# Synthesis of luminescent zirconium thiolate complexes. Crystal structures of $(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$Cl-$p)_2$ and $[(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$OMe-$p)]_2$O

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## Abstract

Several luminescent zirconium thiolate complexes $(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$R-$p)_2$, where R = Cl **(1)**, Me **(2)**, OMe **(3)**, have been synthesized by the reaction of Cp$_2$ZrCl$_2$ with HSC$_6$H$_4$R-$p$ in the presence of Et$_3$N. The crystal structures of $(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$Cl-$p)_2$ and $[(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$OMe-$p)]_2$O **(4)**, which has been isolated as a hydrolysis product of $(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$OMe-$p)_2$, have been determined. Complex **1** crystallizes in the monoclinic space group $P2_1/a$, with $a = 12.182(1)$ Å, $b = 10.674(4)$ Å, $c = 17.131(2)$ Å, $\beta = 103.949(6)°$, $Z = 4$, and $V = 2161.8(6)$ Å$^3$. The Zr atom is in a distorted tetrahedral coordination environment with the thiolate ligands adopting an "endo(anti)" configuration. The two Cp rings have a nearly eclipsed geometry. Complex **4** crystallized in the monoclinic space group $P2_1/c$, with $a = 15.533(1)$ Å, $b = 15.217(4)$ Å, $c = 13.382(2)$ Å, $\beta = 90.00(2)°$, $Z = 4$, and $V = 3162(1)$ Å$^3$. © 1997 Elsevier Science S.A.

*Keywords:* Zirconocene; Zirconium complexes; Thiolate complexes; Crystal structure; Luminescent complexes

## 1. Introduction

The widespread application of early transition metal complexes in catalysis has attracted numerous interests in recent years [1–9]. The structure and bonding properties of metallocenes have also received much attention, in particular, those of the metallocene thiolates [10–14]. Although a number of zirconocene thiolate complexes have been reported [15–22], to our surprise, there have been no reports on the structural characterization of the class of Cp$_2$Zr(SAr)$_2$ compounds despite those of the pentamethylcyclopentadienyl derivatives are known [23]. A possible reason may be due to the fact that the zirconocene thiolate complexes, unlike the titanium mercaptide analogues which are generally air-stable, are very air-sensitive and very susceptible to hydrolysis and formation of coordination polymers [24]. On the other hand, although the structure of an oxo-bridged binuclear zirconocene thiolate $[(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_5)]_2$O has

been reported [25], its related compounds are scarce. As an extension of our continuing effort to explore new classes of luminescent complexes, in particular those of transition metal chalcogenides and chalcogenolates [26–32], we have explored the class of d$^0$ metal chalcogenolates. In this paper we report the first structural characterization of $(\eta^5$-C$_5$H$_5)_2$Zr(SR)$_2$ type complex, $(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$Cl-$p)_2$ together with the structure of $[(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$OMe-$p)]_2$O, a hydrolysis product of $(\eta^5$-C$_5$H$_5)_2$Zr(SC$_6$H$_4$OMe-$p)_2$.

## 2. Experimental

### 2.1. Materials and reagents

Bis(cyclopentadienyl)zirconium dichloride was purchased from Strem Chemicals. 4-Chlorothiophenol, 4-methoxythiophenol, and 4-methylthiophenol were obtained from Lancaster Chemical. Analytical grade toluene and hexane were dried over sodium and distilled over sodium benzophenone ketyl using standard procedures before use.

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## 2.2. Synthesis of zirconium thiolate complexes

All reactions and manipulations were carried out under strictly anaerobic and anhydrous conditions using standard Schlenk technique. The $(\eta^5\text{-}C_5H_5)_2Zr(SAr)_2$ compounds are extremely sensitive to hydrolysis, all glassware used must be carefully flame dried before use.

### 2.2.1. $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4Cl\text{-}p)_2$ (1)

To a toluene solution (15 ml) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (0.28 g, 0.96 mmol) was added a solution of $Et_3NHSC_6H_4Cl\text{-}p$ (1.93 mmol) in toluene (10 ml), prepared in situ from $HSC_6H_4Cl\text{-}p$ (0.28 g, 1.93 mmol) and an excess of $Et_3N$. The reaction mixture was stirred for 12 h at room temperature, after which it was filtered and the filtrate reduced in volume. Addition of hexane to the concentrated solution gave yellow crystals of 1. Yield, 0.34g (70%). $^1$H NMR (300 MHz, $C_6D_6$, 298 K, relative to TMS): $\delta$ 5.57 (s, 10H, Cp), 7.03–7.06 (m, 4 H, aryl protons meta to S), 7.54–7.57 (m, 4H, aryl protons ortho to S). Positive ion EI-MS: $m/z = 508$ {M}$^+$, 363 {M-SC$_6$H$_4$Cl}$^+$. Anal. Found: C, 52.45; H, 3.44. Calc. for $C_{22}H_{18}ZrCl_2S_2$: C, 51.95; H, 3.54.

### 2.2.2. $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4Me\text{-}p)_2$ (2)

The procedure was similar to that of 1 except $HSC_6H_4Me\text{-}p$ (0.24 g, 1.93 mmol) was used in place of $HSC_6H_4Cl\text{-}p$ to give 2 as yellow crystals. Yield, 0.24 g (54%). $^1$H NMR (270 MHz, $C_6D_6$, 298 K, relative to TMS): $\delta$ 2.10 (s, 6H, –Me), 5.72 (s, 10H, Cp), 6.95–6.98 (m, 4H, aryl protons meta to S), 7.81–7.83 (m, 4H, aryl protons ortho to S). Positive ion EI-MS: $m/z = 466$ {M}$^+$, 343 {M-SC$_6$H$_4$Me}$^+$. Anal. Found: C, 61.78; H, 5.14. Calc. for $C_{24}H_{24}ZrS_2$: C, 61.59; H, 5.13.

### 2.2.3. $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4OMe\text{-}p)_2$ (3)

The procedure was similar to that of 1 except $HSC_6H_4OMe\text{-}p$ (0.27 g, 1.93 mmol) was used in place of $HSC_6H_4Cl\text{-}p$ to give 3 as a yellow solid. Yield, 0.25 g (52%). $^1$H NMR (270 MHz, $C_6D_6$, 298 K, relative to TMS): $\delta$ 3.30 (s, 6H, –OMe), 5.73 (s, 10H, Cp), 6.74–6.77 (m, 4H, aryl protons meta to S), 7.78–7.81 (m, 4H, aryl protons ortho to S). Positive ion EI-MS: $m/z = 498$ {M}$^+$, 359 {M-SC$_6$H$_4$OMe}$^+$. Anal. Found: C, 57.49; H, 4.88. Calc. for $C_{24}H_{24}ZrO_2S_2$: C, 57.46; H, 4.80.

### 2.2.4. $[(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4OMe\text{-}p)]_2O$ (4)

This compound was obtained by subjecting a solution of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4OMe\text{-}p)_2$ (0.18 g, 0.36 mmol) in toluene–hexane mixture to hydrolysis by air very slowly. Orange yellow crystals of 4 were obtained. Yield, 0.082 g (61%). Anal. Found: C, 54.89; H, 4.49. Calc. for $C_{34}H_{34}O_3S_2Zr_2$: C, 55.34; H, 4.61.

### 2.2.5. $[(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4Cl\text{-}p)]_2O$ (5)

The procedure was similar to that of 4 except $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4Cl\text{-}p)_2$ (0.14 g, 0.27 mmol) was used in place of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4OMe\text{-}p)_2$ to give pale yellow plates of 5. Yield, 0.045 g (44%). Anal. Found: C, 51.50; H, 3.77. Calc. for $C_{32}H_{28}OCl_2S_2Zr_2$: C, 51.49; H, 3.75.

## 2.3. Physical measurements and instrumentation

UV–visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer and steady state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. $^1$H NMR spectra were recorded on either a Jeol JNM-GSX270 or a Bruker DPX300 Fourier Transform NMR spectrometer. Chemical shifts were reported relative to tetramethylsilane. Positive ion EI mass spectra were recorded on a Finnigan MAT95 mass spectrometer.

## 2.4. Crystal structure determination

### 2.4.1. Crystal data for 1

$C_{22}H_{18}Cl_2S_2Zr$, $M_r = 508.63$, monoclinic, space group $P2_1/a$ (No. 14), $a = 12.182(1)$ Å, $b = 10.674(4)$ Å, $c = 17.131(2)$ Å, $\beta = 103.949(6)°$, $V = 2161.8(6)$ Å$^3$, $Z = 4$, $D_c = 1.563$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 9.53 cm$^{-1}$, $F(000) = 1024$, $T = 298$ K. A yellow crystal of dimensions $0.20 \times 0.15 \times 0.30$ mm mounted inside a glass capillary was used for data collection at 25°C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$–$2\theta$ scans with $\omega$-scan angle $(1.84 + 0.35 \tan\theta)°$ at a scan speed of 16.0 deg min$^{-1}$ (up to four scans for reflection $I < 15\sigma(I)$). Intensity data (in the range of $2\theta_{max} = 52°$; $h$: 0 to 14; $k$: 0 to 13; $l$: $-21$ to 21 and three standard reflections measured after every 300 reflections showed no decay), were corrected for Lorentz and polarization effects, and empirical absorption corrections based on the $\psi$-scan of four strong reflections (minimum and maximum transmission factors 0.869 and 1.000). Upon averaging the 4704 reflections, 4489 of which were uniquely measured, ($R_{int} = 0.025$). 2716 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and the structure solved by heavy-atom Patterson methods and expanded using Fourier techniques [33] and refinement by full-matrix least squares using the MSC-Crystal Structure Package TeXsan [34] on a Silicon Graphics Indy computer. The 27 non-H atoms were refined anisotropically and the 18 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not

Table 1
Crystal and structure determination data for **1**

| Formula | $C_{22}H_{18}Cl_2S_2Zr$ |
|---|---|
| $M_r$ | 508.63 |
| $T$ (K) | 298 |
| $a$ (Å) | 12.182(1) |
| $b$ (Å) | 10.674(4) |
| $c$ (Å) | 17.131(2) |
| $\beta$ (deg) | 103.949(6) |
| $V$ (Å³) | 2162.8(6) |
| Crystal colour and shape | yellow parallelepiped |
| Crystal system | monoclinic |
| Space group | $P2_1/a$ (No. 14) |
| $Z$ | 4 |
| $F(000)$ | 1024 |
| $D_c$ (g cm⁻³) | 1.563 |
| Crystal dimensions (mm) | $0.20 \times 0.15 \times 0.30$ |
| $\lambda$ (Å) (graphite monochromated, Mo-K $\alpha$) | 0.71073 |
| $\mu$ (cm⁻¹) | 9.53 |
| Collection range | $2\theta_{max} = 52°$ ($h$: 0 to 14; $k$: 0 to 13; $l$: −21 to 21) |
| Scan mode and scan speed (deg min⁻¹) | $\omega$–2$\theta$; 16 |
| Scan width (deg) | $1.84 + 0.35 \tan\theta$ |
| No. of data collected | 4704 |
| No. of unique data | 4489 |
| No. of data used in refinement, $m$ | 2716 |
| No. of parameters refined, $p$ | 244 |
| $R$ | 0.032 |
| $wR^a$ | 0.034 |
| goodness-of-fit, $S$ | 2.03 |
| maximum shift $(\Delta/\sigma)_{max}$ | 0.01 |
| Residual extrema in final difference map (e Å⁻³) | +0.36, −0.38 |

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.010\ F_o^2)^2]$ with $I > 3\sigma(I)$.

refined. Convergence for 244 variable parameters by least squares refinement on $F$ with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.010\ F_o^2)^2]$ for 2716 reflections with $I > 3\sigma(I)$ was reached at $R = 0.032$ and

Table 2
Selected bond distances (Å) and bond angles (deg) for **1**[a]

| Zr(1)–S(1) | 2.523(1) | Zr(1)–S(2) | 2.526(1) |
|---|---|---|---|
| Zr(1)–CN(1) | 2.20 | Zr(1)–CN(2) | 2.21 |
| Zr(1)–C(1) | 2.506(4) | Zr(1)–C(2) | 2.505(5) |
| Zr(1)–C(3) | 2.490(5) | Zr(1)–C(4) | 2.494(5) |
| Zr(1)–C(5) | 2.506(5) | S(1)–C(11) | 1.777(4) |
| S(2)–C(17) | 1.774(4) | C(1)–C(2) | 1.389(7) |
| C(2)–C(3) | 1.397(6) | C(3)–C(4) | 1.407(7) |
| C(4)–C(5) | 1.370(7) | C(1)–C(5) | 1.377(7) |
| | | | |
| S(1)–Zr(1)–S(2) | 98.95(4) | CN(1)–Zr–CN(2) | 131.0 |
| S(1)–Zr(1)–CN(1) | 110.6 | S(1)–Zr(1)–CN(2) | 101.1 |
| S(2)–Zr(1)–CN(1) | 101.3 | S(2)–Zr(1)–CN(2) | 109.7 |
| Zr(1)–S(1)–C(11) | 109.7(1) | Zr(1)–S(2)–C(17) | 109.4(1) |

[a] CN(1) and CN(2) are the centroids of the C(1)···C(5) and C(6)···C(10) cyclopentadienyl rings, respectively.

$wR = 0.034$ with a goodness-of-fit of 2.03. $(\Delta/\sigma)_{max} = 0.01$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.36 and 0.38. Crystal and structure determination data for **1** are summarized in Table 1. Selected bond distances and angles are summarized in Table 2.

### 2.4.2. Crystal data for **4**

$C_{34}H_{34}O_3S_2Zr_2$, $M_r = 737.20$, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.533(1)$ Å, $b = 15.217(4)$ Å, $c = 13.382(2)$ Å, $\beta = 90.00(2)°$, $V = 3162(1)$ Å³, $Z = 4$, $D_c = 1.548$ g cm⁻³, $\mu$(Mo-K $\alpha$) = 8.23 cm⁻¹, $F(000) = 1496$, $T = 301$ K. A pale yellow crystal of dimensions $0.25 \times 0.15 \times 0.35$ mm was used for data collection at 28°C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-K $\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$–2$\theta$ scans with $\omega$-scan angle $(0.73 + 0.35 \tan\theta)°$ at a scan speed of 16.0 deg min⁻¹ (up to seven scans for reflection $I < 15\sigma(I)$). Intensity data (in the range of $2\theta_{max} = 45°$; $h$: 0 to 16; $k$: 0 to 16; $l$: −14 to 14 and three standard reflections measured after

Table 3
Crystal and structure determination data for **4**

| Formula | $C_{34}H_{34}O_3S_2Zr_2$ |
|---|---|
| $M_r$ | 737.20 |
| $T$ (K) | 301 |
| $a$ (Å) | 15.533(1) |
| $b$ (Å) | 15.217(4) |
| $c$ (Å) | 13.382(2) |
| $\beta$ (deg) | 90.00(2) |
| $V$ (Å³) | 3162(1) |
| Crystal colour and shape | yellow rod |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ (No. 14) |
| $Z$ | 4 |
| $F(000)$ | 1496 |
| $D_c$ (g cm⁻³) | 1.548 |
| Crystal dimensions (mm) | $0.25 \times 0.15 \times 0.35$ |
| $\lambda$ (Å) (graphite monochromated, Mo-K $\alpha$) | 0.71073 |
| $\mu$ (cm⁻¹) | 8.23 |
| Collection range | $2\theta_{max} = 45°$ (h:0 to 16;k:0 to 16; l:−14 to 14) |
| Scan mode and scan speed (deg min⁻¹) | $\omega$–2$\theta$; 16 |
| Scan width (deg) | $0.73 + 0.35 \tan\theta$ |
| No. of data collected | 4520 |
| No. of unique data | 4332 |
| No. of data used in refinement, $m$ | 3339 |
| No. of parameters refined, $p$ | 370 |
| $R$ | 0.028 |
| $wR^a$ | 0.033 |
| Goodness-of-fit, $S$ | 1.76 |
| Maximum shift, $(\Delta/\sigma)_{max}$ | 0.01 |
| Residual extrema in final difference map (e Å⁻³) | +0.24, −0.24 |

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.008\ F_o^2)^2]$ with $I > 3\sigma(I)$.

Table 4
Selected bond distances (Å) and bond angles (deg) for 4[a]

| Zr(1)–CN(1) | 2.25 | Zr(1)–CN(2) | 2.23 |
|---|---|---|---|
| Zr(2)–CN(3) | 2.22 | Zr(2)–CN(4) | 2.23 |
| Zr(1)–S(1) | 2.542(1) | Zr(2)–S(2) | 2.554(2) |
| Zr(1)–O(2) | 1.964(3) | Zr(2)–O(2) | 1.958(3) |
| S(1)–C(5) | 1.784(5) | S(2)–C(28) | 1.788(6) |
| Zr(1)–C(8) | 2.538(5) | Zr(1)–C(9) | 2.549(5) |
| Zr(1)–C(10) | 2.552(5) | Zr(1)–C(11) | 2.540(5) |
| Zr(1)–C(12) | 2.537(5) | | |
| | | | |
| S(1)–Zr(1)–CN(1) | 108.8 | S(1)–Zr(1)–CN(2) | 98.6 |
| S(2)–Zr(2)–CN(3) | 100.1 | S(2)–Zr(2)–CN(4) | 107.4 |
| CN(1)–Zr(1)–CN(2) | 127.4 | CN(3)–Zr(2)–CN(4) | 129.4 |
| Zr(1)–O(2)–Zr(2) | 169.2(2) | Zr(1)–S(1)–C(5) | 110.2(2) |
| Zr(2)–S(2)–C(28) | 110.0(2) | O(2)–Zr(1)–S(1) | 100.06(9) |
| O(2)–Zr(2)–S(2) | 103.13(10) | | |

[a] CN(1), CN(2), CN(3) and CN(4) are the centroids of the C(8) ··· C(12), C(13) ··· C(17), C(18) ··· C(22) and C(23) ··· C(27) cyclopentadienyl rings, respectively.



Fig. 1. Perspective drawing of 1 with atomic numbering scheme. Thermal ellipsoids are shown at the 40% probability level.

every 300 reflections showed decay of 1.96%), were corrected for decay and for Lorentz and polarization effects, and empirical absorption corrections based on the $\psi$-scan of four strong reflections (minimum and maximum transmission factors 0.934 and 1.000). 4520 reflections were measured, of which 4332 were unique and $R_{int} = 0.070$. 3339 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and the structure solved by Patterson methods and expanded by Fourier techniques [33] and refinement by full-matrix least squares using the MSC-Crystal Structure Package TeXsan [34] on a Silicon Graphics Indy computer. All 41 non-H atoms of an asymmetric unit were refined anisotropically. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 370 variable parameters by least squares refinement on $F$ with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.008\ F_o^2)^2]$ for 3339 reflections with $I > 3\sigma(I)$ was reached at $R = 0.028$ and $wR = 0.033$ with a goodness-of-fit of 1.76. $(\Delta/\sigma)_{max} = 0.01$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.24 and 0.24. Crystal and structure determination data for 4 are summarized in Table 3. Selected bond distances and angles are summarized in Table 4.

## 3. Results and discussion

The compounds $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4R\text{-}p)_2$ [R = Cl (1), Me (2), OMe (3)] were prepared by the reaction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with $HSC_6H_4R\text{-}p$ in the presence of triethylamine in toluene at room temperature, similar to the procedure described for the preparation of $(\eta^5\text{-}C_5H_5)_2Zr(SPh)_2$ [24]. The complexes $[(\eta^5\text{-}$

$C_5H_5)_2Zr(SC_6H_4R\text{-}p)]_2O$ [R = OMe (4), Cl (5)] were obtained by subjecting a solution of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4R\text{-}p)_2$ in toluene–hexane mixture to slow hydrolysis in air. All the newly synthesized complexes gave satisfactory elemental analyses. Complexes 1–3 have also been characterized by ^{1}H NMR spectroscopy, while attempts to record the ^{1}H NMR spectra of 4 and 5 were unsuccessful due to their limited solubility in almost all common solvents. The crystal structures of 1 and 4 have been determined by X-ray crystallography.

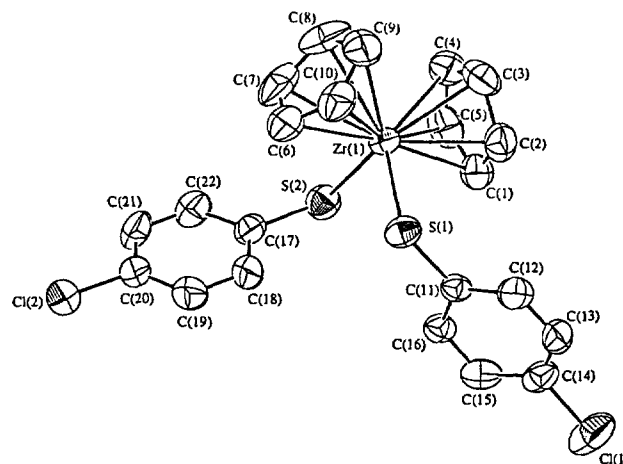The perspective drawings of complexes 1 and 4 are depicted in Figs. 1 and 2, respectively. Complex 1 shows a conformation typical of that found for bent metallocene–thiolate complexes [35,36]. The coordination geometry around the Zr atom is distorted tetrahedron. The two Cp rings are nearly eclipsed relative to each other and the carbon atoms are coplanar with a
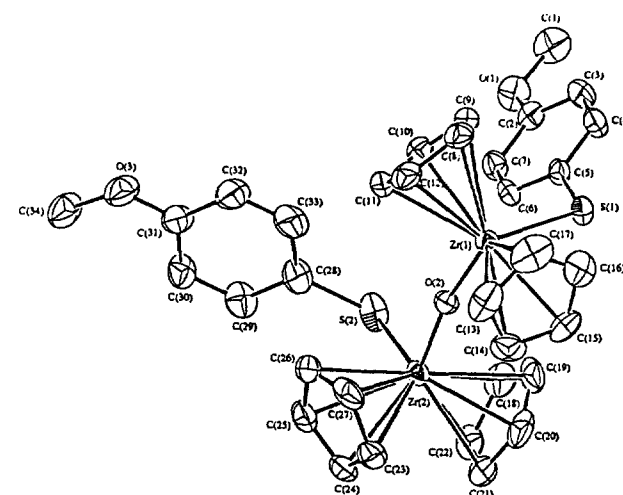


Fig. 2. Perspective drawing of 4 with atomic numbering scheme. Thermal ellipsoids are shown at the 40% probability level.

maximum deviation from the best least-squares planes of 0.004 and 0.002 Å on each ring. The $Cp_{(centroid)}$–Zr–$Cp_{(centroid)}$ angle of 131.0° is normal for zirconocene complexes and the average Zr–$Cp_{(centroid)}$ distance of 2.21 Å is comparable with those of other derivatives [22,35,36]. The thiolate ligands are found to assume an endo(anti) conformation relative to the $Cp_2Zr$ fragment and the S–Zr–S plane, with S(1)–Zr–S(2)–C(17) and S(2)–Zr–S(1)–C(11) torsion angles of 64.4(2) and 69.3(2)°, which is in accord with theoretical calculations on this class of compounds and is commonly adopted by $d^0$ metal centers in order to maximize the $p\pi$–$d\pi$ overlap between sulfur and the metal center [10–14]. The Zr–S bond distances of 2.523(1) and 2.526(1) Å are close to the sum of the respective single bond covalent radii and are comparable to the values observed in $(\eta^5\text{-}C_5Me_5)_2Zr(SPh)_2$ [23]. The S(1)–Zr(1)–S(2) angle of 98.95(4)° is smaller than the angle of 100.9(1)° observed for $(\eta^5\text{-}C_5Me_5)_2Zr(SPh)_2$ and is consistent with $d^0$ metallocene thiolate complexes [35,36]. Similar trend has also been observed in the complexes $(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(OPh)_2$ [23]. The larger deviation from 90° of the S–Zr–S–C torsion angle (49°) in $(\eta^5\text{-}C_5Me_5)_2Zr(SPh)_2$ is in line with the steric requirement of the pentamethylcyclopentadienyl units which direct the phenyl substituents further away from the more sterically demanding pentamethylcyclopentadienyl groups. The smaller displacement of the phenyl substituents from the equatorial plane in **1** is further reflected by the smaller Zr–S(1)–C(11) and Zr–S(2)–C(17) bond angles of 109.7(1)° and 109.4(1)° than those found in the $(\eta^5\text{-}C_5Me_5)_2Zr(SPh)_2$ analogue (119°) [23].

On the other hand, the molecular structure of **4** consists of two $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4OMe\text{-}p)$ molecular units linked together by an oxo-bridge. The structure of the two units are similar with only minor differences. The oxo-bridge oxygen atom together with the thiolate ligand and the two Cp rings complete a distorted tetrahedral arrangement around each Zr atom. The Zr–S bond distances of 2.542(1) and 2.554(2) Å are similar to those found in the related $[(\eta^5\text{-}C_5H_5)_2Zr(SPh)]_2O$ complex [25]. The Zr–O bond distances of 1.964(3) and 1.958(3) Å are also similar to that observed in $[(\eta^5\text{-}C_5H_5)_2Zr(SPh)]_2O$ and slightly shorter than those found in $(\eta^5\text{-}C_5H_5)_2Zr(OPh)_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(OPh)_2$ [23,25]. The average Zr–$Cp_{(centroid)}$ distance of 2.23 Å compares well with those of other zirconocene derivatives [22,35,36]. Unlike the Zr–S bond, the Zr–O bond distance is much shorter than the sum of the covalent bond radii for zirconium and oxygen, which may be attributed to a consequence of partial ionic character in the Zr–O bond rather than an enhanced oxygen to zirconium $p\pi$–$d\pi$ bonding [23,25,37,38]. The Zr–O–Zr bridging angle of 169.2(2)° is slightly larger than that in

$[(\eta^5\text{-}C_5H_5)_2Zr(SPh)]_2O$ [165.8(2)°] [25]. The two $Cp_{(centroid)}$–Zr–$Cp_{(centroid)}$ angles of 127.4° and 129.1° are similar and only slightly smaller than that in **1**. The two slightly different S–Zr–O bond angles [S(1)–Zr(1)–O(2) 100.06(9)°, S(2)–Zr(2)–O(2) 103.13(10)°] are another difference found in the two $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_4OMe\text{-}p)$ molecular units.

It is interesting to find that complexes **1–5** exhibit intense yellow-green to orange-red emission ($\lambda_{em}$ 520–620 nm) upon visible light excitation in the solid state both at room temperature and at 77 K. The corresponding $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ were found to emit at 452 and 494 nm, respectively. It is likely that the emission observed in $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ arises from the respective Cp $\rightarrow$ Zr and $Cp^* \rightarrow$ Zr ligand-to-metal charge transfer (LMCT) states. Similar findings have been reported for the titanocene derivatives [39–41]. The much lower emission energies in **1–5** relative to $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ may suggest an emission of different origin. Preliminary results suggest that the emission in **1–5** may originate from a thiolate-to-metal LMCT excited state. Detailed spectroscopic studies to elucidate the origin of such emission are in progress.

## 4. Supplement material available

Tables giving fractional coordinates and thermal parameters, general displacement parameter expressions (U), all bond distances and bond angles, and observed and calculated structure factors for **1** and **4** (65 pages).

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