

Fig. 2. The neighbourhood of the H₂O groups; (a) H₂O(10) and (b) H₂O(20).

Cl—N distance of 3.49 Å, which is in the typical range for interionic charge-transfer salts. A detailed publication with respect to the theoretical approach to the effect is in preparation.

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Long Zr—S Bonds in the Structure of the Stereochemically Nonrigid Complex, Bis(η^5 -cyclopentadienyl)(*N,N*-dimethyldithiocarbamato)phenoxyzirconium(IV)

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Abstract. C₁₉H₂₁NOS₂Zr, *M_r* = 434.73, monoclinic, *P*2₁/*n*, *a* = 8.126 (6), *b* = 8.692 (7), *c* = 26.626 (12) Å, β = 98.19 (5)°, *V* = 1861 (3) Å³, *Z* = 4, *D_m* = 1.53,

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D_x = 1.55 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 8.0 cm⁻¹, *F*(000) = 888, *T* = 295 K, *R* = 0.12 for 5313 unique data, 2082 of which were observed. The expected bent-metallocene geometry is observed. The Zr—S bonds to the bidentate dithiocarbamate ligand (2.656 and 2.789 Å) are unusually long, thus

accounting for the observed rapid rates of *N*-methyl group exchange.

Introduction. The structure and dynamics of one class of five-coordinate bent-metallocene complexes of the titanium family, Cp₂Zr(*X*)(S₂CNMe₂) (Cp = η⁵-C₅H₅), where *X* runs the gamut from halide to aryloxy to alkyl ligands, have been studied extensively in our laboratories (Silver, Eisenstein & Fay, 1983; Femec, Silver & Fay, 1989). This paper reports the crystal structure of the most dynamically active complex of this class known to date: Cp₂Zr(OPh)(S₂CNMe₂) (Femec, Silver & Fay, 1989). A 10³- to 10⁴-fold increase in the rate of *N*-methyl group exchange on going from Cp₂ZrCl(S₂CNMe₂) to Cp₂Zr(OPh)(S₂CNMe₂) suggested unusually loose Zr—S bonding in the phenoxy complex (Femec, Silver & Fay, 1989).

Experimental. Preparation of crystals. Suitable crystals obtained by slow evaporation of solvent from a solution of the compound in dry, deoxygenated tetrahydrofuran; density by flotation in chloroform/1,2-dibromopropane; clear, colorless, irregularly shaped single crystal chosen; dimensions 0.2 × 0.3 × 0.5 mm; mounted on the end of a 0.3 mm diameter, X-ray-grade glass capillary, sealed inside a 0.5 mm diameter capillary.

Structure determination. Nicolet R3m/V2000 diffractometer; unit-cell dimensions determined from 21 reflections in the 2θ range 5.5–20.0°; intensities collected with Mo Kα radiation; 3.5 < 2θ < 60°; ω scan; data scaled, based on three intensity standards (012̄, 105̄, 111̄) measured every fifty reflections, intensity corrections ranged from 0.9972 to 1.0251; range of *hkl*, chosen for high χ for consistency with azimuthal scans: *h* –12–12, *k* –13–0, *l* –38–0; empirical absorption correction applied, using azimuthal scans of nine intense reflections with χ in the ranges 70–90° or –70––90° (0,2,11̄; 0,2,16̄; 019̄; 1,3,22̄; 116̄; 2,2,12̄; 2,2,19̄; 2,1,14̄; 3,2,13̄), mean μ_r of 0.20 chosen on basis of minimum merging *R*, transmission range of 0.582–0.636; systematic absences (*h*0*l*, *h* + *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) indicated space group P2₁/*n*; Lorentz and polarization corrections were applied; data with |*F*_o| > 3σ(*F*) considered observed (2082 of 5313 unique data); structure partially solved by direct methods (all non-H atoms except for nitrogen, both methyl C atoms and two cyclopentadienyl C atoms, found from the solution with the highest FOM), remaining non-H atoms located from difference Fourier maps; final refined structure obtained by full-matrix least squares on *F* using anisotropic thermal parameters and anomalous-dispersion corrections for non-H atoms, H atoms floated at 0.96 Å from attached C atom with fixed isotropic thermal parameters (*U* = 0.08 Å²); overall

extinction correction χ = 0.00002 [*F** = *F*_o(1 + 0.002χ*F*_o²/sin2θ)^{-1/4}]; goodness-of-fit, *S* = 1.73, final conventional *R* = 0.12, *wR* = 0.07, *w* = [σ(*F*)² + *c*|*F*_o|²]⁻¹, *c* refined to 0.000031; largest peak in final difference map = 1 e Å⁻³; final cycle largest shift/e.s.d. = 0.049. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Crystallographic calculations were performed on a MicroVAX 2000 computer using programs from the Nicolet *SHELXTL-Plus* structure refinement package (Sheldrick, 1988).

Discussion. Table 1 lists the final atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms and Table 2 gives the bond distances and angles for all atoms.† A perspective view of the molecule, including the atom-numbering scheme, is presented in Fig. 1 and a stereoview of the unit-cell contents is shown in Fig. 2.

The expected bent-metallocene geometry is readily evident. The phenoxide O atom and the heavy atoms of the dithiocarbamate ligand all lie in or near the quasi-mirror plane which reflects one cyclopentadienyl ring into the other. The phenyl ring is rotated about the Zr—O bond out of this plane. The crowding in the ZrOS₂C₁₀ coordination group is as pronounced as in the ZrClS₂C₁₀ coordination group of Cp₂ZrCl(S₂CNEt₂) (Silver, Eisenstein & Fay, 1983) (see Table 1).

The Zr—O bond length and Zr—O—C(1*c*) bond angle are typical for zirconium-alkoxide complexes (Matchett, Norton & Anderson, 1988; Chamberlain, Durfee, Fanwick, Kobriger, Latesky, McMullen, Rothwell, Foltig, Huffman, Streib & Wang, 1987). The dihedral angle between the ZrOC(1*c*) plane and the ZrOS(1)S(2) plane is 53°, a compromise between maximizing the π overlap between the 1*a*_g orbital of the Cp₂Zr fragment and the *p* orbitals of the O atom and minimizing steric repulsions between the phenyl ring and the nearest cyclopentadienyl ring (Silver, Eisenstein & Fay, 1983; Erker, Dorf, Krueger & Tsay, 1987).

Both Zr—S bonds are longer than the corresponding bonds in Cp₂ZrCl(S₂CNEt₂) (Silver, Eisenstein & Fay, 1983). The lateral Zr—S(1) bond (2.789 Å) is the longest terminal Zr—S bond observed to date. The Zr—S bond lengths in the analogous bidentate bis(trimethylsilyl)phosphinodithioformate complex, Cp₂ZrCl[S₂CP(SiMe₃)₂] (Hey, Lappert, Atwood & Bott, 1987), are nearly identical to those observed in Cp₂ZrCl(S₂CNEt₂), while the Zr—S distances to the

† Lists of structure factors, anisotropic thermal parameters, select mean planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53873 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cp}_2\text{Zr}(\text{OPh})(\text{S}_2\text{CNMe}_2)$, with *e.s.d.*'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Zr	4651 (1)	2112 (1)	1600 (1)	43 (1)
S(1)	4439 (4)	1801 (4)	600 (1)	56 (1)
S(2)	6819 (4)	3907 (4)	1124 (1)	62 (1)
C(1)	6079 (12)	3033 (13)	569 (4)	42 (4)
N	6723 (11)	3243 (11)	146 (4)	57 (4)
C(2)	6026 (13)	2486 (14)	-333 (4)	69 (6)
C(3)	8134 (14)	4247 (14)	114 (5)	73 (6)
O	2883 (9)	486 (9)	1422 (3)	60 (4)
C(1c)	1511 (14)	-206 (15)	1185 (5)	43 (5)
C(2c)	499 (15)	426 (15)	787 (5)	57 (6)
C(3c)	-868 (16)	-410 (18)	556 (5)	65 (6)
C(4c)	-1235 (16)	-1821 (18)	733 (6)	76 (7)
C(5c)	-206 (16)	-2453 (15)	1136 (5)	70 (7)
C(6c)	1192 (14)	-1665 (14)	1367 (4)	52 (5)
C(1a)	7511 (16)	1721 (16)	2109 (6)	72 (6)
C(2a)	6419 (20)	1364 (24)	2412 (6)	103 (10)
C(3a)	5553 (19)	71 (26)	2253 (8)	114 (11)
C(4a)	6160 (21)	-349 (18)	1814 (8)	91 (9)
C(5a)	7367 (16)	648 (19)	1721 (5)	60 (6)
C(1b)	4227 (22)	4937 (18)	1844 (11)	96 (10)
C(2b)	4047 (23)	4047 (24)	2248 (7)	88 (9)
C(3b)	2655 (25)	3188 (19)	2127 (8)	88 (8)
C(4b)	1933 (17)	3472 (23)	1653 (8)	100 (9)
C(5b)	2950 (28)	4544 (22)	1461 (7)	85 (9)

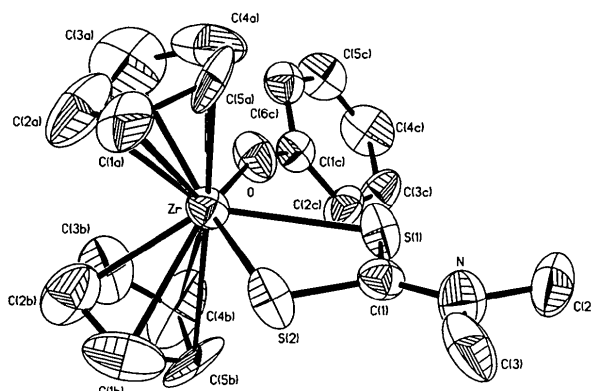


Fig. 1. Thermal ellipsoid plot of $\text{Cp}_2\text{Zr}(\text{OPh})(\text{S}_2\text{CNMe}_2)$. Thermal ellipsoids are shown at the 50% probability level.

μ^3 -bound *tert*-butyl thiolate ligand in the $\text{Zr}_3(\text{S})(\text{tert}\text{-BuS})_{10}$ cluster average 2.765 Å (Cocouvanis, Hadji-kyriacou & Kanatzidis, 1985). Further, the bonding of the dithiocarbamate ligand to the metal atom is more unsymmetrical than previously observed. This weaker chelation is consistent with the accelerated exchange rate for the *N*-methyl groups in the phenoxide complex (Femec, Silver & Fay, 1989). The better π -donor ligand (phenoxide) increases the electron density at the metal center, thereby weakening the Zr—S bonds and hence the chelate interaction. This can be traced to the principal σ -bonding interaction between the a'_π orbital of the Cp_2ZrX^+ fragment and the b_2 orbital of the dithiocarbamate ligand (Silver, Eisenstein & Fay, 1983). On improv-

Table 2. Bond distances (Å) and angles ($^\circ$) in $\text{Cp}_2\text{Zr}(\text{OPh})(\text{S}_2\text{CNMe}_2)$ with *e.s.d.*'s in parentheses

Zr—S(1)	2.656 (4)	C(1c)—C(6c)	1.395 (18)
Zr—S(2)	2.789 (4)	C(2c)—C(3c)	1.395 (18)
Zr—O	2.023 (8)	C(3c)—C(4c)	1.363 (22)
Zr—C(1a)	2.541 (13)	C(4c)—C(5c)	1.376 (19)
Zr—C(2a)	2.506 (16)	C(5c)—C(6c)	1.393 (17)
Zr—C(3a)	2.519 (12)	S(2)—C(1a)†	3.222 (15)
Zr—C(4a)	2.491 (16)	S(2)—C(5a)†	3.248 (16)
Zr—C(5a)	2.528 (14)	O—C(3a)†	2.892 (19)
Zr—C(1b)	2.576 (17)	O—C(4a)†	2.813 (17)
Zr—C(2b)	2.509 (20)	C(1a)—C(2a)	1.320 (23)
Zr—C(3b)	2.474 (21)	C(1a)—C(5a)	1.383 (20)
Zr—C(4b)	2.526 (16)	C(2a)—C(3a)	1.361 (28)
Zr—C(5b)	2.524 (20)	C(3a)—C(4a)	1.380 (30)
S(1)—S(2)*	2.875 (6)	C(4a)—C(5a)	1.358 (22)
S(1)—C(1)	1.721 (11)	S(2)—C(1b)†	3.173 (25)
S(2)—C(1)	1.694 (11)	O—C(4b)†	2.801 (22)
C(1)—N	1.319 (15)	C(2a)—C(2b)†	3.017 (27)
N—C(2)	1.475 (15)	C(1b)—C(2b)	1.350 (32)
N—C(3)	1.453 (15)	C(1b)—C(5b)	1.391 (29)
S(1)—O†	2.911 (10)	C(2b)—C(3b)	1.355 (27)
O—C(1c)	1.342 (14)	C(3b)—C(4b)	1.337 (28)
C(1c)—C(2c)	1.361 (17)	C(4b)—C(5b)	1.391 (28)
S(1)—Zr—S(2)	63.7 (1)	C(2c)—C(3c)—C(4c)	121.1 (12)
S(1)—Zr—O	75.6 (3)	C(3c)—C(4c)—C(5c)	119.3 (12)
S(2)—Zr—O	139.3 (3)	C(4c)—C(5c)—C(6c)	121.0 (12)
Zr—S(1)—C(1)	92.6 (4)	C(5c)—C(6c)—C(1c)	118.3 (11)
Zr—S(2)—C(1)	88.7 (4)	C(6c)—C(1c)—C(2c)	121.0 (11)
S(1)—C(1)—S(2)	114.7 (7)	C(1a)—C(2a)—C(3a)	111.4 (17)
S(1)—C(1)—N	122.1 (8)	C(2a)—C(3a)—C(4a)	104.6 (16)
S(2)—C(1)—N	123.2 (8)	C(3a)—C(4a)—C(5a)	109.8 (15)
C(1)—N—C(2)	121.7 (9)	C(4a)—C(5a)—C(1a)	106.3 (13)
C(1)—N—C(3)	123.1 (10)	C(5a)—C(1a)—C(2a)	107.8 (13)
C(2)—N—C(3)	115.2 (10)	C(1b)—C(2b)—C(3b)	107.9 (16)
Zr—O—C(1c)	159.7 (8)	C(2b)—C(3b)—C(4b)	111.2 (17)
O—C(1c)—C(2c)	123.7 (11)	C(3b)—C(4b)—C(5b)	105.5 (15)
O—C(1c)—C(6c)	115.3 (10)	C(4b)—C(5b)—C(1b)	108.3 (17)
C(1c)—C(2c)—C(3c)	119.2 (12)	C(5b)—C(1b)—C(2b)	106.9 (16)

* The bite of the ligand.

† Close contacts within the $\text{ZrOS}_2\text{C}_{10}$ coordination group.

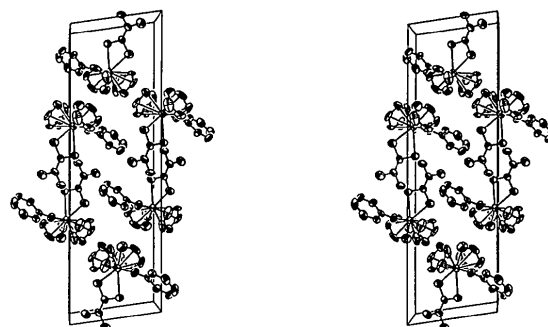


Fig. 2. Stereoview of the unit-cell contents for $\text{Cp}_2\text{Zr}(\text{OPh})(\text{S}_2\text{CNMe}_2)$, looking down the *b* axis, with the *a* axis horizontal and the *c* axis vertical. Thermal ellipsoids are shown at the 50% probability level.

ing the π -donating ability of *X*, the a'_π orbital is raised in energy away from the b_2 orbital, weakening the bonding interaction.

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A Mixed Bridged Trinuclear Copper(II) Complex with Diethylaminoethanolato and 3-Methylbenzoato Ligands

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Abstract. Bis[μ -2-(diethylamino)ethanolato-*O,N*]-bis(methanol)-bis(μ -3-methylbenzoato-*O,O'*)-bis(3-methylbenzoato-*O*)-tricopper(II), [Cu₃(C₆H₁₄NO)₂(C₈H₇O₂)₄(CH₄O)₂], *M_r* = 1027.6, monoclinic, *P*2₁/*c*, *a* = 8.302 (2), *b* = 30.794 (8), *c* = 10.688 (3) Å, β = 110.12 (1)°, *V* = 2565.7 Å³, *Z* = 2, *D_x* = 1.330 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 1.231 mm⁻¹, *F*(000) = 1074, *T* = 297 K. Final *R* = 0.059 for 3145 independent reflections [*F_o* > 2σ(*F_o*)]. Linear Cu₃ arrangement; adjacent copper centres are bridged by a bidentate carboxylato group and an aminoethanolato oxygen atom.

Introduction. Trinuclear copper(II) complexes with benzoato/diethylaminoethanolato bridging, [Cu₃{(C₂H₅)₂NC₂H₄O}₂(C₆H₅CO₂)₄(CH₃OH)₂] (Haase & Gehring, 1985) or benzoato/dibutylaminoethanolato bridging, [Cu₃{(n-C₄H₉)₂NC₂H₄O}₂(C₆H₅CO₂)₄(C₂H₅OH)₂] (Muhonen, Pajunen & Hämäläinen, 1980), are systems with a quartet spin ground state due to a ferromagnetic exchange coupling in the Cu^{II}—RO/RCO₂—Cu^{II} moiety (Gehring & Haase, 1990). As part of these investigations (Gehring, 1990) we synthesized new Cu₃ complexes with methyl-substituted benzoato ligands as reported in a preliminary

communication (Gehring, Paulus, Haase, Bill & Trautwein, 1990). The present work deals with the molecular structure of the 3-methyl derivative.

Experimental. Cu₂CO₃(OH)₂ (0.05 mol) was stirred into a melt of 3-methylbenzoic acid (0.2 mol) to prepare the starting material Cu(3-CH₃-C₆H₄CO₂)₂. The reaction was completed by further heating of the powdered mixture to 423–443 K (0.5 h). Residual acid was removed by washing with dichloromethane or ether. For purification, the crude product (50 g) was treated with acetone (analytical grade, 300 ml) in a Soxhlet extractor and dried *in vacuo*.

Diethylaminoethanol (3.90 mmol in 5 ml methanol) was added to a methanolic suspension of Cu(3-CH₃-C₆H₄CO₂)₂ (1.95 mmol in 50 ml). After filtration blue single crystals precipitated from the turquoise solution standing at 279 K. Elemental analysis, calculated values for Cu₃(C₄₆H₆₄N₂O₁₂) in parentheses: C 53.76 (53.76), H 6.08 (6.28), N 2.75 (2.73)%.

For data collection a single crystal with the approximate dimensions 0.3 × 0.4 × 1 mm was sealed in a Lindemann capillary containing mother liquor. Lattice constants determined on a Stoe-Siemens AED2 diffractometer by a least-squares treatment of the setting angles of 56 reflections in the

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