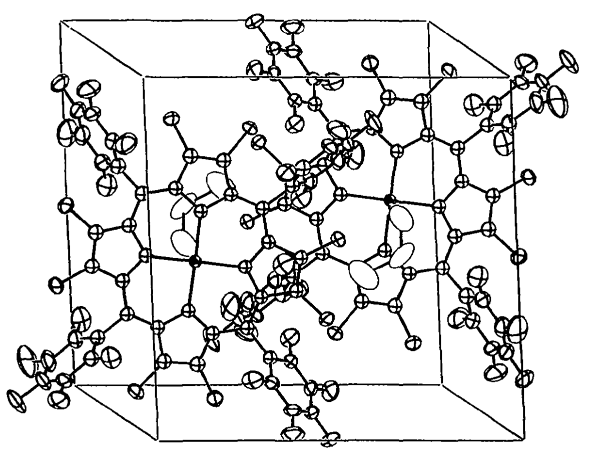

Fig. 3. An *ORTEP*II drawing showing the packing in the crystal. The contents of one unit cell is shown (50% probability ellipsoids) with a unit cell outlined. H atoms on the CH_2Cl_2 molecule are not shown. The Cu atoms have shaded octants, the porphyrin atoms outlined octants and the solvent atoms are unadorned. The view is perpendicular to the *bc* plane, with the *c* axis horizontal.

Experimental

Crystal data

$[Cu(C_{44}Cl_8F_{20}N_4)].CH_2Cl_2$
M_r = 1396.58
Triclinic
$P\bar{1}$
a = 11.794 (5) Å
b = 14.492 (4) Å
c = 14.731 (2) Å
α = 87.51 (5)°
β = 73.48 (5)°
γ = 78.40 (3)°
V = 2364 (3) Å^3
Z = 2
D_x = 1.96 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 16.5–18°
μ = 1.15 mm^{-1}
T = 294 K
Irregular five-sided prism
0.63 × 0.52 × 0.33 mm
Reddish

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical
T_{min} = 0.953, T_{max} = 1.042
16705 measured reflections
8290 independent reflections
8290 observed reflections [all relections used]
R_{int} = 0.016
θ_{max} = 25°
$h = -14 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 166.66 min
intensity variation: within counting statistics

Refinement

Refinement on F^2
Final R = 0.052 (on F) for 6908 reflections with $F_o^2 > 3\sigma(F_o^2)$
wR = 0.014 (on F^2)
S = 3.75
8290 reflections
582 parameters
No H atoms included in model
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.03 for porphyrin, 0.35 for solvent
$\Delta\rho_{max}$ = 1.36 e Å^{-3}
$\Delta\rho_{min}$ = −1.29 e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient (secondary): 0.61 (7) × 10^{-6}

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

A dagger indicates an isotropic B parameter; for the other atoms $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B or U_{eq}
Cu	0.2200 (4)	0.46010 (3)	0.83050 (3)	0.0284 (1)
Cl1	0.1502 (1)	0.3108 (1)	0.4943 (1)	0.0502 (3)
Cl2	0.1485 (1)	0.5302 (1)	0.4548 (1)	0.0458 (2)
Cl3	0.3138 (1)	0.8111 (1)	0.6452 (1)	0.0504 (3)
Cl4	0.3000 (1)	0.8401 (1)	0.8604 (1)	0.0624 (3)
Cl5	0.0840 (1)	0.6347 (1)	1.2058 (1)	0.0578 (3)
Cl6	0.0844 (1)	0.4147 (1)	1.2421 (1)	0.0512 (3)
Cl7	0.3341 (1)	0.0848 (1)	0.9803 (1)	0.0603 (4)
Cl8	0.3747 (1)	0.0593 (1)	0.7574 (1)	0.0620 (4)
N1	0.2238 (3)	0.4426 (3)	0.6950 (2)	2.3 (1)†
N2	0.2238 (3)	0.5969 (2)	0.8080 (2)	2.3 (1)†
N3	0.1922 (3)	0.4798 (2)	0.9700 (2)	2.4 (1)†
N4	0.2361 (3)	0.3210 (2)	0.8506 (2)	2.3 (1)†
C1	0.2172 (3)	0.3605 (2)	0.6552 (3)	2.3 (1)†
C2	0.1868 (3)	0.3822 (3)	0.5671 (3)	2.5 (1)†
C3	0.1853 (3)	0.4743 (3)	0.5508 (3)	2.5 (1)†

C4	0.2118 (3)	0.5126 (3)	0.6307 (3)	2.4 (1)†
C5	0.2308 (3)	0.6032 (3)	0.6380 (3)	2.3 (1)†
C6	0.2432 (3)	0.6398 (3)	0.7206 (3)	2.3 (1)†
C7	0.2727 (3)	0.7301 (3)	0.7300 (3)	2.6 (1)†
C8	0.2674 (3)	0.7421 (3)	0.8211 (3)	2.8 (1)†
C9	0.2332 (3)	0.6592 (3)	0.8719 (3)	2.5 (1)†
C10	0.2041 (3)	0.6473 (3)	0.9698 (3)	2.6 (1)†
C11	0.1740 (3)	0.5650 (3)	1.0150 (3)	2.6 (1)†
C12	0.1328 (4)	0.5522 (3)	1.1160 (3)	2.9 (1)†
C13	0.1325 (3)	0.4599 (3)	1.1310 (3)	2.8 (1)†
C14	0.1753 (3)	0.4130 (3)	1.0393 (3)	2.4 (1)†
C15	0.2087 (3)	0.3161 (3)	1.0227 (3)	2.5 (1)†
C16	0.2457 (3)	0.2743 (3)	0.9331 (3)	2.5 (1)†
C17	0.2932 (4)	0.1751 (3)	0.9100 (3)	2.9 (1)†
C18	0.3084 (4)	0.1635 (3)	0.8165 (3)	2.9 (1)†
C19	0.2660 (3)	0.2544 (3)	0.7801 (3)	2.4 (1)†
C20	0.2467 (3)	0.2710 (3)	0.6907 (3)	2.4 (1)†
C21	0.2368 (3)	0.6654 (3)	0.5532 (3)	2.7 (1)†
C22	0.1373 (4)	0.7286 (3)	0.5455 (3)	0.0458 (11)
F22	0.0327 (2)	0.7326 (2)	0.6132 (2)	0.0592 (7)
C23	0.1391 (6)	0.7873 (3)	0.4692 (4)	0.0651 (14)
F23	0.0398 (4)	0.8477 (2)	0.4642 (3)	0.1041 (11
C24	0.2440 (7)	0.7813 (4)	0.3985 (4)	0.0777 (18)
F24	0.2471 (5)	0.8389 (3)	0.3234 (3)	0.1272 (14)
C25	0.3458 (6)	0.7201 (4)	0.4029 (3)	0.0682 (17)
F25	0.4501 (4)	0.7160 (3)	0.3338 (2)	0.1140 (15)
C26	0.3425 (5)	0.6610 (3)	0.4803 (3)	0.0492 (12)
F26	0.4423 (3)	0.6016 (2)	0.4850 (2)	0.0731 (9)
C31	0.2205 (4)	0.7224 (3)	1.0290 (3)	3.1 (1)†
C32	0.3285 (5)	0.7155 (3)	1.0480 (3)	0.0524 (12)
F32	0.4153 (3)	0.6390 (2)	1.0180 (2)	0.0709 (8)
C33	0.3553 (6)	0.7860 (4)	1.0938 (3)	0.0671 (15)
F33	0.4629 (4)	0.7762 (3)	1.1104 (3)	0.1064 (12)
C34	0.2710 (8)	0.8667 (4)	1.1204 (4)	0.0773 (19)
F34	0.2965 (4)	0.9375 (2)	1.1613 (2)	0.1116 (13)
C35	0.1596 (7)	0.8747 (3)	1.1064 (3)	0.0709 (19)
F35	0.0764 (4)	0.9541 (2)	1.1320 (3)	0.1129 (14)
C36	0.1342 (5)	0.8031 (3)	1.0617 (3)	0.0557 (13)
F36	0.0257 (3)	0.8127 (2)	1.0478 (2)	0.0792 (9)
C41	0.2076 (3)	0.2529 (3)	1.1066 (3)	2.7 (1)†
C42	0.1113 (4)	0.2106 (3)	1.1482 (3)	0.0420 (10)
F42	0.0158 (3)	0.2278 (2)	1.1148 (2)	0.0670 (8)
C43	0.1096 (5)	0.1516 (3)	1.2244 (3)	0.0559 (14)
F43	0.0142 (3)	0.1129 (2)	1.2622 (2)	0.0882 (10)
C44	0.2062 (6)	0.1356 (4)	1.2610 (3)	0.0689 (17)
F44	0.2039 (4)	0.0791 (3)	1.3361 (2)	0.1153 (14)
C45	0.3026 (5)	0.1755 (4)	1.2230 (4)	0.0654 (14)
F45	0.3967 (4)	0.1587 (3)	1.2585 (3)	0.1169 (13)
C46	0.3029 (4)	0.2341 (3)	1.1454 (3)	0.0490 (11)
F46	0.4000 (3)	0.2726 (2)	1.1070 (2)	0.0759 (9)
C51	0.2593 (3)	0.1880 (3)	0.6289 (3)	2.4 (1)†
C52	0.3594 (4)	0.1634 (3)	0.5518 (3)	0.0345 (9)
F52	0.4449 (2)	0.2148 (2)	0.5311 (2)	0.0538 (6)
C53	0.3734 (4)	0.0868 (3)	0.4957 (3)	0.0407 (10)
F53	0.4724 (3)	0.0641 (2)	0.4216 (2)	0.0627 (8)
C54	0.2877 (4)	0.0329 (3)	0.5155 (3)	0.0451 (11)
F54	0.3029 (3)	−0.0439 (2)	0.4622 (2)	0.0729 (9)
C55	0.1864 (4)	0.0554 (3)	0.5904 (3)	0.0455 (11)
F55	0.1018 (3)	0.0025 (2)	0.6088 (2)	0.0717 (8)
C56	0.1733 (4)	0.1327 (3)	0.6462 (3)	0.0393 (10)
F56	0.0734 (2)	0.1551 (2)	0.7189 (2)	0.0631 (7)
C(*S*1)	0.4144 (11)	0.4448 (10)	0.2258 (10)	0.2054 (50)
Cl(*S*1)	0.4351 (2)	0.3873 (3)	0.3268 (3)	0.2286 (15)
Cl(*S*2)	0.4720 (4)	0.5382 (3)	0.2089 (4)	0.2479 (19)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Cu—N1	2.010 (3)	C2—C3	1.342 (5)
Cu—N2	2.003 (3)	C3—C4	1.459 (5)
Cu—N3	2.011 (3)	C4—C5	1.388 (5)
Cu—N4	2.003 (3)	C5—C6	1.405 (5)
Cl1—C2	1.717 (4)	C5—C21	1.502 (5)
Cl2—C3	1.719 (4)	C6—C7	1.441 (5)
Cl3—C7	1.712 (4)	C7—C8	1.343 (5)
Cl4—C8	1.707 (4)	C8—C9	1.453 (5)
Cl5—C12	1.714 (4)	C9—C10	1.395 (5)
Cl6—C13	1.719 (4)	C10—C11	1.400 (5)
Cl7—C17	1.713 (4)	C10—C31	1.500 (6)
Cl8—C18	1.704 (4)	C11—C12	1.444 (6)
N1—C1	1.374 (5)	C12—C13	1.347 (6)
N1—C4	1.371 (5)	C13—C14	1.447 (5)
N2—C6	1.385 (5)	C14—C15	1.393 (5)
N2—C9	1.373 (5)	C15—C16	1.392 (5)
N3—C11	1.375 (5)	C15—C41	1.504 (5)
N3—C14	1.376 (5)	C16—C17	1.451 (5)
N4—C16	1.387 (5)	C17—C18	1.350 (6)
N4—C19	1.371 (5)	C18—C19	1.449 (5)
C1—C2	1.448 (5)	C19—C20	1.401 (5)
C1—C20	1.394 (5)	C20—C51	1.498 (5)
N2—Cu—N1	90.3 (1)	C7—C8—Cl4	122.1 (3)
N3—Cu—N1	172.3 (1)	C9—C8—Cl4	130.3 (3)
N4—Cu—N1	90.5 (1)	C9—C8—C7	107.6 (3)
N3—Cu—N2	90.4 (1)	C8—C9—N2	108.4 (3)
N4—Cu—N2	173.7 (1)	C10—C9—N2	125.0 (3)
N4—Cu—N3	89.7 (1)	C10—C9—C8	126.3 (3)
C1—N1—Cu	125.6 (2)	C11—C10—C9	124.0 (4)
C4—N1—Cu	126.3 (2)	C31—C10—C9	117.9 (3)
C4—N1—C1	107.1 (3)	C31—C10—C11	117.7 (3)
C6—N2—Cu	125.5 (2)	C10—C11—N3	124.7 (3)
C9—N2—Cu	125.7 (2)	C12—C11—N3	108.8 (3)
C9—N2—C6	107.6 (3)	C12—C11—C10	126.1 (4)
C11—N3—Cu	125.9 (2)	C11—C12—Cl5	129.4 (3)
C14—N3—Cu	126.7 (2)	C13—C12—Cl5	122.9 (3)
C14—N3—C11	107.1 (3)	C13—C12—C11	107.6 (3)
C16—N4—Cu	126.1 (2)	C12—C13—Cl6	122.8 (3)
C19—N4—Cu	125.1 (2)	C14—C13—Cl6	130.0 (3)
C19—N4—C16	107.5 (3)	C14—C13—C12	107.2 (3)
C2—C1—N1	108.9 (3)	C13—C14—N3	108.8 (3)
C20—C1—N1	124.5 (3)	C15—C14—N3	124.6 (3)
C20—C1—C2	126.4 (3)	C15—C14—C13	126.1 (3)
C1—C2—Cl1	129.5 (3)	C16—C15—C14	123.9 (3)
C3—C2—Cl1	122.7 (3)	C41—C15—C14	118.1 (3)
C3—C2—C1	107.7 (3)	C41—C15—C16	118.0 (3)
C2—C3—Cl2	122.9 (3)	C15—C16—N4	124.8 (3)
C4—C3—Cl2	130.0 (3)	C17—C16—N4	108.3 (3)
C4—C3—C2	107.0 (3)	C17—C16—C15	126.8 (3)
C3—C4—N1	108.9 (3)	C16—C17—Cl7	129.6 (3)
C5—C4—N1	125.1 (3)	C18—C17—Cl7	122.7 (3)
C5—C4—C3	125.8 (3)	C18—C17—C16	107.6 (3)
C6—C5—C4	123.5 (3)	C17—C18—Cl8	123.2 (3)
C21—C5—C4	118.1 (3)	C19—C18—Cl8	129.3 (3)
C21—C5—C6	118.4 (3)	C19—C18—C17	107.4 (3)
C5—C6—N2	125.6 (3)	C18—C19—N4	108.9 (3)
C7—C6—N2	108.4 (3)	C20—C19—N4	124.8 (3)
C7—C6—C5	125.9 (3)	C20—C19—C18	126.0 (3)
C6—C7—Cl3	129.6 (3)	C19—C20—C1	123.8 (3)
C8—C7—Cl3	122.4 (3)	C51—C20—C1	117.7 (3)
C8—C7—C6	107.9 (3)	C51—C20—C19	118.5 (3)

The two H atoms on CH_2Cl_2 were ignored. The structure was solved by *MULTAN*88 (Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988) which located the Cu and Cl atoms of the porphyrin and 15 light atoms. F^2 magnitudes were used in full-matrix least-squares refinement of 582 parameters: positional and isotropic displacement parameters for the light atoms of the porphyrin ring and the phenyl C atoms bonded to it, positional and anisotropic displacement parameters for all other atoms, a scale factor and a secondary-extinction parameter. A population parameter for the solvent molecule refined to 1.0 within 2.5 e.s.d. and it was set to 1.0 for the final cycles. The weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\bar{I})^2$. Atomic scattering factors and values for f' were taken from Cromer & Waber (1974) and Cromer (1974). The largest peaks and valleys in the final difference map were all within 1.5 Å of the solvent atom. The programs used were those of *CRYM* (Duchamp, 1964) and *ORTEP*II (Johnson, 1976).

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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]

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

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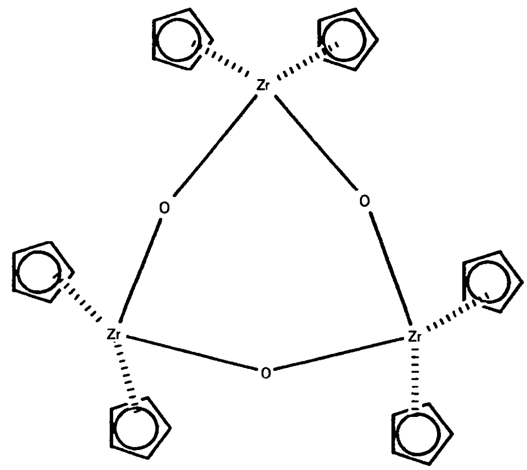
Abstract

The title compound, *cyclo*-tri-μ-oxo-tris[bis(η^5-cyclopentadienyl)zirconium] benzene solvate, obtained from the reaction of zirconocene hydride with CO_2, is shown to contain planar Zr_3O_3 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. Cp_2ZrO units are often found to be associated in trimeric molecules where Zr_3O_3 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* $Cp_2Zr(CO)_2$ reaction with CO_2 and characterized by means of X-ray structure analysis (Fachinetti, Floriani, Chiesi-Villa & Guastini, 1979).



(I)

Our investigations of carbon dioxide interaction with zirconocene and hafnocene hydrides have shown that $[Cp_2ZrH_2]_n$ readily reacts with CO_2 at room temperature and atmospheric pressure yielding the benzene solvate of the oxo-zirconocene trimer, (II). Its cystal 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 $[Cp_2ZrO]_3$ and solvating benzene molecules. The Zr_3O_3 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-CH_2O)-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 amost equal and close to those observed in (I) (average