This equation may be rearranged by dividing numerator and denominator by k_{41} and noting that $k_{14}/k_{41} = K_{14}/(\mathrm{H}^+)$, and $(k_{14} + k_{41})/k_{41} = (K_{14} + (\mathrm{H}^+)/(\mathrm{H}^+)$ and that $k_{32} = k_{23}(\mathrm{H}^+)/K_{23}$. In addition from the point of view of the present work it is useful to divide numerator and denominator by $k_{21}(k_{34} + k_{35})$ to obtain eq A5.

$$k_{\mathrm{obsd}}\,\frac{K_{14} + (\mathrm{H}^+)}{(\mathrm{H}^+)} = \frac{\dfrac{k_{23}}{(k_{35} + k_{34})}\left\{\dfrac{k_{12}}{k_{21}}k_{35} + \dfrac{K_{14}}{K_{23}}\right\} + k_{46}\dfrac{K_{14}}{(\mathrm{H}^+)}\left\{\dfrac{(k_{23} + k_{21})}{k_{21}}\left[k_{46} + \dfrac{k_{35}k_{43}}{(k_{35} + k_{34})}\right]\right\}}{1 + k_{23} \quad k_{21} + k_{23}(\mathrm{H}^+)/K_{23}(k_{35} + k_{34})} \tag{A5}$$

The first term in brackets in the numerator can be written as $(K_{14}/K_{23})\{(k_{43}k_{35}/k_{43} + k_{46}\}$. It seems reasonable that $k_{43} \approx k_{46}$, and $k_{35} \gg k_{34}$, in which case eq A5 reduces to eq 11. It should be noted that the last two assumptions do not affect the (H^+) dependence predicted by eq A5, but simply produce a more tractable equation.

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Synthesis, Characterization, and X-Ray Structure of η^5-Cyclopentadienyltris(*N,N*-dimethyldithiocarbamato)zirconium(IV)

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Abstract: η^5-Cyclopentadienyltris(*N,N*-dimethyldithiocarbamato)zirconium(IV), $(\eta^5\text{-C}_5\text{H}_5)\text{Zr}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$, has been prepared by reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ with anhydrous $\text{NaS}_2\text{CN}(\text{CH}_3)_2$ in refluxing dichloromethane and has been characterized by analysis, ^{1}H NMR, and infrared spectroscopy. The structure of this molecule has been determined by a single-crystal x-ray diffraction study of the chlorobenzene solvate, $(\eta^5\text{-C}_5\text{H}_5)\text{Zr}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\cdot\text{C}_6\text{H}_5\text{Cl}$. The solvate crystallizes in the monoclinic space group $P2_1/c$ with four formula units in a unit cell of dimensions: $a = 11.582$ (2), $b = 16.756$ (3), $c = 14.016$ (2) Å; $\beta = 90.58$ (1)° ($\rho_{\text{obsd}} = 1.545$, $\rho_{\text{calcd}} = 1.537$ g cm^{-3}). The final anisotropic least-squares refinement, which employed 7384 independent diffractometer-recorded reflections having $2\theta_{\text{Mo}K\bar{\alpha}} \leq 62.07°$ and $I \geq 2.0\sigma(I)$, afforded residuals $R_1 = 0.079$ and $R_2 = 0.090$. The crystal contains discrete seven-coordinate molecules of the zirconium complex which have a pentagonal bipyramidal structure of approximate symmetry C_s-m. The η^5-cyclopentadienyl ligand occupies one axial position (Zr–C = 2.511–2.519 Å), dithiocarbamate ligand a spans the other axial position and one equatorial position, while dithiocarbamate ligands b and c take the remaining equatorial positions. Zr–S bond lengths vary from 2.655 (1) to 2.717 (2) Å (av value, 2.690 Å). The chief distortions from ideal pentagonal bipyramidal geometry are rotation of the axial Zr–S bond off the quasi-fivefold axis (by 8.9°) and displacement of the Zr atom from the plane of the equatorial sulfur atoms (by 0.60 Å) in the direction of the C_5H_5 group. As expected, there is considerable crowding in the ZrS_6C_5 coordination group, most of the S···S and C···S nonbonded contacts being less than the sum of the van der Waals radii.

In the course of our investigations of *N,N*-dialkyldithiocarbamate complexes of early transition metals[1-3] we have prepared the potentially seven-coordinate cyclopentadienylzirconium(IV) complex $(\eta^5\text{-C}_5\text{H}_5)\text{Zr}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$. This compound is closely related to the dithiocarbamate complexes $\text{Ti}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3\text{Cl}$,[1,2] $\text{VO}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$,[4] $\text{NbO}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$,[4] and $\text{Mo(NO)}[\text{S}_2\text{CN}(n\text{-C}_4\text{H}_9)_2]_3$[5] and to the cyclopentadienyltris(hexafluoroacetylacetonate) $(\eta^5\text{-C}_5\text{H}_5)\text{Zr(hfac)}_3$,[6] all of which have been shown by x-ray diffraction to possess pentagonal bipyramidal structures in which the monodentate ligand occupies an axial position. A similar structure for $(\eta^5\text{-C}_5\text{H}_5)\text{Zr}[\text{S}_2\text{CN}(\text{CH}_3)_2]_3$ is suggested by the proton NMR spectrum which exhibits four methyl resonances of relative intensity 2:1:2:1 at ambient probe temperature (37 °C). Thus, this compound is of special interest since it is one of only a few seven-coordinate complexes which are stereochemically rigid on the NMR time scale;[7-14] in contrast, $Ti[S_2CN(CH_3)_2]_3Cl$ is nonrigid at −90 °C.[1]

In order to establish the detailed stereochemistry of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ and to provide a basis for interpreting future kinetic studies of stereochemical rearrangement at elevated temperatures, the structure of this molecule in crystalline $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$ has been determined by x-ray diffraction. Another point of interest here is the amount of crowding in the ZrS_6C_5 coordination group since some unusually short S···S contacts have been found in the TiS_6Cl coordination group of $Ti[S_2CN(CH_3)_2]_3Cl$.[2]

Experimental Section

Preparation and Physical Data. η^5-Cyclopentadienyltris(*N,N*-dimethyldithiocarbamato)zirconium(IV) was prepared under dry nitrogen by reaction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (1.78 g, 6.1 mmol) and anhydrous $NaS_2CN(CH_3)_2$ (2.58 g, 18.0 mmol) in refluxing, dry dichloromethane. After a reflux time of 42 h the resulting yellow solution was filtered, and the crude product was isolated as yellow crystals in 47% yield by adding dry hexane and allowing the mixture to stand overnight. Recrystallization from dichloromethane–hexane (~3:1 v/v) afforded colorless crystals of the desired compound as a dichloromethane solvate. Anal. Calcd for $(C_5H_5)Zr(C_3H_6NS_2)_3\cdot CH_2Cl_2$: C, 29.93; H, 4.19; Cl, 11.78; N, 6.98; S, 31.96. Found: C, 30.21; H, 4.24; Cl, 11.37; N, 6.92; S, 31.03. The compound decomposes (chars) without melting at 270–275 °C. The proton NMR spectrum of a $CDCl_3$ solution (5.8 g/100 ml) at 37 °C exhibits a single cyclopentadienyl resonance at −6.13 ppm and four dithiocarbamate methyl resonances of relative intensity 2:1:2:1 at −3.36, −3.35, −3.30, and −3.29 ppm; chemical shifts are expressed relative to an internal reference of tetramethylsilane (1% by volume). The NMR spectrum also shows the presence of 1 mol of CH_2Cl_2 per mole of complex. Infrared frequencies at 1510 and 350 cm^{-1} (Nujol mull) may be assigned to $\nu(C\overset{...}{-}N)$ and ν(Zr—S), respectively.

Crystallography. Because of decomposition in the x-ray beam, crystals of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot CH_2Cl_2$ did not prove to be suitable for x-ray structural determination. However, the following crystal data were determined prior to discovery of stable crystals of a chlorobenzene solvate. Crystal data: $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot CH_2Cl_2$; M = 601.90; triclinic; a = 9.975 (2), b = 14.258 (3), c = 9.627 (2) Å; α = 97.53 (2), β = 110.16 (1), γ = 92.70 (2)°; d_m = 1.568 g cm^{-3}, Z = 2, d_c = 1.576 g cm^{-3}.

Dissolution of the triclinic crystals of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot CH_2Cl_2$ in chlorobenzene and subsequent crystallization under dry nitrogen afforded monoclinic crystals of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$. The crystals used for x-ray study were first coated with Krylon, a clear electrically insulating substance, in order to prevent hydrolysis. Subsequent Weissenberg and precession photographs revealed systematic absences, $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$; these uniquely determine the space group to be $P2_1/c\text{-}C_{2h}{}^5$ (No. 14).[15] Using Zr-filtered Mo $K\bar{\alpha}$ radiation (λ 0.710 69 Å), 12 high-angle reflections ($2\theta > 30°$) were chosen to obtain an adequate sampling of reciprocal space and then centered on a computer-controlled four-circle Picker FACS-I diffractometer. The least-squares refinement of the diffraction geometry for these reflections yielded the following values for the lattice parameters: a = 11.582 (2), b = 16.756 (3), c = 14.016 (2) Å; and β = 90.58 (1)°. The density calculated on the basis of four formula units of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$ (M = 629.52) per unit cell is 1.537 g cm^{-3}, which is in excellent agreement with the observed density of 1.545 g cm^{-3} measured by flotation in a solution of carbon tetrachloride and hexane.

Intensity data were similarly collected on a Picker FACS-I diffractometer using Zr-filtered Mo $K\bar{\alpha}$ radiation. The crystal, of dimensions 0.37 × 0.17 × 0.25 mm parallel to the a, b, and c axes, respectively, was mounted on a glass fiber such that the a axis was parallel to φ. The θ–2θ scanning technique was utilized with a takeoff angle of 3°. A scan angle of 1.2° was used in conjunction with a scan rate of 1°/min. Background counts, each of 20-s duration, were taken at both ends of the scan. Reflections having counting rates greater than 20 000 cps were automatically attenuated by inserting copper foil into the path of the diffracted beam until the intensity was reduced to less than that value. The intensities of three standard reflections were monitored periodically at intervals of 50 reflections; for each standard reflection the maximum deviation from the mean intensity was less than 3.5%.

Table I. Residuals for Anisotropic Refinements

sinθ/λ Min	sinθ/λ Max	No. of reflections	R_1	R_2
0.00	0.47	2183	0.052	0.083
0.44	0.73	5622	0.097	0.088
0.00	0.73	7384	0.079	0.090

A total of 8722 reflections having $2\theta \leq 62.07°$ (1.4 times the number of data in the limiting Cu $K\bar{\alpha}$ sphere) was collected in concentric shells of increasing 2θ containing approximately 725 reflections each. The data were corrected for background, use of attenuators, and Lorentz and polarization factors. Absorption corrections were not made since the linear absorption coefficient for Mo $K\bar{\alpha}$ radiation is 9.50 cm^{-1} and the maximum error resulting from neglect of absorption corrections is <4% in any intensity or <2% in any amplitude for the crystal used.

A rejection criterion of $I < 2.0\sigma(I)$ was employed to determine which of those reflections collected were to be considered unobserved. The standard deviation in an intensity, $\sigma(I)$, was computed from

$$\sigma^2(I) = (C_t + k^2B)$$

where C_t is the total count from scanning, k is the ratio of scanning time to total background time, and B is the total background count. Of the 8722 reflections collected, 1338 had $I < 2.0\sigma(I)$, leaving 7384 objectively observed, independent reflections.

Structure Determination and Refinement. The structure was solved by application of the heavy-atom method. Straightforward interpretation of a Patterson synthesis of the $|F_o|^2$ data revealed the position of the Zr atom, and several subsequent Fourier syntheses sufficed to locate the remaining 30 non-hydrogen atoms.

Unit-weighted full-matrix least-squares refinement of the coordinates and isotropic thermal parameters of the 31 atoms was carried out using the 1760 reflections having $0 < 2\theta \leq 36.09°$. The function minimized in this and all subsequent refinements was $\Sigma w(|F_o| - |F_c|)^2$. Upon convergence, the residuals

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

were 0.095 and 0.099, respectively. Subsequent refinements of the positional and anisotropic thermal parameters of all 31 non-hydrogen atoms employed a block-diagonal matrix method and empirical weights, $w = [\sigma(|F_o|)]^{-2}$, obtained from the counting statistics. Three refinements were carried out, with the results presented in Table I. The initial refinement employed only the inner sphere data. A refinement using the outer sphere data was carried out in order to define as precisely as possible the coordinates of the heavy atoms. However, because of high thermal parameters for the η^5-cyclopentadienyl carbon atoms and the angular dependence of the carbon atom scattering factor curve, the outer sphere data proved to be insufficient for determination of accurate atomic coordinates and thermal parameters for those carbon atoms; C–C bond distances within the cyclopentadienyl ring varied from 1.26 to 1.44 Å and esd's were larger than for the first refinement. Consequently, a final anisotropic refinement was carried out which employed all of the data. This refinement afforded the smallest esd's and chemically reasonable values for all bond lengths. In the final cycle of refinement, no coordinate shifted by more than 0.21σ, with the average shift being 0.03σ. A final difference Fourier showed no anomalous features; the three strongest peaks (1.4–1.6 e/Å^3) were near the Zr position.

Scattering factors for Zr^0, Cl^0, S^0, N^0, and C^0 were taken from Cromer and Mann.[16] Anomalous dispersion corrections, real and imaginary, for Zr, Cl, and S were obtained from Cromer.[17] Calculations were performed on an IBM 370/168 computer using the following programs: DIFFDATA, a local data reduction program; FOURIER, a local version of the Zalkin Fourier program; ORFLSE, full-matrix least-squares structure refinement program, a modified version of Busing, Martin, and Levy's original ORFLS; REFINE, a local block-diagonal least-squares structure refinement program; ORFEE,

Table II. Final Atomic Fractional Coordinates for Crystalline $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$[a]

Atom	$10^4 x$	$10^4 y$	$10^4 z$
Zr	2379.4 (0.4)	1286.2 (0.3)	2466.8 (0.3)
S_{a1}	3079 (1)	1432 (1)	658 (1)
S_{a2}	4573 (1)	890 (1)	2208 (1)
S_{b1}	343 (1)	826 (1)	1709 (1)
S_{b2}	2284 (1)	−244 (1)	1833 (1)
S_{c1}	1111 (1)	2563 (1)	1968 (1)
S_{c2}	3528 (1)	2700 (1)	2461 (1)
N_a	5295 (4)	1034 (3)	413 (3)
N_b	203 (4)	−693 (3)	1163 (3)
N_c	2273 (4)	3935 (3)	1792 (3)
C_a	4419 (4)	1111 (3)	1017 (4)
C_b	866 (4)	−117 (3)	1531 (3)
C_c	2305 (5)	3169 (3)	2051 (4)
C_{a1}	5156 (5)	1211 (4)	−624 (4)
C_{a2}	6449 (5)	797 (4)	726 (5)
C_{b1}	−1028 (5)	−562 (4)	936 (4)
C_{b2}	678 (6)	−1489 (3)	948 (5)
C_{c1}	1212 (6)	4311 (4)	1447 (4)
C_{c2}	3314 (6)	4443 (4)	1823 (5)
C_1	3031 (6)	1405 (5)	4175 (4)
C_2	2854 (7)	605 (6)	4023 (4)
C_3	1664 (8)	498 (5)	3872 (4)
C_4	1174 (6)	1218 (6)	3945 (5)
C_5	1990 (7)	1771 (4)	4132 (4)
C_6	8248 (6)	1819 (4)	5311 (5)
C_7	7807 (6)	1938 (5)	6209 (6)
C_8	6627 (7)	1960 (5)	6340 (6)
C_9	5865 (7)	1872 (6)	5556 (6)
C_{10}	6282 (6)	1734 (5)	4650 (6)
C_{11}	7481 (6)	1709 (4)	4544 (5)
Cl	8015 (2)	1577 (1)	3392 (2)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure.

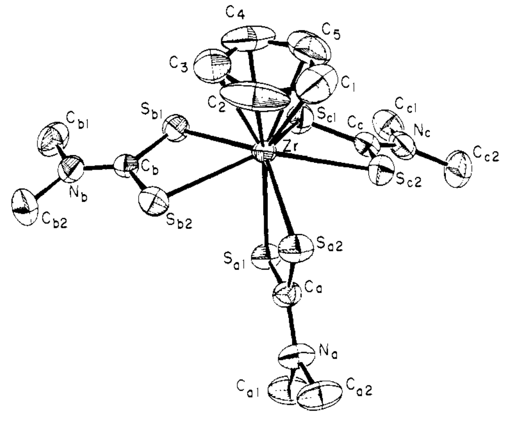

Figure 1. Model in persepctive of the $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ molecule. Each atom is represented by an ellipsoid consistent with the thermal parameters in Table III.

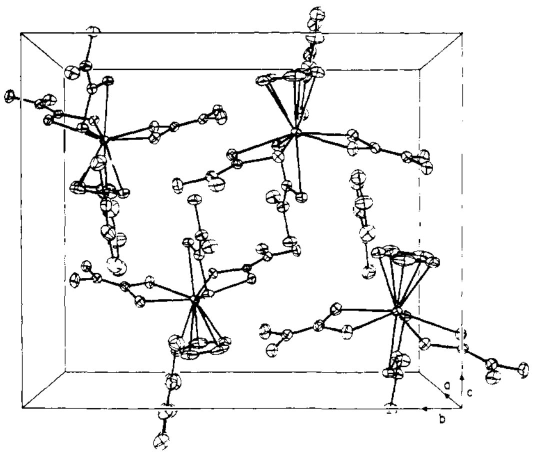

Figure 2. Model in perspective to illustrate the packing of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ and C_6H_5Cl molecules in the crystal. The contents of one unit cell are viewed normal to the (100) plane.

bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP, the C. K. Johnson thermal ellipsoid plotting program; and MEAN PLANES, a local least-squares mean plane calculation program.

Results

Final atomic coordinates and thermal parameters for crystalline $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$ are presented in Tables II and III, respectively.[18] The geometry of the $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ molecule and the atom numbering scheme are shown in Figure 1; atoms of the three *N,N*-dimethyldithiocarbamate ligands are distinguished by a literal subscript (a, b, or c). Bond distances, polyhedral edge lengths, and bond angles in the ZrS_6C_5 coordination group are given in Table IV. Bond lengths and bond angles for the *N,N*-dimethyldithiocarbamate ligands, the cyclopentadienyl ligand, and the chlorobenzene solvate molecule are presented in Tables V and VI, and the results of selected mean plane calculations are summarized in Table VII.

All of the parameters listed in Tables II-VII are based on the final refinement (Table I), which employed all 7384 reflections. Bond distances obtained from the inner sphere refinement (2183 reflections) differed from those obtained in the final refinement by $\lesssim 1\sigma$, except for the N—CH_3 distances which differed by as much as 7σ (average difference 2.3σ). Differences between bond distances obtained from the outer sphere refinement (5622 reflections) and those obtained from the final refinement were $\lesssim 1\sigma$ for the Zr—S and C—S bonds, 1σ-2σ for the Zr—C and C$\overset{...}{-}$N bonds, 1σ-5σ for the N—CH_3 and chlorobenzene C—C bonds (av 2.7σ and 1.7σ, respectively), and 2σ-6σ (av 3.5σ) for the cyclopentadienyl C—C bonds. In these comparisons σ is the esd obtained in the final refinement. In general, the final refinement gave smaller esd's (~ 0.6 × those obtained in the inner sphere refinement) and more uniform distances for chemically equivalent bonds.

The packing of the $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ and C_6H_5Cl molecules in the unit cell is depicted in Figure 2. There are two intermolecular contacts which are 0.3 Å less than the sum of the van der Waals radii; however, both of these are $CH_3 \cdots CH_3$ contacts. All other relatively close intermolecular contacts involve at least one methyl group, and none is more than 0.15 Å less than the sum of the van der Waals radii.

Discussion

$(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ exists in the crystalline chlorobenzene solvate as discrete molecules in which the zirconium atom is symmetrically attached to the planar cyclopentadienyl ring and to six sulfur atoms from the three bidentate *N,N*-dimethyldithiocarbamate ligands (Figure 1). The zirconium atom is therefore formally 11-coordinate, and the ZrS_6C_6 coordination polyhedron could be described as a distorted icosahedron with one vertex suppressed. However, because of the relatively small size of the cyclopentadienyl group, the coordination polyhedron is more conveniently viewed as a pentagonal bipyramid in which the $\eta^5\text{-}C_5H_5$ ligand is considered to occupy a single axial coordination site. The other axial position and one equatorial position are spanned by dithiocarbamate ligand a, while the remaining equatorial positions are occupied by dithiocarbamate ligands b and c.

The molecules (four per unit cell) occupy general positions of the space group $P2_1/c$ and are not required to have any

Table III. Final Thermal Parameters for $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$[a]

Atom	Anisotropic parameters, Å^2						Equiv isotropic B,[b] Å^2
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
Zr	2.36 (2)	2.93 (2)	2.31 (2)	0.03 (1)	0.25 (1)	−0.31 (1)	2.50
S_{a1}	2.74 (5)	4.15 (6)	2.65 (5)	0.40 (4)	0.04 (4)	0.09 (4)	3.10
S_{a2}	2.73 (5)	4.70 (6)	2.76 (5)	0.60 (5)	−0.06 (4)	0.26 (5)	3.25
S_{b1}	2.86 (5)	3.47 (5)	3.45 (5)	−0.03 (4)	0.03 (4)	−0.47 (4)	3.23
S_{b2}	3.50 (5)	3.22 (5)	3.70 (6)	0.37 (4)	0.32 (4)	−0.33 (5)	3.43
S_{c1}	2.92 (5)	3.30 (6)	5.13 (7)	0.21 (4)	0.20 (5)	−0.24 (5)	3.66
S_{c2}	3.33 (5)	3.86 (6)	4.32 (7)	−0.66 (5)	−0.05 (5)	−0.51 (5)	3.75
N_a	2.7 (2)	4.8 (2)	3.3 (2)	0.8 (2)	0.7 (1)	0.3 (2)	3.4
N_b	4.4 (2)	3.8 (2)	3.2 (2)	−1.1 (2)	0.6 (2)	−0.3 (2)	3.7
N_c	5.7 (3)	3.2 (2)	3.4 (2)	−0.4 (2)	0.6 (2)	−0.6 (2)	3.9
C_a	2.4 (2)	3.5 (2)	3.2 (2)	0.2 (2)	0.1 (2)	−0.1 (2)	3.0
C_b	3.1 (2)	3.1 (2)	2.2 (2)	−0.4 (2)	0.5 (1)	−0.1 (1)	2.7
C_c	4.0 (2)	3.1 (2)	3.4 (2)	− 0.1 (2)	0.8 (2)	−0.8 (2)	3.3
C_{a1}	4.8 (3)	6.6 (4)	2.9 (2)	1.0 (3)	0.7 (2)	0.4 (2)	4.4
C_{a2}	2.6 (2)	7.2 (4)	5.1 (3)	1.6 (2)	0.8 (2)	0.6 (3)	4.3
C_{b1}	4.0 (3)	6.3 (4)	4.1 (3)	−1.9 (3)	−0.4 (2)	0.1 (3)	4.4
C_{b2}	7.2 (4)	2.8 (2)	5.9 (4)	−0.6 (2)	1.0 (3)	−0.7 (2)	4.8
C_{c1}	6.4 (4)	3.6 (3)	4.4 (3)	1.1 (2)	−0.3 (3)	0.1 (2)	4.6
C_{c2}	6.7 (4)	3.8 (3)	6.5 (4)	−2.0 (3)	0.5 (3)	−0.1 (3)	5.2
C_1	5.5 (4)	11.3 (6)	2.7 (2)	−3.1 (4)	−0.9 (2)	0.5 (3)	5.1
C_2	9.7 (5)	11.2 (6)	2.5 (2)	6.6 (5)	1.8 (3)	2.0 (3)	5.2
C_3	10.3 (5)	6.4 (4)	2.8 (2)	−3.1 (4)	1.7 (3)	0.1 (3)	5.2
C_4	4.4 (3)	13.0 (7)	3.1 (3)	0.7 (4)	1.5 (2)	0.2 (4)	5.3
C_5	10.3 (6)	5.5 (4)	3.1 (3)	0.5 (4)	1.4 (3)	−0.4 (3)	5.4
C_6	4.8 (3)	6.0 (4)	6.0 (4)	0.7 (3)	−0.2 (3)	1.4 (3)	5.4
C_7	6.2 (4)	7.0 (5)	6.1 (4)	0.2 (4)	0.3 (3)	0.8 (4)	6.4
C_8	6.7 (4)	7.2 (5)	7.1 (5)	0.2 (4)	1.8 (4)	0.2 (4)	6.8
C_9	5.5 (4)	10.3 (6)	5.9 (4)	0.0 (3)	1.1 (3)	−0.6 (4)	6.9
C_{10}	3.9 (3)	8.6 (5)	8.1 (5)	−0.1 (3)	0.9 (3)	−0.7 (4)	6.4
C_{11}	5.6 (3)	3.7 (3)	6.3 (4)	0.3 (2)	1.5 (3)	0.3 (3)	5.0
Cl	7.1 (1)	6.9 (1)	6.3 (1)	−0.4 (1)	1.5 (1)	−0.9 (1)	6.6

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

symmetry. However, the maximum permissible symmetry for this configuration, C_s-m, is closely approximated, with the zirconium atom, the centroid of the cyclopentadienyl ring (Cent Cp), and dithiocarbamate ligand a lying in the mirror plane, and dithiocarbamate ligands b and c being symmetrically disposed about this plane. The symmetry of the coordination group is illustrated in Figure 3, which is a projection of the ZrS_6C_5 core onto the quasi-mirror plane containing Zr, S_{a1}, S_{a2}, and Cent Cp; the mean displacement of these atoms from the quasi-mirror plane is 0.004 Å (cf. Table VII). The five equatorial sulfur atoms are nearly coplanar (displacements $\leq$ 0.11 Å; mean displacement 0.07 Å; cf. Table VII), and the dihedral angle between the equatorial plane and the quasi-mirror plane is 88.8° (90° for an ideal pentagonal bipyramid). The dihedral angle between the plane of the cyclopentadienyl ligand and the quasi-mirror plane is 89.8°, with displacements of the five carbon atoms from the mean plane of the ligand being $\leq$0.004 Å (cf. Table VII). The centroid of the cyclopentadienyl ring lies just slightly (1.9°) off the quasi-fivefold axis established by the equatorial plane, and the dihedral angle between the cyclopentadienyl ligand and the equatorial plane is 2.5°.

The chief distortions from ideal pentagonal bipyramidal geometry are rotation of the axial Zr–S_{a1} bond off the quasi-fivefold axis (by 8.9°) and displacement of the Zr atom from the equatorial plane (by 0.60 Å) in the direction of the C_5H_5 group. The former distortion arises because of the relatively small "bite" of the dithiocarbamate ligand; the latter results from a bending of the equatorial Zr–S bonds away from the C_5H_5 ligand so as to increase the C···S contacts. Despite this distortion, five of the ten C···S distances (cf. Table IV) are 0.1–0.2 Å less than the sum of the van der Waals radii (3.43 Å).[19-22] A similar, though smaller, displacement (0.39 Å) of the Zr atom from the equatorial plane has been observed in $(\eta^5\text{-}C_5H_5)Zr(hfac)_3$;[6] the displacement is larger in $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ because of the greater steric requirements of sulfur. The five Zr–C bond distances in the dithiocarbamate complex are extremely uniform (2.511–2.519 Å, av 2.515 Å; cf. Table IV) and compare well with the aver-

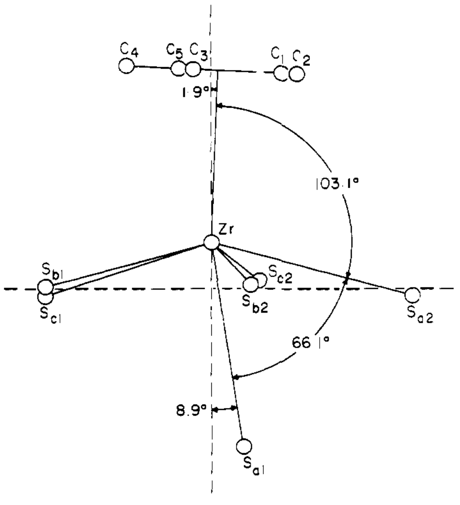

Figure 3. Projection of the ZrS_6C_5 coordination group of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ on the quasi-mirror plane.

Table IV. Bond Distances, Polyhedral Edge Lengths, and Bond Angles Subtended at the Zr(IV) Atom in the Coordination Group of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$[a]

Atoms	Length, Å	Atoms	Angle, deg
Zr-S$_{a1}$	2.681 (1)		
Zr-S$_{a2}$	2.655 (1)		
Zr-S$_{b1}$	2.690 (1)		
Zr-S$_{b2}$	2.715 (1)		
Zr-S$_{c1}$	2.683 (2)		
Zr-S$_{c2}$	2.717 (2)		
Zr-C$_1$	2.511 (6)	C$_1$-Zr-C$_2$	31.7 (3)
Zr-C$_2$	2.517 (6)	C$_2$-Zr-C$_3$	32.4 (3)
Zr-C$_3$	2.519 (6)	C$_3$-Zr-C$_4$	30.8 (3)
Zr-C$_4$	2.512 (6)	C$_4$-Zr-C$_5$	31.1 (3)
Zr-C$_5$	2.516 (6)	C$_5$-Zr-C$_1$	31.3 (3)
S$_{a1}$···S$_{a2}$[b]	2.910 (2)	S$_{a1}$-Zr-S$_{a2}$	66.10 (4)
S$_{a1}$···S$_{b1}$	3.652 (2)	S$_{a1}$-Zr-S$_{b1}$	85.67 (4)
S$_{a1}$···S$_{b2}$	3.388 (2)	S$_{a1}$-Zr-S$_{b2}$	77.76 (4)
S$_{a1}$···S$_{c1}$	3.499 (2)	S$_{a1}$-Zr-S$_{c1}$	81.43 (5)
S$_{a1}$···S$_{c2}$	3.339 (2)	S$_{a1}$-Zr-S$_{c2}$	76.42 (5)
S$_{a2}$···S$_{b2}$	3.300 (2)	S$_{a2}$-Zr-S$_{b2}$	75.81 (4)
S$_{a2}$···S$_{c2}$	3.286 (2)	S$_{a2}$-Zr-S$_{c2}$	75.43 (4)
S$_{b1}$···S$_{b2}$[b]	2.879 (2)	S$_{b1}$-Zr-S$_{b2}$	64.36 (4)
S$_{b1}$···S$_{c1}$	3.064 (2)	S$_{b1}$-Zr-S$_{c1}$	69.53 (4)
S$_{c1}$···S$_{c2}$[b]	2.886 (2)	S$_{c1}$-Zr-S$_{c2}$	64.60 (4)
C$_1$···S$_{c2}$	3.294 (8)	C$_1$-Zr-S$_{c2}$	78.0 (2)
C$_1$···S$_{a2}$	3.411 (8)	C$_1$-Zr-S$_{a2}$	82.6 (2)
C$_2$···S$_{a2}$	3.280 (7)	C$_2$-Zr-S$_{a2}$	78.7 (2)
C$_2$···S$_{b2}$	3.442 (9)	C$_2$-Zr-S$_{b2}$	82.1 (2)
C$_3$···S$_{b2}$	3.206 (7)	C$_3$-Zr-S$_{b2}$	75.4 (2)
C$_3$···S$_{b1}$	3.426 (8)	C$_3$-Zr-S$_{b1}$	82.2 (2)
C$_4$···S$_{b1}$	3.335 (8)	C$_4$-Zr-S$_{b1}$	79.7 (2)
C$_4$···S$_{c1}$	3.571 (8)	C$_4$-Zr-S$_{c1}$	86.8 (2)
C$_5$···S$_{c1}$	3.454 (8)	C$_5$-Zr-S$_{c1}$	83.2 (2)
C$_5$···S$_{c2}$	3.341 (8)	C$_5$-Zr-S$_{c2}$	79.3 (2)
Zr-Cent Cp[c]	2.232 (6)	Cent Cp-Zr-S$_{a1}$	169.1 (2)
Cent Cp···S$_{a2}$	3.836 (8)	Cent Cp-Zr-S$_{a2}$	103.1 (2)
Cent Cp···S$_{b1}$	3.872 (8)	Cent Cp-Zr-S$_{b1}$	103.4 (2)
Cent Cp···S$_{b2}$	3.819 (8)	Cent Cp-Zr-S$_{b2}$	100.6 (2)
Cent Cp···S$_{c1}$	3.964 (8)	Cent Cp-Zr-S$_{c1}$	107.2 (2)
Cent Cp···S$_{c2}$	3.831 (8)	Cent Cp-Zr-S$_{c2}$	101.0 (2)
Av values[d]			
Zr-S	2.690 (1, 18, 35)		
Zr-C	2.515 (6, 3, 4)	C-Zr-C	31.4 (3, 5, 10)
S$_{a1}$···S$_{eq}$[e]	3.36 (0.2, 19, 45)	S$_{a1}$-Zr-S$_{eq}$	77.5 (0.4, 50, 114)
S$_{eq}$···S$_{eq}$	3.08 (0.2, 17, 22)	S$_{eq}$-Zr-S$_{eq}$	69.9 (0.4, 45, 59)
C···S$_{eq}$	3.38 (0.8, 9, 20)	C-Zr-S$_{eq}$	80.8 (2, 26, 60)
Cent Cp···S$_{eq}$	3.86 (0.8, 4, 10)	Cent Cp-Zr-S$_{eq}$	103.1 (2, 18, 41)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The "bite" of the ligand. [c] Cent refers to the centroid of the cyclopentadienyl ring. [d] The numbers in parentheses following each averaged value are the root mean square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value. [e] The subscript eq refers to the equatorial sulfur atoms S$_{a2}$, S$_{b1}$, S$_{b2}$, S$_{c1}$, and S$_{c2}$.

aged Zr-C distance in the hexafluoroacetylacetonate (2.527 Å[6]). The distance from the Zr atom to the centroid of the C_5H_5 ring is 2.232 (6) Å.

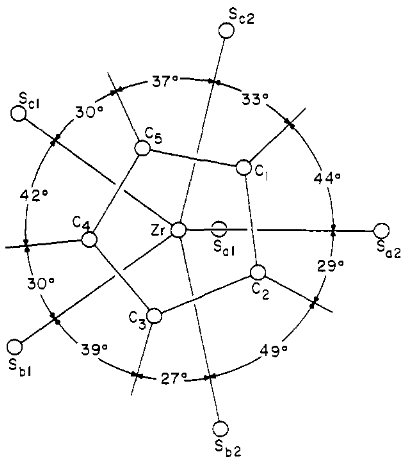

Figure 4. Projection of the ZrS_6C_5 coordination group of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ on the plane of the η^5-cyclopentadienyl ligand.

Carbon-carbon bond distances within the cyclopentadienyl ligand (Table VI) vary from 1.338 to 1.404 Å. However, this variation is not considered significant in view of the 0.013-Å esd's on these distances and the highly anisotropic thermal parameters (Table III) observed for the cyclopentadienyl carbon atoms. The orientation of the thermal ellipsoids for these atoms (Figures 1 and 2) suggests that there is considerable librational motion of the cyclopentadienyl ring about the Zr-Cent Cp axis, as has been observed in $(\eta^5\text{-}C_5H_5)_2ZrI_2$[23] and $(\eta^5\text{-}C_5H_5)_2ZrCl[Si(C_6H_5)_3]$.[24] The averaged C-C bond distance (1.363 Å) is comparable to averaged values of 1.35 and 1.37 Å found for $(\eta^5\text{-}C_5H_5)_2ZrI_2$ and $(\eta^5\text{-}C_5H_5)_2ZrF_2$, respectively.[23] Correction for the effects of librational motion[25] would increase the averaged C-C bond length to ~1.41 Å, in satisfactory agreement with the expected value[26] of ~1.42 Å. It is interesting to note (Figure 4) that the cyclopentadienyl ring is slightly rotated out of the exactly staggered configuration (by ~6°). This distortion presumably improves crystal packing since it increases the differences between adjacent C···S contacts (Table IV), thus increasing intramolecular repulsive interactions.

It was anticipated that bending of the equatorial Zr-S bonds away from the C_5H_5 ligand (Figure 3) might lead to some unusually short S···S contacts in the equatorial plane. Indeed the three inter-ring S···S distances (3.064, 3.286, and 3.300 Å) are appreciably less than the van der Waals contact (3.45 Å[20]), though they are not as short as the corresponding S···S distances in $Ti[S_2CN(CH_3)_2]_3Cl$ (2.951, 3.088, and 3.101 Å[2]). The averaged Zr-S bond length (2.690 Å; cf. Table IV) exceeds the averaged Ti-S bond length in $Ti[S_2CN(CH_3)_2]_3Cl$ (2.512 Å[2]) by 0.18 Å, and the resultant expansion of the pentagonal girdle in the zirconium compound suffices to increase the nonbonded S···S contacts in the equatorial plane, despite the bending of the equatorial Zr-S bonds away from the C_5H_5 ligand. On the basis of the 0.12-Å difference between the ionic (or covalent) radii of Zr(IV) and Ti(IV),[27] one might have expected an averaged Zr-S bond length of ~2.63 Å; the observed value in $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ is 0.06 Å longer, presumably because of the steric requirements of the C_5H_5 group. Unfortunately, no structures of discrete seven-coordinate complexes having Zr-S bonds are available for comparison. In the six-coordinate benzenedithiolato complex, $[Zr(S_2C_6H_4)_3]^{2-}$, the Zr-S distance (2.544 Å[28]) is substantially shorter, as expected.

The individual Zr-S bond lengths range from 2.655 (1) to 2.717 (2) Å, and the variations are such as to preserve the quasi-mirror symmetry of the coordination group. The symmetrically disposed bonds Zr-S$_{b1}$ and Zr-S$_{c1}$ have essentially equal lengths (av. 2.687 Å), as do Zr-S$_{b2}$ and Zr-S$_{c2}$ (2.716 Å); however, the latter are significantly longer than the former, presumably because of the off-axis positioning of the axial sulfur atom S$_{a1}$ (Figure 3). The S$_{a1}$···S$_{b2}$ and S$_{a1}$···S$_{c2}$ distances

Table V. Bond Lengths (Å) and Bond Angles (deg) in the *N,N*-Dimethyldithiocarbamate Ligands[a]

Bond	Ligand a	Ligand b	Ligand c	Av[b]	Angle	Ligand a	Ligand b	Ligand c	Av[b]
$S_1 \cdots S_2$[c]	2.910 (2)	2.879 (2)	2.886 (2)	2.883 (2, 4, 4)[d]	S_1-C-S_2	116.0 (3)	114.9 (3)	114.4 (3)	114.7 (3, 3, 3)[d]
C-S_1	1.713 (5)	1.711 (5)	1.719 (5)	1.713 (5, 4, 8)	C-S_1-Zr	88.6 (2)	90.7 (2)	90.9 (2)	90.4 (2, 4, 5)[d]
C-S_2	1.718 (5)	1.705 (5)	1.713 (6)		C-S_2-Zr	89.4 (2)	90.0 (2)	89.9 (2)	
C-N	1.333 (6)	1.334 (6)	1.336 (7)	1.334 (6, 1, 2)	S_1-C-N	122.5 (4)	121.4 (4)	121.9 (4)	122.4 (4, 9, 14)
					S_2-C-N	121.5 (4)	123.8 (4)	123.6 (4)	
C_1-N	1.492 (7)	1.474 (8)	1.459 (8)	1.472 (8, 10, 20)	C_1-N-C	121.5 (4)	121.9 (5)	121.8 (5)	121.8 (5, 3, 7)
C_2-N	1.457 (7)	1.476 (8)	1.476 (8)		C_2-N-C	122.5 (5)	121.2 (5)	121.7 (5)	
					C_1-N-C_2	115.9 (4)	116.8 (5)	116.5 (5)	116.4 (5, 3, 5)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The numbers in parentheses following each averaged value are the root mean square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value; the averaging assumes C_2 symmetry for each ligand. [c] The bite of the ligand. [d] Average for ligands b and c.

Table VI. Bond Lengths and Bond Angles in the η^5-Cyclopentadienyl Ligand and the Chlorobenzene Solvate Molecule[a]

Atoms	Length, Å	Atoms	Angle, deg
(a) η^5-C_5H_5			
C_1-C_2	1.371 (13)	C_1-C_2-C_3	107.0 (6)
C_2-C_3	1.404 (13)	C_2-C_3-C_4	106.8 (7)
C_3-C_4	1.338 (13)	C_3-C_4-C_5	109.8 (7)
C_4-C_5	1.347 (12)	C_4-C_5-C_1	108.6 (7)
C_5-C_1	1.354 (12)	C_5-C_1-C_2	107.7 (6)
Av C-C:[b]	1.363 (13, 20, 41)	Av C-C-C:[b]	108.0 (7, 10, 18)
(b) C_6H_5Cl			
Cl-C_{11}	1.749 (7)	Cl-C_{11}-C_6	119.8 (5)
		Cl-C_{11}-C_{10}	117.6 (6)
C_6-C_7	1.378 (11)	C_6-C_7-C_8	120.1 (7)
C_7-C_8	1.382 (11)	C_7-C_8-C_9	120.4 (7)
C_8-C_9	1.410 (12)	C_8-C_9-C_{10}	120.8 (7)
C_9-C_{10}	1.383 (12)	C_9-C_{10}-C_{11}	117.3 (7)
C_{10}-C_{11}	1.399 (10)	C_{10}-C_{11}-C_6	122.5 (7)
C_{11}-C_6	1.400 (10)	C_{11}-C_6-C_7	118.8 (6)
Av C-C:[b]	1.392 (11, 11, 18)	Av C-C-C:[b]	120.0 (7, 13, 27)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The numbers in parentheses following each averaged value are the root mean square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value.

(Table IV) are less than the van der Waals contact and are less than $S_{a1} \cdots S_{b1}$ and $S_{a1} \cdots S_{c1}$ by ~0.2 Å; C⋯S contacts are also shorter, on average, for S_{b2} and S_{c2}. It is interesting to note that the axial Zr-S bond, Zr-S_{a1} (2.681 (1) Å), is *not* appreciably shorter than the averaged length of the five equatorial Zr-S bonds (2.692 Å), as is the case for $(\eta^5\text{-}C_5H_5)Zr(hfac)_3$[6] and several other pentagonal bipyramidal chelate structures.[2,29,30] Some lengthening of Zr-S_{a1} would appear to be necessitated by the substantial bending of the equatorial bonds away from the C_5H_5 ligand.

Bond distances and angles within the dithiocarbamate ligands (Table V) are in agreement with the values found in other dithiocarbamate structures.[2-5,31-37] Ligand a, which spans the axial and an equatorial position, has a slightly larger bite (by 0.027 Å), a larger S-C-S bite angle (by 1.3°), and correspondingly smaller C-S-Zr angles than ligands b and c. Otherwise, the dimensions of the three dithiocarbamate ligands are essentially identical. A larger bite for the "spanning" ligand (ligand a) is a common feature of pentagonal bipyramidal dithiocarbamate structures;[2,4,5] the larger bite presumably reflects an attempt by the spanning ligand to locate its sulfur atoms as near the ideal axial and equatorial sites as the relatively rigid geometry of the dithiocarbamate ligand will allow. Delocalized π bonding in the S_2CN portion of the ligand is indicated by the C—N (av 1.334 Å) and C—S (av 1.713 Å) distances, which are intermediate between single-bond and double-bond distances (C—N, 1.47 Å; C=N, 1.27 Å; C—S,

Table VII. Least-Squares Mean Planes of the Form $AX + BY + CZ = D$[a]

Plane no.	Atoms	*A*	*B*	*C*	*D*
1	S_{a2}, S_{b1}, S_{b2}, S_{c1}, S_{c2}	0.1607	0.1142	−0.9809	−2.1034
2	Zr, S_{a1}, S_{a2}, Cent Cp	−0.2742	−0.9452	−0.1773	−3.4026
3	S_{a1}, S_{a2}, C_a, N_a, C_{a1}, C_{a2}	−0.2561	−0.9506	−0.1754	−3.3285
4	S_{b1}, S_{b2}, C_b, N_b, C_{b1}, C_{b2}	0.2658	0.2798	−0.9225	−1.7614
5	S_{c1}, S_{c2}, C_c, N_c, C_{c1}, C_{c2}	0.2414	−0.2552	−0.9363	−3.3959
6	C_1, C_2, C_3, C_4, C_5	0.1280	0.1427	−0.9815	−4.9695
7	C_6, C_7, C_8, C_9, C_{10}, C_{11}, Cl	0.0071	0.9880	−0.1542	1.9283
	Atoms and Their Displacements from Planes, Å				
1	S_{a2}, −0.086; S_{b1}, 0.027; S_{b2}, 0.041; S_{c1}, −0.092; S_{c2}, 0.110; Zr, 0.603				
2	Zr, −0.007; S_{a1}, 0.003; S_{a2}, −0.001; Cent Cp, 0.004				
3	S_{a1}, 0.024; S_{a2}, −0.020; C_a, −0.002; N_a, −0.011; C_{a1}, −0.021; C_{a2}, 0.030; Zr, 0.023				
4	S_{b1}, −0.038; S_{b2}, 0.027; C_b, 0.013; N_b, 0.009; C_{b1}, 0.032; C_{b2}, −0.042; Zr, 0.102				
5	S_{c1}, −0.021; S_{c2}, 0.010; C_c, 0.013; N_c, 0.009; C_{c1}, 0.013; C_{c2}, −0.023; Zr, −0.266				
6	C_1, − 0.004; C_2, 0.003; C_3, −0.002; C_4, 0.000; C_5, 0.003				
7	C_6, −0.002; C_7, −0.001; C_8, 0.001; C_9, −0.016; C_{10}, 0.013; C_{11}, 0.021; Cl, −0.015				

[a] *X*, *Y*, and *Z* are orthogonal coordinates measured in Å along *a*, *b*, and *c**, respectively, of the crystallographic coordinate system.

1.81 Å; C=S, 1.61 Å).[38] Brenan and Bernal[5] have reported that the two C—S bond distances within each ligand of $Mo(NO)[S_2CN(n\text{-}C_4H_9)_2]_3$ differ from each other by 0.05 Å; no significant differences between any of the C—S distances are observed in the more accurately determined structure of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ (cf. Table V).

The six atoms of the S_2CNC_2 dithiocarbamate skeleton are nearly coplanar (Table VII), the average displacement of the 18 atoms of the three ligands from their respective mean planes being 0.020 Å (maximum displacement, 0.042 Å). Such departures from planarity as are observed correspond to a slight twisting of the ligands about the C—N bond; dihedral angles between the S_2CN and CNC_2 mean planes are 2.1, 3.1, and 1.7° for ligands a, b, and c, respectively. The Zr atom is displaced from the ligand planes by 0.023, 0.102, and 0.266 Å, respectively, which implies a small folding of the chelate rings about the edges (S···S) of the coordination polyhedron; the corresponding dihedral angles between the ligand planes and the appropriate ZrS_2 plane are 1.0, 3.0, and 6.6° for ligands a, b, and c, respectively. Ring c is folded so as to bend the uncoordinated part of the ligand away from the C_5H_5 group; however, ring b is bent toward the C_5H_5 group. The ring folding and the $S_2C\text{-}NC_2$ twisting are probably due to crystal packing.

The chlorobenzene solvate molecule is planar (Table VII), and the six C-C bond distances (Table VI) are equal within experimental uncertainty. The averaged C-C bond length (1.392 Å) is in excellent agreement with literature values of 1.397 Å[39] for gaseous benzene, 1.392 Å[40] for crystalline benzene, and 1.399 Å[41] for gaseous chlorobenzene. In gaseous chlorobenzene the C-Cl bond distance is believed to be in the range 1.712–1.730 Å;[41] the C-Cl distance in the chlorobenzene solvate is 1.749 (7) Å.

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Supplementary Material Available: A listing of structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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