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Articles

Synthesis, Emission, and Molecular Orbital Studies of Luminescent Hafnium Thiolate Complexes. Crystal Structures of (η^5-C_5Me_5)$_2$Hf(SR)$_2$ (R = ^{n}Bu, C_6H_5, C_6H_4OMe-*p*)

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A series of luminescent hafnium thiolate complexes (η^5-C_5Me_5)$_2$Hf(SR)$_2$ (R = ^{n}Bu, C_6H_5, C_6H_4OMe-*p*, $C_6H_4{}^t$Bu-*p*) have been synthesized by the reaction of (η^5-C_5Me_5)$_2$HfCl$_2$ with LiSR and shown to exhibit rich luminescence behavior. The crystal structures of (η^5-C_5Me_5)$_2$Hf(S^{n}Bu)$_2$, (η^5-C_5Me_5)$_2$Hf(SC_6H_5)$_2$, and (η^5-C_5Me_5)$_2$Hf(SC_6H_4OMe-*p*)$_2$ have been determined. Fenske−Hall molecular orbital calculations on the hafnium thiolate complexes reveal a thiolate-based HOMO and a LUMO that is mainly composed of hafnium d character.

Introduction

In contrast to the metal-to-ligand charge-transfer (MLCT) excited states, which have been the dominant subjects of study in inorganic photochemistry over the past two decades,[1] complexes that show ligand-to-metal charge-transfer (LMCT) emissive states are very scarce.[2] We have explored the class of d^0 zirconium chalcogenolates,[3] as part of our efforts in the study of metal chalcogenides and chalcogenolates,[4] because the chalcogenolates, being good σ-donor type ligands, together with the good electron-accepting ability of d^0 metal centers, may give rise to low-lying emissive LMCT excited states. To extend our research efforts in luminescent metal chalcogenolates, herein, we report the synthesis and luminescence studies of a series of hafnium thiolates, (η^5-C_5Me_5)$_2$Hf(SR)$_2$ (R = ^{n}Bu, C_6H_5, C_6H_4OMe-*p*, $C_6H_4{}^t$Bu-*p*). The X-ray crystal structures of (η^5-C_5Me_5)$_2$Hf(S^{n}Bu)$_2$, (η^5-C_5Me_5)$_2$Hf(SC_6H_5)$_2$, and (η^5-C_5Me_5)$_2$Hf(SC_6H_4OMe-*p*)$_2$ have been determined. The electronic structures and the nature of the excited states of these luminescent complexes have been probed by Fenske−Hall molecular orbital calculations.

Experimental Section

Materials and Reagents. Bis(pentamethylcyclopentadienyl)hafnium dichloride was purchased from Strem Chemicals Inc. 1-Butanethiol, thiophenol, 4-methoxythiophenol, and 4-*tert*-butylthiophenol were obtained from Lancaster Synthesis Ltd. *n*-Butyllithium was purchased from Aldrich Chemical Co. Analytical grade toluene, dimethoxyethane, and hexane were dried over sodium and distilled over sodium benzophenone ketyl using standard procedures before use.

Synthesis of Hafnium Thiolate Complexes. All reactions and manipulations were carried out under strictly anaerobic and anhydrous conditions using standard Schlenk technique.

(η^5-C_5Me_5)$_2$Hf(S^{n}Bu)$_2$ (1). To a solution of (η^5-C_5Me_5)$_2$HfCl$_2$ (0.14 g, 0.27 mmol) in DME (15 mL) at 0 °C was added LiS^{n}Bu (0.60 mmol) in DME (20 mL), prepared *in situ* at 0 °C from HS^{n}Bu (0.054 g, 0.60 mmol) and ^{n}BuLi (0.60 mmol in *n*-hexane). The reaction mixture was slowly warmed to 50 °C and stirred at that temperature for 48 h. After removal of the solvent under reduced pressure, the solid residue was extracted with toluene. The toluene extract was subsequently concentrated and addition of hexane followed by cooling gave **1** as pale yellow crystals. Yield: 0.11 g (65%). ^{1}H NMR (300 MHz, C_6D_6, 298 K, relative to Me$_4$Si): δ 0.95 (t, 6H, CH$_3$), 1.53 (m, 4H, CH$_3$*CH$_2$*), 1.73 (m, 4H, CH$_3$CH$_2$*CH$_2$*), 2.06 (s, 30H, C_5-Me$_5$), 2.99 (t, 4H, *CH$_2$*S). UV−vis in toluene (298 K), λ_{max}/nm

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(ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 318 (4300), 368 (2300). Positive ion EI-MS: $m/z = 628$ $\{M\}^+$, 571 $\{M - C_4H_9\}^+$, 538$\{M - SC_4H_9\}^+$, 481 $\{M - SC_4H_9 - C_4H_9\}^+$. Anal. Found: C, 53.41; H, 7.67. Calcd for $C_{28}H_{48}S_2Hf$: C, 53.56; H, 7.65.

$(\eta^5\text{-}C_5Me_5)_2Hf(SC_6H_5)_2$ (2). The procedure was similar to that of **1** except HSC_6H_5 (0.066 g, 0.60 mmol) was used in place of HS^{n}Bu to give **2** as yellow crystals. Yield: 0.12 g (67%). ^{1}H NMR (300 MHz, C_6D_6, 298 K, relative to Me_4Si): δ 1.93 (s, 30H, C_5Me_5), 6.89 (t, $J = 8$ Hz, 2H, aryl protons *para* to S), 6.97 (t, $J = 8$ Hz, 4H, aryl protons *meta* to S), 7.86 (d, $J = 8$ Hz, 4H, aryl protons *ortho* to S). UV−vis in toluene (298 K), λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 332 (11000), 392 (7600). Positive ion EI-MS: $m/z = 668$ $\{M\}^+$, 559 $\{M - SC_6H_5\}^+$, 533 $\{M - Cp^*\}^+$. Anal. Found: C, 57.56; H, 5.92. Calcd for $C_{32}H_{40}S_2Hf$: C, 57.58; H, 5.99.

$(\eta^5\text{-}C_5Me_5)_2Hf(SC_6H_4OMe\text{-}p)_2$ (3). The procedure was similar to that of **1** except HSC_6H_4OMe-*p* (0.084 g, 0.60 mmol) was used in place of HS^{n}Bu to give **3** as pale yellow green crystals. Yield: 0.13 g (66%). ^{1}H NMR (300 MHz, C_6D_6, 298 K, relative to Me_4Si): δ 1.97 (s, 30H, C_5Me_5), 3.25 (s, 6H, OMe), 6.63 (d, $J = 8$ Hz, 4H, aryl protons *meta* to S), 7.77 (d, $J = 8$ Hz, 4H, aryl protons *ortho* to S). UV−vis in toluene (298 K), λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 330 (8800), 396 (5600). Positive ion EI-MS: $m/z = 728$ $\{M\}^+$, 589 $\{M - SC_6H_4OMe\text{-}p\}^+$. Anal. Found: C, 56.28; H, 6.07. Calcd for $C_{34}H_{44}O_2S_2Hf$: C, 56.16; H, 6.06.

$(\eta^5\text{-}C_5Me_5)_2Hf(SC_6H_4{}^tBu\text{-}p)_2$ (4). The procedure was similar to that of **1** except $HSC_6H_4{}^tBu$-*p* (0.10 g, 0.60 mmol) was used in place of HS^{n}Bu to give **4** as pale yellow crystals. Yield: 0.15 g (71%). ^{1}H NMR (300 MHz, C_6D_6, 298 K, relative to Me_4Si): δ 1.14 (s, 18H, ^{t}Bu), 1.99 (s, 30H, C_5Me_5), 7.03 (d, $J = 8$ Hz, 4H, aryl protons *meta* to S), 7.84 (d, $J = 8$ Hz, 4H, aryl protons *ortho* to S). UV−vis in toluene (298 K), λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 332 (9700), 394 (6200). Positive ion EI-MS: $m/z = 780$ $\{M\}^+$, 615 $\{M - SC_6H_4{}^tBu\text{-}p\}^+$. Anal. Found: C, 61.77; H, 7.29. Calcd for $C_{40}H_{56}S_2Hf$: C, 61.66; H, 7.19.

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 tube detector. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^{1}H NMR spectra were recorded on 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.

Crystal Structure Determination. Crystal Data for 1: $C_{28}H_{48}S_2Hf$, $M_r = 627.30$, monoclinic, space group *C*2/*c* (No. 15), $a = 14.843(3)$ Å, $b = 13.233(2)$ Å, $c = 16.332(5)$ Å, $\beta = 116.07(2)°$, $V = 2881(1)$ Å^3, $Z = 4$, $D_c = 1.446$ g cm^{-3}, μ(Mo Kα) = 37.72 cm^{-1}, $F(000) = 1280$, $T = 301$ K. A pale yellow crystal of dimensions 0.15 × 0.15 × 0.30 mm mounted on a glass fiber was used for data collection at 28 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) using $\omega-2\theta$ scans with ω-scan angle $(0.80 + 0.35 \tan\theta)°$ at a scan speed of 1.50−8.24 deg min^{-1}. Intensity data (in the range of $2\theta_{max} = 48°$; *h*, 0 to 17; *k*, 0 to 15; *l*, −18 to 18 and 3 standard reflections measured after every 300 reflections showed decay of 4.75%) were corrected for decay and for Lorentz and polarization effects and empirical absorption corrections based on the ψ-scan of four strong reflections (minimum and maximum transmission factors 0.836 and 1.000). A total of 2479 reflections were measured, of which 2416 were unique and $R_{int} = 0.010$; 2167 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined on the basis of systematic absences and a statistical analysis of intensity distribution, and the successful refinement of the structure was solved by direct methods (*SIR92*)[5a] and expanded by the Fourier method; refinement was by full-matrix least squares using the software package *TeXsan*[5b] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of half of one molecule with the Hf atom at special position. All 16 non-H atoms of the asymmetric unit were refined anisotropically, and the 24 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 141 variable parameters by least-squares refinement on *F* with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.020\ F_o^2)^2]$ for 2167 reflections with $I > 3\sigma(I)$ was reached at $R = 0.019$ and $wR = 0.025$ with a goodness-of-fit of 1.58. $(\Delta/\sigma)_{max} = 0.01$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.51 and 0.55 e Å^{-3}, respectively.

Crystal Data for 2: $C_{32}H_{40}S_2Hf$, $M_r = 667.28$, monoclinic, space group *C*2/*c* (No. 15), $a = 14.414(5)$ Å, $b = 11.466(3)$ Å, $c = 18.190(3)$ Å, $\beta = 103.18(2)°$, $V = 2927(1)$ Å^3, $Z = 4$, $D_c = 1.732$ g cm^{-3}, μ(Mo Kα) = 37.18 cm^{-1}, $F(000) = 1344$, $T = 301$ K. A yellow crystal of dimensions 0.25 × 0.20 × 0.35 mm mounted on a glass fiber was used for data collection at 28 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) using $\omega-2\theta$ scans with ω-scan angle $(0.66 + 0.35 \tan\theta)°$ at a scan speed of 1.18−5.49 deg min^{-1}. Intensity data (in the range of $2\theta_{max} = 50°$; *h*, 0 to 17; *k*, 0 to 13; *l*, −21 to 21 and 3 standard reflections measured after every 300 reflections showed no decay) were corrected for Lorentz and polarization effects and empirical absorption corrections based on the ψ-scan of four strong reflections (minimum and maximum transmission factors 0.833 and 1.000). A total of 2831 reflections were measured, of which 2732 were unique and $R_{int} = 0.011$; 2484 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined on the basis of systematic absences and a statistical analysis of intensity distribution, and the successful refinement of the structure was solved by direct methods (*SIR92*)[5a] and expanded by the Fourier method; refinement was by full-matrix least squares using the software package *TeXsan*[5b] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of half of one molecule with the Hf atom at special position. All 18 non-H atoms of the asymmetric unit were refined anisotropically, and the 20 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 159 variable parameters by least-squares refinement on *F* with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.028F_o^2)^2]$ for 2484 reflections with $I > 3\sigma(I)$ was reached at $R = 0.024$ and $wR = 0.038$ with a goodness-of-fit of 2.17. $(\Delta/\sigma)_{max} = 0.02$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.61 and 1.18 e Å^{-3}, respectively.

Crystal Data for 3: $C_{32}H_{44}O_2S_2Hf$, $M_r = 727.33$, monoclinic, space group *C*2/*c* (No. 15), $a = 18.034(3)$ Å, $b = 11.105(2)$ Å, $c = 16.835(3)$ Å, $\beta = 109.69(2)°$, $V = 3174(1)$ Å^3, $Z = 4$, $D_c = 1.522$ g cm^{-3}, μ(Mo Kα) = 34.40 cm^{-1}, $F(000) = 1472$, $T = 301$ K. A yellow green crystal of dimensions 0.25 × 0.15 × 0.30 mm on a glass fiber was used for data collection at 28 °C on an MAR diffractometer with a 300 mm image plate detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data collection was made with 3° oscillation (60 images) at 120 mm distance and 280 s exposure. The images were interpreted and intensities integrated using the program *DENZO*.[5c] A total of 3073 unique reflections were obtained

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from a total of 13 424 measured reflections ($R_{int} = 0.033$); 2863 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. These reflections were in the range *h*, 0 to 21; *k*, 0 to 13; *l*, −20 to 20 with $2\theta_{max} = 51.0°$. The space group was determined on the basis of systematic absences and a statistical analysis of intensity distribution, and the successful refinement of the structure was solved by direct methods (*SIR92*)[5a] and expanded by the Fourier method; refinement was by full-matrix least squares using the software package *TeXsan*[5b] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of half of one molecule with the Hf atom at special position. In the least-squares refinement, all 20 non-H atoms were refined anisotropically, and the 22 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 177 variable parameters by least-squares refinement on *F* with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.032F_o^2)^2]$ for 2863 reflections with $I > 3\sigma(I)$ was reached at $R = 0.025$ and $wR = 0.044$ with a goodness-of-fit of 1.92. $(\Delta/\sigma)_{max} = 0.01$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.78 and 1.51 e Å^{-3}, respectively.

Computational Details. Nonparametrized Fenske−Hall MO calculations[6] were carried out on the complex $(\eta^5\text{-}C_5Me_5)_2Hf(S^nBu)_2$. This method is based on a self-consistent-field method, which is an approximation of the Hartree−Fock−Roothaan procedure. The molecular geometry and the atomic basis sets used completely determine the resulting eigenvalues and eigenvectors. The calculation was based upon crystallographic data of $(\eta^5\text{-}C_5Me_5)_2Hf(S^nBu)_2$. The relative positions of the two S atoms and the two centroids of Cp* were adjusted to an idealized microsymmetry of C_s (C_1 for overall symmetry, two Cp* rings being staggered). The idealized atomic coordinates were taken such that the *x* direction of the master coordinate system originating on the Hf atom bisects the S−Hf−S bond angle, the *y* direction is normal to the HfS_2 plane, and the *z* direction is normal to the plane that bisects the S−Hf−S angle. The basis sets used were those provided with the Fenske−Hall program package version 5.1. All calculations were carried out on a VAX 780 computer at The University of Hong Kong.

Results and Discussion

Reaction of $(\eta^5\text{-}C_5Me_5)_2HfCl_2$ with 2.2 equiv of LiSR in DME gave $(\eta^5\text{-}C_5Me_5)_2Hf(SR)_2$ [R = ^{n}Bu (**1**), C_6H_5 (**2**), $C_6H_4OMe\text{-}p$ (**3**), $C_6H_4{}^tBu\text{-}p$ (**4**)] in reasonable yield. However, unlike the zirconium analogues,[3] reaction of $(\eta^5\text{-}C_5Me_5)_2HfCl_2$ with NaSR instead of LiSR did not give the desired $(\eta^5\text{-}C_5Me_5)_2Hf(SR)_2$ complexes. Instead only the monosubstituted $(\eta^5\text{-}C_5Me_5)_2Hf(SR)Cl$ was obtained. All the newly synthesized complexes gave satisfactory elemental analyses and were characterized by ^{1}H NMR spectroscopy and EI mass spectrometry. The structures of **1**−**3** have been determined by X-ray crystallography and represent the first report on the X-ray structure of this class of $(\eta^5\text{-}Cp')_2Hf(SR)_2$ (Cp′ = C_5Me_5 or C_5H_5) compounds.

The perspective drawings of complexes **1**−**3** are depicted in Figures 1−3. The crystal and structure determination data for these complexes are collected in Table 1. Selected bond distances and angles are summarized in Tables 2, 3, and 4, respectively. For all three complexes, the coordination geometries about the Hf atom, defined by the pentamethylcyclopentadienyl ring centroids and the S atoms, are distorted tetrahedral. A projection onto the Hf−S(1)−S(1*) plane shows that the pentamethylcyclopentadienyl rings have a staggered conformation. The Hf−S distances in **1**−**3** of 2.4761(9), 2.502(1), and 2.5044(8) Å are comparable to the values observed in $(\eta^5\text{-}C_5H_5)_2HfS_5$ of 2.512 Å,[7] while as

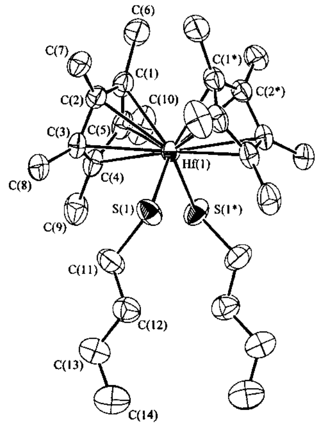

Figure 1. Perspective drawing of **1** with atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability level. Starred atoms have coordinates at −*x*, *y*, 0.5−*z*.

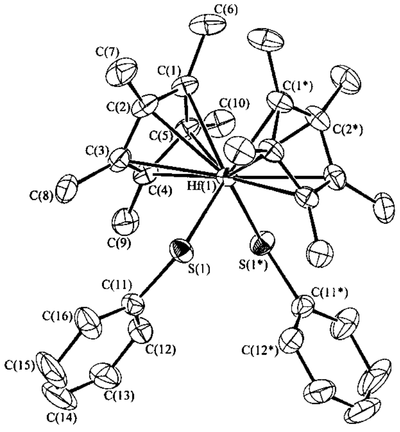

Figure 2. Perspective drawing of **2** with atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability level. Starred atoms have coordinates at −*x*, *y*, 0.5−*z*.

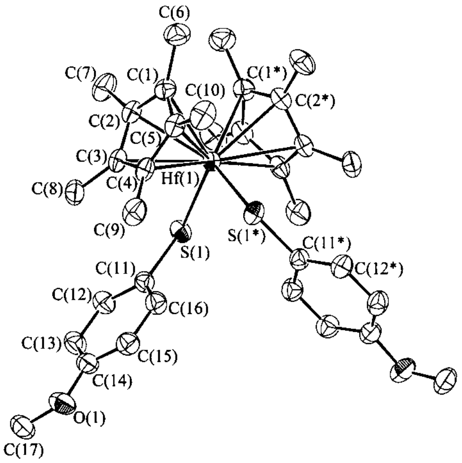

Figure 3. Perspective drawing of **3** with atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability level. Starred atoms have coordinates at −*x*, *y*, 0.5−*z*.

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[6] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

[7] Shaver, A.; McCall, J. M.; Day, V. W.; Vollmer, S. *Can. J. Chem.* **1987**, *65*, 1676.

Table 1. Crystal and Structure Determination Data for Complexes 1-3

	$Cp^*_2Hf(S^nBu)_2$ (**1**)	$Cp^*_2Hf(SC_6H_5)_2$ (**2**)	$Cp^*_2Hf(SC_6H_4OMe\text{-}p)_2$ (**3**)
mol formula	$C_{28}H_{48}S_2Hf$	$C_{32}H_{40}S_2Hf$	$C_{34}H_{44}O_2S_2Hf$
M_r	627.3	667.28	727.33
T, K	301	301	301
a, Å	14.843(3)	14.414(5)	18.034(3)
b, Å	13.233(2)	11.466(3)	11.105(2)
c, Å	16.332(5)	18.190(3)	16.835(3)
β, deg	116.07(2)	103.18(2)	109.69(2)
V, Å^3	2881(1)	2927(1)	3174(1)
cryst color	pale yellow	yellow	yellow green
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
Z	4	4	4
$F(000)$	1280	1344	1472
D_c, g cm^{-3}	1.446	1.732	1.522
cryst dimens, mm	0.15 × 0.15 × 0.30	0.25 × 0.20 × 0.35	0.25 × 0.15 × 0.30
λ, Å (graphite-monochromated, Mo Kα)	0.710 73	0.710 73	0.710 73
μ(Mo Kα), cm^{-1}	37.72	37.18	34.40
collection range	$2\theta_{max} = 48°$ (h, 0 to 17; k, 0 to 15; l, −18 to 18)	$2\theta_{max} = 50°$ (h, 0 to 17; k, 0 to 13; l, −21 to 21)	$2\theta_{max} = 51°$ (h, 0 to 21; k, 0 to 13; l, −20 to 20)
scan mode and scan speed, deg min^{-1}	$\omega-2\theta$; 1.50−8.24	$\omega-2\theta$; 1.18−5.49	oscillation
scan width, deg	0.80 + 0.35 tan θ	0.66 + 0.35 tan θ	
no. of data collected	2479	2831	13 424
no of unique data	2416	2732	3073
no. of data used in refinement, m	2167	2484	2863
no. of parameters refined, p	141	159	177
R^a	0.019	0.024	0.025
wR^a	0.025	0.038	0.044
goodness-of-fit, S	1.58	2.17	1.92
maximum shift, $(\Delta/\sigma)_{max}$	0.01	0.02	0.01
residual maximum in final difference map, e Å^{-3}	+0.51, −0.55	+0.61, −1.18	+0.78, −1.51

[a] $w = 4F_o^2/\sigma^2(F_o)^2$, where $\sigma^2(F_o)^2 = [\sigma^2(I) + (0.020F_o^2)^2]$ with $I > 3\sigma(I)$ for **1**; $w = 4F_o^2/\sigma^2(F_o)^2$, where $\sigma^2(F_o)^2 = [\sigma^2(I) + (0.028F_o^2)^2]$ with $I > 3\sigma(I)$ for **2**; $w = 4F_o^2/\sigma^2(F_o)^2$, where $\sigma^2(F_o)^2 = [\sigma^2(I) + (0.032F_o^2)^2]$ with $I > 3\sigma(I)$ for **3**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1

Hf(1)−S(1)	2.4761(9)	Hf(1)−C(1)	2.546(3)
Hf(1)−C(2)	2.529(3)	Hf(1)−C(3)	2.577(3)
Hf(1)−C(4)	2.596(4)	Hf(1)−C(5)	2.555(4)
Hf−$Cp^*_{centroid}$	2.269	S(1)−C(11)	1.828(4)
C(1)−C(2)	1.410(5)	C(2)−C(3)	1.415(5)
C(3)−C(4)	1.410(5)	C(4)−C(5)	1.430(5)
C(1)−C(5)	1.402(5)	C(1)−C(6)	1.507(5)
C(2)−C(7)	1.506(5)	C(3)−C(8)	1.502(5)
C(4)−C(9)	1.500(5)	C(5)−C(10)	1.503(5)
C(11)−C(12)	1.477(6)	C(12)−C(13)	1.536(7)
C(13)−C(14)	1.447(8)		
S(1)−Hf(1)−S(1*)	95.90(6)	Hf(1)−S(1)−C(11)	111.6(2)
S(1)−C(11)−C(12)	112.5(3)	C(11)−C(12)−C(13)	111.8(4)
C(12)−C(13)−C(14)	113.2(5)	$Cp^*_{centroid}$−Hf−$Cp^*_{centroid}$	135.1

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 2

Hf(1)−S(1)	2.502(1)	Hf(1)−C(1)	2.545(4)
Hf(1)−C(2)	2.504(4)	Hf(1)−C(3)	2.566(5)
Hf(1)−C(4)	2.595(4)	Hf(1)−C(5)	2.560(4)
Hf−$Cp^*_{centroid}$	2.261	S(1)−C(11)	1.778(4)
C(1)−C(2)	1.425(7)	C(2)−C(3)	1.436(6)
C(3)−C(4)	1.406(7)	C(4)−C(5)	1.442(6)
C(1)−C(5)	1.416(6)	C(1)−C(6)	1.507(6)
C(2)−C(7)	1.498(7)	C(3)−C(8)	1.510(7)
C(4)−C(9)	1.506(6)	C(5)−C(10)	1.480(5)
C(11)−C(12)	1.390(8)	C(12)−C(13)	1.367(7)
C(13)−C(14)	1.412(10)	C(14)−C(15)	1.340(1)
C(15)−C(16)	1.429(9)		
S(1)−Hf(1)−S(1*)	100.52(5)	Hf(1)−S(1)−C(11)	119.0(1)
S(1)−C(11)−C(12)	123.4(3)	S(1)−C(11)−C(16)	116.6(4)
$Cp^*_{centroid}$−Hf−$Cp^*_{centroid}$	135.54		

a result of lanthanide contraction effect, they are slightly shorter than the Zr−S distances observed in the related zirconocene thiolate complexes $(\eta^5\text{-}C_5Me_5)_2Zr(SR)_2$ [R = ^{n}Bu (2.4987(8) Å);[3] R = C_6H_5 (2.522(1) Å)[8]]. The S(1)−Hf(1)−S(1*) angles of 95.90(6)°, 100.52(5)°, and 100.62(4)° in **1**−**3** are comparable to the corresponding S(1)−Zr(1)−S(1*) angles in $(\eta^5\text{-}C_5Me_5)_2Zr(SR)_2$ [R = ^{n}Bu (96.14°);[3] R = C_6H_5 (101°)[8]] and are consistentwith the difference in the steric demand of the −S^{n}Bu and −SPh moieties. The Hf−$Cp^*_{centroid}$ distances in **1**−**3** of 2.269, 2.261, and 2.265 Å are slightly shorter than the Zr−$Cp^*_{centroid}$ distances of 2.27 Å in $(\eta^5\text{-}C_5Me_5)_2Zr(S^nBu)_2$.[3] The $Cp^*_{centroid}$−M−$Cp^*_{centroid}$ angles (M = Zr,[3] Hf) are also similar and are consistent with the steric demand of the ligands. Similar to the zirconium analogues,[3,8] complexes **1**−**3** exhibit an *endo* conformation as reflected by their S(1*)−Hf−S(1)−C(11) torsion angles of 48.17°, 48.79°, and 52.07°, respectively. This is in accord with theoretical calculations on this class of compounds and is favored by d^0 metal centers in order to maximize the pπ−dπ overlap between sulfur and the metal center.[9] The larger deviation from 90° of the S−Hf−S−C torsion angle in **1**−**3** is in line with the steric requirement of the pentamethylcyclopentadienyl units, which direct the alkyl/phenyl substituents further away from the more sterically demanding pentamethylcyclopentadienyl groups.

The luminescent behavior of complexes **1**−**4** has been studied. Their photophysical data together with those of the precursor complex $(\eta^5\text{-}C_5Me_5)_2HfCl_2$ and the

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Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 3

Hf(1)−S(1)	2.5044(8)	Hf(1)−C(1)	2.549(4)
Hf(1)−C(2)	2.508(4)	Hf(1)−C(3)	2.576(4)
Hf(1)−C(4)	2.598(4)	Hf(1)−C(5)	2.548(3)
Hf−Cp*$_{centroid}$	2.265	S(1)−C(11)	1.787(3)
C(1)−C(2)	1.418(6)	C(2)−C(3)	1.421(6)
C(3)−C(4)	1.427(6)	C(4)−C(5)	1.423(6)
C(1)−C(5)	1.421(6)	C(1)−C(6)	1.501(5)
C(2)−C(7)	1.496(6)	C(3)−C(8)	1.495(6)
C(4)−C(9)	1.492(5)	C(5)−C(10)	1.510(4)
C(11)−C(12)	1.388(5)	C(12)−C(13)	1.396(6)
C(13)−C(14)	1.387(6)	C(14)−C(15)	1.376(5)
C(15)−C(16)	1.392(6)	O(1)−C(14)	1.376(5)
O(1)−C(17)	1.419(5)		
S(1)−Hf(1)−S(1*)	100.62(4)	Hf(1)−S(1)−C(11)	117.4(1)
S(1)−C(11)−C(12)	118.3(3)	S(1)−C(11)−C(16)	122.7(4)
Cp*$_{centroid}$−Hf−Cp*$_{centroid}$	134.5		

Table 5. Photophysical Data for Hafnium Thiolate Complexes

compound	medium (T/K)	emission (λ_{em}/nm)	lifetime (τ_o/μs)
1	PE/Tol (v/v 10:1) glass (77)	542	
	solid (77)	538	
2	Tol (298)	540	<0.1
	PE/Tol (v/v 10:1) glass (77)	526	
	solid (77)	522	
	solid (298)	513	1.5 ± 0.1
3	PE/Tol (v/v 10:1) glass (77)	545	
	solid (77)	527	
	solid (298)	520	9.0 ± 0.5
4	PE/Tol (v/v 10:1) glass (77)	528	
	solid (77)	532	
	solid (298)	513	<0.1
(η^5-C_5Me_5)$_2$HfCl$_2$	solid (77)	455	
(η^5-C_5H_5)$_2$HfCl$_2$	solid (77)	427	
(η^5-C_5Me_5)$_2$ZrCl$_2$[a]	solid (77)	494	
(η^5-C_5H_5)$_2$ZrCl$_2$[a]	solid (77)	452	

[a] From ref 3.

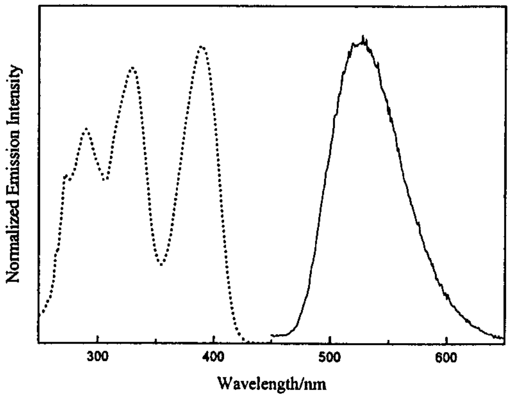

Figure 4. Excitation spectrum (···) and emission spectrum (—) of **2** in petroleum ether/toluene (v/v 10:1) glass at 77 K.

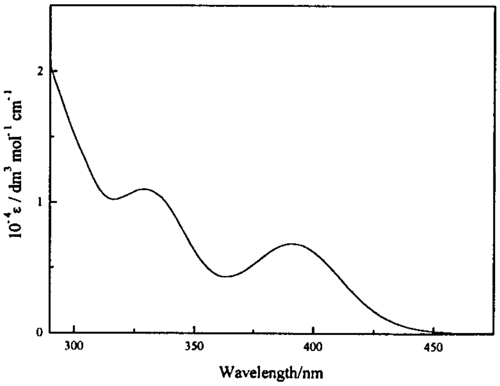

Figure 5. Electronic absorption spectrum of **2** in toluene at room temperature.

Table 6. Idealized Bond Lengths (Å) and Angles (deg) of 1 Used for Nonparametrized Fenske−Hall MO Calculations

Hf−Cp*$_{centroid}$	2.269
Hf−S	2.48
S−C	1.83
Cp*$_{centroid}$−Hf−Cp*$_{centroid}$	135.1
S−Hf−S	95.90
Hf−S−C$_{11}$	111.6
C$_{11}$−S−Hf−S*	48.17
C$_{12}$−C$_{11}$−S*−Hf	44.82

related complexes (η^5-C_5H_5)$_2$HfCl$_2$, (η^5-C_5Me_5)$_2$ZrCl$_2$, and (η^5-C_5H_5)$_2$ZrCl$_2$ are collected in Table 5. The excitation and emission spectra of **2** in petroleum ether/Et$_2$O glass at 77 K are shown in Figure 4. The excitation spectrum closely resembles that of the electronic absorption spectrum (Figure 5). The complexes (η^5-C_5Me_5)$_2$HfCl$_2$, (η^5-C_5H_5)$_2$HfCl$_2$, (η^5-C_5Me_5)$_2$ZrCl$_2$, and (η^5-C_5H_5)$_2$ZrCl$_2$ emit at 455, 427, 494, and 452 nm, respectively, in the solid state at 77 K. A comparison of their emission spectra shows that the emission energy follows the order Hf > Zr and C_5H_5 > C_5Me_5. With reference to previous spectroscopic work on the related titanocene derivatives[10] and the observed emission trends, the emissions observed in (η^5-C_5Me_5)$_2$MCl$_2$ are tentatively assigned as derived from the respective C_5Me_5 → M ligand-to-metal charge-transfer (LMCT) states. Complexes **1**−**4** exhibit intense emission at ca. 520−540 nm upon visible light excitation in the solid state at 77 K. The much lower emission energies in **1**−**4** relative to (η^5-C_5Me_5)$_2$HfCl$_2$ may suggest an emission of different origin. An assignment of the emission origin in complexes **1**−**4** as derived from the C_5Me_5 → Hf LMCT transition is not favored since the thiolate ligands, being a better σ-donor than the electronegative chloro group, would be expected to render the Hf center less electron deficient and, hence, a poorer electron acceptor. This would cause the C_5Me_5 → Hf LMCT transition to shift to higher energies instead. The observation of an opposite trend would disfavor such an assignment. A comparison of the emission energies of the complexes in the solid state at 77 K shows that **1** < **4** < **3** < **2**, which is in line with the σ-donating effect of the thiolate ligands S^{n}Bu > SC$_6$H$_4$^{t}Bu-*p* > SC$_6$H$_4$OMe-*p* > SC$_6$H$_5$. A similar trend has also been found in the related zirconium chalcogenolate complexes.[3] The observation of such an emission trend is suggestive of either a thiolate to hafnium (SR → Hf) LMCT origin or a thiolate to pentamethylcyclopentadienyl (SR → C_5Me_5) LLCT origin. Although one cannot exclude the possibility of a LLCT state, we prefer its assignment as an origin with predominant LMCT character since the emission energies are found to be sensitive to the nature of the metal center. A comparison of the emission

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(10) See for example: (a) Kenney, J. W., III; Boone, D. R.; Striplin, D. R.; Chen, Y. H.; Hamar, K. B. *Organometallics* **1993**, *12*, 3671. (b) Bruce, M. R. M.; Sclafani, A.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2546. (c) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639.

Table 7. Energies and Percent Compositions for the Frontier Orbitals of $(\eta^5\text{-}C_5Me_5)_2Hf(S^nBu)_2$

molecular orbital	energy (eV)	% composition		
		SR	Hf	C_5Me_5
HOMO(88)	−9.48	77.4	0.8	21.8
LUMO(89)	−2.65	16.4	73.2	10.4

spectra of $(\eta^5\text{-}C_5Me_5)_2M(SR)_2$ shows that, for the same thiolate ligand, the emission for the hafnium complexes occurs at a higher energy than that of the zirconium counterparts. For example, the 77 K solid-state emission of $(\eta^5\text{-}C_5Me_5)_2Hf(S^nBu)_2$ occurs at 538 nm, while that of $(\eta^5\text{-}C_5Me_5)_2Zr(S^nBu)_2$ occurs at 610 nm.[3]

The electronic structures of this class of compounds have been probed by Fenske−Hall molecular orbital calculation on complex **1**. Table 6 summarizes the idealized bond lengths and angles used for the MO calculations. Table 7 shows the percent composition for the frontier molecular orbitals of complex **1**. The calculation results show that the composition of the HOMO is approximately 77% S^nBu and 22% C_5Me_5 in character, while that of the LUMO is approximately 73% Hf and 10% C_5Me_5. The large percent composition of thiolate character in the HOMO has also been found in the analogous $(\eta^5\text{-}C_5Me_5)_2Zr(S^nBu)_2$[3] and in the related $(\eta^5\text{-}C_5H_5)_2Ti(SH)_2$.[11] Based on the results of the calculations, an assignment of the origin of emission as derived from a predominant thiolate-to-hafnium (RS → Hf) LMCT state mixed with some C_5Me_5 → Hf LMCT character is favored. A similar assignment has been made for the related zirconium complexes.[3]

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Supporting Information Available: Tables giving fractional coordinates and thermal parameters, general displacement parameter expressions (*U*), and all bond distances and bond angles for **1**−**3** (28 pages). Ordering information is given on any current masthead page.

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