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Crystal and Molecular Structure of η^5-Cyclopentadienyltris(*N*,*N*-dimethyldithiocarbamato)titanium(IV), a Stereochemically Rigid Seven-Coordinate Chelate

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The crystal and molecular structure of the benzene solvate of η^5-cyclopentadienyltris(*N*,*N*-dimethyldithiocarbamato)titanium(IV), $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$, has been determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units in a cell having dimensions a = 10.154 (1) Å, b = 11.444 (2) Å, c = 22.411 (2) Å, and β = 97.11 (6)° (ρ_{obsd} = 1.44, ρ_{calcd} = 1.418 g cm^{-3}). Least-squares refinement, which employed 5072 independent diffractometer-recorded reflections having $2\theta_{Mo\,K\bar{\alpha}} \leq 54.83°$ and $|F_o| > 1.58\sigma_F$, afforded residuals R_1 = 0.077 and R_2 = 0.079. Anisotropic thermal parameters were used for Ti, S, and the five C atoms of the cyclopentadienyl ligand; isotropic thermal parameters were employed for the remaining nonhydrogen atoms. The crystal contains discrete seven-coordinate molecules which have pentagonal-bipyramidal geometry and approximate symmetry C_s-m. The η^5-cyclopentadienyl ligand occupies one axial position (Ti–C = 2.420–2.425 Å), one bidentate dithiocarbamate ligand spans the other axial position and one equatorial position, and the other two bidentate dithiocarbamate ligands take the remaining equatorial positions. As expected, the TiS_6C_5 coordination group is extremely crowded, with all of the S···S and C···S nonbonded contacts being less than the sum of the van der Waals radii. Because of the crowding, the Ti–S bond distances are unusually long; the average Ti–S bond length of 2.611 Å is 0.10 Å longer than that in the closely related compound $Ti[S_2CN(CH_3)_2]_3Cl$. Nonbonded repulsions are reduced, primarily, by expansion of the Ti–S bonds to the two equatorial ligands; these bonds average ~0.07 Å longer than the Ti–S bonds to the spanning ligand.

Introduction

η^5-Cyclopentadienyltris(*N*,*N*-dialkyldithiocarbamato)metal complexes, $(\eta^5\text{-}C_5H_5)M(S_2CNR_2)_3$ (M = Ti, Zr, Hf),[1-3] are of interest as examples of seven-coordinate chelates that are stereochemically rigid on the NMR time scale. The number of seven-coordinate complexes for which limiting slow-exchange NMR spectra have been reported is still quite small.[1-10]

We have previously reported the NMR spectrum and the X-ray structure of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$.[1] This compound exhibits four methyl proton resonances of relative intensity 2:1:2:1 at ambient probe temperature (37 °C), consistent with the pentagonal-bipyramidal structure found in the solid state; as expected, the η^5-C_5H_5 ligand occupies an axial position. The four-line spectrum coalesces to a single time-averaged resonance line at ~91° due to a metal-centered rearrangement process. The Ti(IV) analogue, $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$, exhibits a similar 2:1:2:1 pattern of methyl proton resonances at −55 °C, but these coalesce to give three lines of relative intensity 4:1:1 at 17°; only at higher temperatures (~58 °C) do the three resonances coalesce into a single time-averaged resonance line.[3] The NMR spectra of the Ti complex clearly point to the existence of a low-temperature kinetic process that exchanges methyl groups between the two inequivalent sites in the equatorial plane of the pentagonal bipyramid. The low-temperature process is not observed for the Zr complex. An X-ray diffraction study of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ was undertaken in order to provide a structural basis for interpreting this interesting difference in kinetic behavior.

A second reason for investigating the solid-state structure of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ derives from the results of previous X-ray studies of seven-coordinate pentagonal-bipyramidal chelates of the type $M(S_2CNR_2)_3X$ (X = Cl,[11,12] I,[13] O,[14] S,[15] NO,[16] CO,[17] η^5-C_5H_5[1]). The structures of these complexes are characterized by severe crowding in the equatorial plane. For example, $Ti[S_2CN(CH_3)_2]_3Cl$ has a 2.951-Å interligand S···S contact, which is 0.50 Å less than the sum of the van der Waals radii.[18] Because the η^5-C_5H_5 ligand is more bulky than a Cl atom, it was expected that the TiS_6C_5 coordination group of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ would be exceedingly crowded if its structure is closely similar to that found for $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$.[1] Steric crowding might be relieved by alteration of the structure (e.g., η^1 attachment of the C_5H_5 ligand or unsymmetrical attachment of the bidentate dithiocarbamate ligands) or by a more or less symmetrical expansion of the Ti–S bonds to the equatorial ligands. The observed structure of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ exhibits the latter feature, and the unusually long Ti–S bonds to the two equatorial ligands may provide a rationale for the above mentioned difference in kinetic behavior.

Experimental Section

η^5-Cyclopentadienyltris(*N*,*N*-dimethyldithiocarbamato)titanium(IV) was prepared in this laboratory by Weir[3] by reaction for 16 h at room temperature under an argon atmosphere of a 1:2:0.5 molar ratio of $(\eta^5\text{-}C_5H_5)_2TiCl_2$, anhydrous $NaS_2CN(CH_3)_2$, and tetramethylthiuram disulfide in dry, degassed tetrahydrofuran. Recrystallization from a dichloromethane/benzene mixture afforded air-sensitive, yellow-orange crystals of the benzene solvate, $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3 \cdot C_6H_6$. The crystals were sealed in 0.3-mm diameter Lindemann glass capillaries under an atmosphere of dry nitrogen.

Weissenberg and precession photographs indicated the crystal system to be monoclinic, and the systematically absent reflections ($h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$) indicated the space group to be $P2_1/c$-C_{2h}^5 (No. 14).[21] The lattice constants of a = 10.154 (1) Å, b = 11.444 (2) Å, c = 22.411 (2) Å, and β = 97.11 (6)° were determined by least-squares refinement of the diffraction geometry for 12 reflections ($2\theta > 30°$) centered on a computer-controlled, four-circle Picker FACS-I diffractometer using Zr-filtered Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å). The calculated density based on one molecule of benzene solvate (mol wt = 78.11) per molecule of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ (mol wt = 473.62) and Z = 4 is 1.418 g cm^{-3}; the observed density, measured by flotation using a solution of carbon tetrachloride and hexane, was 1.44 g cm^{-3}.

A needle-shaped crystal of dimensions 0.50 × 0.21 × 0.12 mm was chosen for collection of intensity data. The data were collected on the Picker FACS-I diffractometer using the θ–2θ scan technique with Zr-filtered Mo K$\bar{\alpha}$ radiation at a takeoff angle of ~2°. The range of each scan, taken at 1°/min, consisted of an estimated base width of 1.8° at 2θ = 0° and an increment of $\Delta(2\theta) = (0.692 \tan \theta)°$ to allow for spectral dispersion; background counts of 40-s duration were taken at both limits of the scan. Reflections with counting rates greater than 10000 counts/s were automatically attenuated by insertion of 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 measured at 50-reflection intervals to monitor the stability of the system. The sum of the three intensities showed a

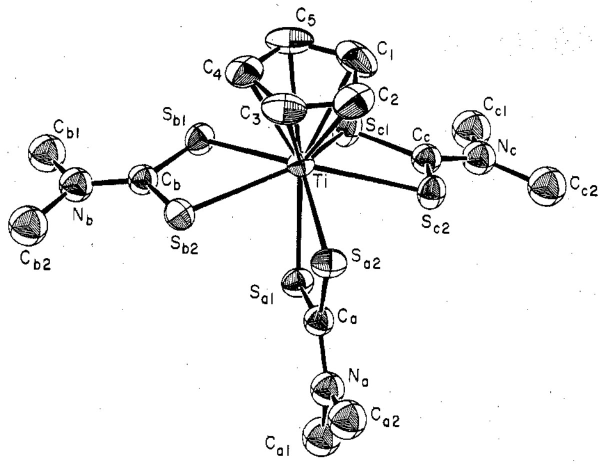

Figure 1. Model in perspective of the $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ molecule. Each atom is represented by an ellipsoid or sphere consistent with the thermal parameters in Tables I and II.

Table I. Final Atomic Fractional Coordinates and Isotropic Thermal Parameters for $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3\cdot C_6H_6$[a]

atom	10^4x	10^4y	10^4z	B,[b] $Å^2$
Ti	3843.3 (8)	2427.2 (8)	909.0 (4)	2.13 (2)
S_{a1}	1464 (1)	2979 (1)	1069 (1)	2.86 (3)
S_{a2}	3281 (1)	4544 (1)	590 (1)	2.92 (4)
S_{b1}	2740 (1)	404 (1)	643 (1)	2.94 (3)
S_{b2}	2549 (1)	2274 (1)	−198 (1)	3.13 (4)
S_{c1}	3630 (2)	1221 (1)	1882 (1)	2.95 (4)
S_{c2}	4178 (1)	3654 (1)	1915 (1)	2.96 (3)
N_a	797 (5)	5191 (5)	750 (2)	3.7 (1)
N_b	1459 (5)	155 (5)	−469 (2)	3.5 (1)
N_c	3927 (5)	2423 (5)	2917 (2)	3.5 (1)
C_a	1719 (5)	4340 (5)	800 (2)	2.7 (1)
C_b	2173 (5)	856 (5)	−69 (2)	2.7 (1)
C_c	3931 (5)	2438 (5)	2318 (2)	2.8 (1)
C_{a1}	−514 (7)	5015 (7)	956 (3)	4.5 (1)
C_{a2}	1073 (7)	6365 (7)	529 (3)	4.8 (1)
C_{b1}	1169 (7)	−1068 (6)	−331 (3)	4.4 (1)
C_{b2}	878 (7)	598 (7)	−1062 (3)	4.9 (1)
C_{c1}	3669 (7)	1343 (7)	3244 (3)	4.7 (1)
C_{c2}	4149 (7)	3516 (7)	3275 (3)	4.7 (1)
C_1	6181 (6)	2187 (9)	1257 (3)	4.3 (2)
C_2	6052 (6)	3217 (6)	894 (4)	4.1 (3)
C_3	5596 (6)	2868 (6)	301 (3)	3.7 (2)
C_4	5439 (6)	1643 (6)	297 (3)	3.4 (2)
C_5	5801 (6)	1229 (6)	885 (3)	3.6 (2)
C_6	−1450 (10)	3982 (9)	−2339 (5)	7.0 (2)
C_7	−2402 (9)	3365 (9)	−2100 (4)	6.4 (2)
C_8	−2343 (9)	2139 (9)	−2096 (4)	6.6 (2)
C_9	−1337 (10)	1554 (9)	−2330 (5)	7.1 (2)
C_{10}	−365 (10)	2171 (10)	−2559 (5)	7.3 (2)
C_{11}	−409 (10)	3405 (10)	−2564 (5)	7.4 (2)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Isotropic thermal parameters for Ti, the six S atoms, and the five C atoms of the cyclopentadienyl ligand were calculated from $B = 4[V^2\det(\beta_{ij})]^{1/3}$. See Table II for anisotropic thermal parameters.

Table II. Final Anisotropic Thermal Parameters for $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	2.06 (3)	1.94 (3)	2.48 (4)	0.10 (3)	0.41 (3)	0.08 (3)
S_{a1}	2.49 (5)	2.70 (5)	3.62 (6)	0.10 (4)	0.68 (4)	0.00 (5)
S_{a2}	3.20 (6)	2.26 (5)	3.72 (6)	0.16 (5)	0.56 (4)	0.69 (4)
S_{b1}	3.22 (6)	2.38 (5)	3.34 (6)	−0.22 (5)	0.46 (4)	−0.19 (4)
S_{b2}	3.35 (6)	3.29 (6)	2.77 (6)	0.24 (5)	0.12 (4)	0.06 (5)
S_{c1}	4.54 (7)	2.14 (5)	2.67 (6)	0.00 (5)	0.56 (4)	0.08 (4)
S_{c2}	3.71 (6)	2.31 (5)	3.03 (6)	−0.24 (5)	0.32 (4)	−0.09 (4)
C_1	2.1 (2)	10.1 (6)	4.0 (3)	1.1 (3)	0.4 (2)	−0.3 (4)
C_2	2.4 (2)	4.4 (3)	8.4 (5)	−1.0 (2)	1.7 (3)	−1.6 (3)
C_3	2.7 (2)	4.7 (3)	5.3 (3)	0.3 (2)	1.8 (2)	1.4 (3)
C_4	2.5 (2)	4.5 (3)	4.6 (3)	0.2 (2)	1.6 (2)	−0.4 (2)
C_5	2.7 (2)	4.2 (3)	5.8 (4)	1.1 (2)	1.7 (2)	1.7 (3)

[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 $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$.

slight (~4%) but systematic decrease throughout the first half of the data collection; the data were appropriately adjusted by a least-squares procedure.

A total of 5916 unique reflections having $2\theta \leq 54.83°$ (the number of data in the limiting Cu $K\alpha$ sphere) was scanned. Based on the cited dimensions of the crystal and a linear absorption coefficient of $8.2\ cm^{-1}$, the maximum error resulting from neglect of absorption corrections was estimated to be <10% in any intensity and <5% in any structure amplitude. Since the crystal was mounted in a glass capillary, reliable determination of the indices of the crystal faces was difficult. Thus, an absorption correction was not made. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factors. Those 5072 reflections having $|F_o| > 1.58\sigma_F$, where σ_F is defined elsewhere,[22] were retained as "observed" for the structure analysis.

The structure was solved by application of Patterson and Fourier techniques and was refined by full-matrix least squares using anisotropic thermal parameters for Ti, the six S atoms, and the five C atoms of the cyclopentadienyl ligand; isotropic thermal parameters were employed for the remaining 12 nonhydrogen atoms of the dithiocarbamate ligands and the six C atoms of the benzene molecule. Unit weighting was used throughout the refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$. In the final cycle of refinement no parameter varied by more then 0.32 (the average was 0.06) of its estimated standard deviation, and the discrepancy indices

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

and

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

were 0.077 and 0.079, respectively. A final difference Fourier showed no anomalous features; the strongest peak (0.80 e/Å^3) was near the position of a methyl carbon atom.

Scattering factors for Ti^0, S^0, N^0, and C^0 were taken from Cromer and Mann.[23] Anomalous dispersion corrections, real and imaginary, for Ti and S were obtained from Cromer.[24] Calculations were performed on Prime 300 and IBM 370/168 computers using programs listed in a previous paper.[1]

Results

Final atomic coordinates and isotropic thermal parameters for $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3\cdot C_6H_6$ are presented in Table I; anisotropic thermal parameters for the titanium, sulfur, and the carbon atoms of the cyclopentadienyl ligand are given in Table II.[25] The molecular geometry 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 TiS_6C_5 coordination group are listed in Table III, while distances and angles in the *N*,*N*-dimethyldithiocarbamate ligands, the cyclopentadienyl ligand, and the benzene solvate molecule are presented in Tables IV and V. The results of selected mean plane calculations are summarized in Table VI.

A packing diagram is presented in Figure 2. There are only four nonbonded intermolecular contacts that are appreciably less than the sum of the van der Waals radii: $C_4\cdots C_{b1}$ (3.50 Å), $C_5\cdots C_{b1}$ (3.46 Å), $C_{a1}\cdots C_{a2}$ (3.67 Å), and $C_{a2}\cdots C_{b1}$ (3.52 Å). All of these contacts involve at least one methyl group.

Discussion

Crystals of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3\cdot C_6H_6$ contain discrete molecules of the complex in which the titanium atom is symmetrically bound to the planar cyclopentadienyl ligand and to the six sulfur atoms of the three bidentate *N*,*N*-dimethyldithiocarbamate ligands (Figure 1). If the cyclo-

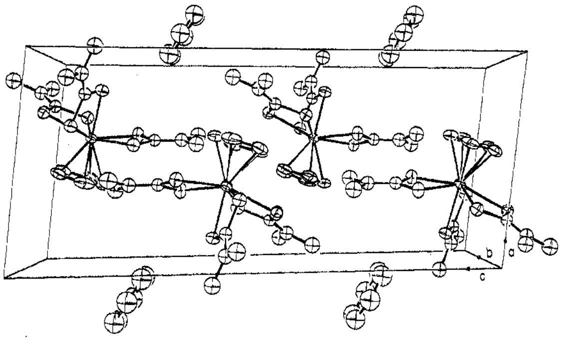

Figure 2. Model in perspective to illustrate the packing of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ and C_6H_6 molecules in the crystal. The contents of one unit cell are viewed normal to the (010) plane.

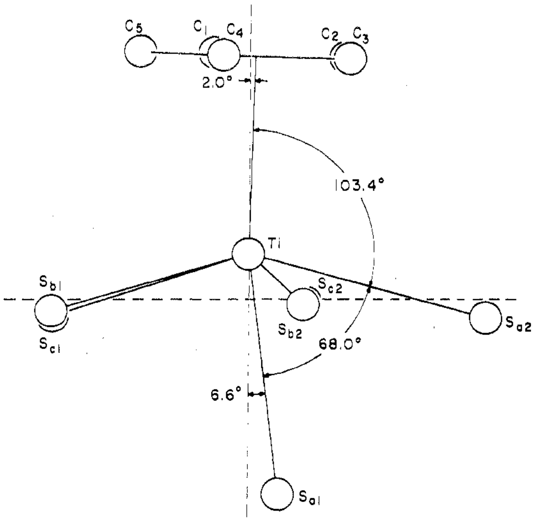

Figure 3. Projection of the TiS_6C_5 coordination group of $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ on the quasi-mirror plane.

pentadienyl ligand is considered to occupy a single coordination site,[1] the titanium atom is seven-coordinate and the molecule possesses an approximate pentagonal-bipyramidal structure. The $\eta^5\text{-}C_5H_5$ ligand occupies an axial position; dithiocarbamate ligand a spans the other axial position and one equatorial position, while dithiocarbamate ligands b and c take the remaining equatorial positions.

The maximum permissible symmetry for this configuration, $C_s\text{-}m$, is closely approximated, with the titanium atom, the centroid of the cyclopentadienyl ring (Cent Cp), and sulfur atoms S_{a1} and S_{a2} lying in the quasi-mirror plane, and dithiocarbamate ligands b and c being symmetrically disposed about this plane. A projection of the TiS_6C_5 coordination group onto the quasi-mirror plane is shown in Figure 3; the mean displacement of the atoms Ti, S_{a1}, S_{a2}, and Cent Cp from this plane is 0.002 Å (cf. Table VI). The five equatorial sulfur atoms are coplanar to within 0.09 Å (cf. Table VI), and the equatorial plane is virtually perpendicular to the quasi-mirror plane (dihedral angle, 89.4°). The dihedral angle between the plane of the cyclopentadienyl ligand and the quasi-mirror plane is 90.0°, with displacements of the five carbon atoms from the mean plane of the ligand being ≤0.002 Å (cf. Table VI). The dihedral angle between the plane of the cyclopentadienyl ligand and the equatorial plane is 2.1°.

The coordination polyhedron may be further characterized by values of the δ shape parameters defined by Muetterties and Guggenberger.[26] Observed δ values are 48.4, 47.5, and −74.4° for the polyhedral faces which intersect along the edges $S_{a1}\cdots S_{b2}$, $S_{a1}\cdots S_{c2}$, and $S_{b2}\cdots S_{c2}$, respectively; the third δ value is negative because the edge $S_{b2}\cdots S_{c2}$ is not an exterior polyhedral edge. In view of the presence of chelating ligands, the observed δ values are in satisfactory agreement with those expected (54.4, 54.4, and −72.8°) for an idealzed D_{5h} pentagonal bipyramid. The observed δ values differ markedly from theoretical values for the C_{3v} monocapped octahedron (16.2, 16.2, and 16.2°) and the C_{2v} monocapped trigonal prism (0.0, 0.0, and 41.5°).

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

atoms	length, A	atoms	angle, deg
Ti-S_{a1}	2.565 (2)		
Ti-S_{a2}	2.570 (2)		
Ti-S_{b1}	2.609 (2)		
Ti-S_{b2}	2.666 (2)		
Ti-S_{c1}	2.612 (2)		
Ti-S_{c2}	2.643 (2)		
Ti-C_1	2.420 (6)	C_1-Ti-C_2	34.3 (3)
Ti-C_2	2.422 (6)	C_2-Ti-C_3	33.8 (2)
Ti-C_3	2.425 (6)	C_3-Ti-C_4	33.9 (2)
Ti-C_4	2.421 (6)	C_4-Ti-C_5	33.7 (2)
Ti-C_5	2.421 (6)	C_5-Ti-C_1	33.7 (3)
$S_{a1}\cdots S_{a2}$[b]	2.872 (2)	S_{a1}-Ti-S_{a2}	68.03 (5)
$S_{a1}\cdots S_{b1}$	3.403 (2)	S_{a1}-Ti-S_{b1}	82.26 (5)
$S_{a1}\cdots S_{b2}$	3.271 (2)	S_{a1}-Ti-S_{b2}	77.39 (5)
$S_{a1}\cdots S_{c1}$	3.348 (2)	S_{a1}-Ti-S_{c1}	80.60 (5)
$S_{a1}\cdots S_{c2}$	3.239 (2)	S_{a1}-Ti-S_{c2}	76.92 (5)
$S_{a2}\cdots S_{b2}$	3.177 (2)	S_{a2}-Ti-S_{b2}	74.69 (5)
$S_{a2}\cdots S_{c2}$	3.166 (2)	S_{a2}-Ti-S_{c2}	74.78 (5)
$S_{b1}\cdots S_{b2}$[b]	2.842 (2)	S_{b1}-Ti-S_{b2}	65.19 (5)
$S_{b1}\cdots S_{c1}$	2.963 (2)	S_{b1}-Ti-S_{c1}	69.16 (5)
$S_{c1}\cdots S_{c2}$[b]	2.838 (2)	S_{c1}-Ti-S_{c2}	65.38 (5)
$C_1\cdots S_{c1}$	3.285 (7)	C_1-Ti-S_{c1}	81.4 (2)
$C_1\cdots S_{c2}$	3.143 (7)	C_1-Ti-S_{c2}	76.6 (2)
$C_2\cdots S_{c2}$	3.193 (7)	C_2-Ti-S_{c2}	78.0 (2)
$C_2\cdots S_{a2}$	3.195 (7)	C_2-Ti-S_{a2}	79.5 (2)
$C_3\cdots S_{a2}$	3.162 (6)	C_3-Ti-S_{a2}	78.5 (2)
$C_3\cdots S_{b2}$	3.229 (7)	C_3-Ti-S_{b2}	78.6 (2)
$C_4\cdots S_{b2}$	3.092 (6)	C_4-Ti-S_{b2}	74.7 (2)
$C_4\cdots S_{b1}$	3.262 (6)	C_4-Ti-S_{b1}	80 8 (2)
$C_5\cdots S_{b1}$	3.229 (7)	C_5-Ti-S_{b1}	79.8 (2)
$C_5\cdots S_{c1}$	3.328 (6)	C_5-Ti-S_{c1}	82.7 (2)
Ti-Cent Cp[c]	2.103 (6)	Cent Cp-Ti-S_{a1}	171.4 (2)
Cent Cp$\cdots S_{a2}$	3.678 (7)	Cent Cp-Ti-S_{a2}	103.4 (2)
Cent Cp$\cdots S_{b1}$	3.740 (7)	Cent Cp-Ti-S_{b1}	104.6 (2)
Cent Cp$\cdots S_{b2}$	3.686 (7)	Cent Cp-Ti-S_{b2}	100.6 (2)
Cent Cp$\cdots S_{c1}$	3.791 (7)	Cent Cp-Ti-S_{c1}	106.5 (2)
Cent Cp$\cdots S_{c2}$	3.690 (7)	Cent Cp-Ti-S_{c2}	101.4 (2)
	Av Values[d]		
Ti-S	2.611 (2, 30, 55)		
Ti-C	2.422 (6, 1, 3)	C-Ti-C	33.9 (2, 2, 4)
$S_{a1}\cdots S_{eq}$[e]	3.23 (0.2, 14, 36)	S_{a1}-Ti-S_{eq}	77.0 (0.5, 37, 90)
$S_{eq}\cdots S_{eq}$	3.00 (0.2, 14, 18)	S_{eq}-Ti-S_{eq}	69.8 (0.5, 39, 71)
C$\cdots S_{eq}$	3.21 (0.7, 6, 12)	C-Ti-S_{eq}	79.1 (2, 18, 44)
Cent Cp$\cdots S_{eq}$	3.72 (0.7, 4, 7)	Cent Cp-Ti-S_{eq}	103.3 (2, 18, 32)

[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}.

The principal distortions from ideal pentagonal-bipyramidal geometry are very similar to those observed for the isostructural $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$.[1] In both structures, the metal atom is displaced from the equatorial plane by the same amount (0.60 Å) in the direction of the C_5H_5 ligand. The centroid of the C_5H_5 ring is rotated off the quasi-fivefold

Table IV. Bond Lengths (A) 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]	2.872 (2)	2.842 (2)	2.838 (2)	2.840 (2, 2, 2)[d]	S_1-C-S_2	114.0 (3)	113.0 (3)	113.2 (3)	113.1 (3, 1, 1)[d]
C-S_1	1.701 (6)	1.708 (6)	1.707 (6)	1.706 (6, 8, 19)	C-S_1-Ti	89.3 (2)	91.8 (2)	91.1 (2)	90.8 (2, 7, 10)[d]
C-S_2	1.725 (5)	1.700 (6)	1.694 (6)		C-S_2-Ti	88.7 (2)	90.0 (2)	90.3 (2)	
C-N	1.347 (7)	1.346 (7)	1.343 (7)	1.345 (7, 2, 2)	S_1-C-N	123.8 (4)	122.2 (4)	122.7 (4)	123.3 (4, 9, 15)
					S_2-C-N	122.2 (4)	124.8 (4)	124.1 (4)	
C_1-N	1.476 (8)	1.471 (9)	1.477 (9)	1.477 (9, 4, 11)	C_1-N-C	121.3 (5)	122.1 (5)	121.9 (5)	121.5 (5, 5, 9)
C_2-N	1.471 (9)	1.476 (9)	1.488 (9)		C_2-N-C	122.0 (5)	121.2 (5)	120.6 (5)	
					C_1-N-C_2	116.6 (5)	116.6 (5)	117.4 (5)	116.9 (5, 4, 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 V. Bond Lengths and Bond Angles in the η^5-Cyclopentadienyl Ligand and the Benzene Solvate Molecule[a]

atoms	length, A	atoms	angle, deg
	(a) η^5-C_5H_5		
C_1-C_2	1.429 (11)	C_1-C_2-C_3	107.4 (6)
C_2-C_3	1.410 (10)	C_2-C_3-C_4	108.1 (6)
C_3-C_4	1.411 (9)	C_3-C_4-C_5	108.3 (6)
C_4-C_5	1.405 (9)	C_4-C_5-C_1	108.3 (6)
C_5-C_1	1.403 (11)	C_5-C_1-C_2	107.9 (6)
av C-C[b]	1.412 (10, 7, 17)	av C-C-C[b]	108.0 (6, 3, 6)
	(b) C_6H_6		
C_6-C_7	1.359 (13)	C_6-C_7-C_8	119.3 (9)
C_7-C_8	1.404 (13)	C_7-C_8-C_9	121.1 (10)
C_8-C_9	1.378 (13)	C_8-C_9-C_{10}	119.8 (10)
C_9-C_{10}	1.364 (13)	C_9-C_{10}-C_{11}	119.8 (10)
C_{10}-C_{11}	1.414 (14)	C_{10}-C_{11}-C_6	119.7 (10)
C_{11}-C_6	1.393 (13)	C_{11}-C_6-C_7	120.4 (10)
av C-C[b]	1.385 (13, 18, 29)	av C-C-C[b]	120.0 (10, 5, 11)

[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 VI

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}	0.9760	−0.1367	−0.1696	2.2414
2	Ti, S_{a1}, S_{a2}, Cent Cp	−0.2156	−0.3129	−0.9250	−3.5233
3	S_{a1}, S_{a2}, C_a, N_a, C_{a1}, C_{a2}	−0.2302	−0.3022	−0.9250	−3.5032
4	S_{b1}, S_{b2}, C_b, N_b, C_{b1}, C_{b2}	0.8906	−0.2918	−0.3489	1.7273
5	S_{c1}, S_{c2}, C_c, N_c, C_{c1}, C_{c2}	−0.9740	0.1930	−0.1191	−3.3198
6	C_1, C_2, C_3, C_4, C_5	0.9758	−0.1074	−0.1906	4.9816
7	C_6, C_7, C_8, C_9, C_{10}, C_{11}	−0.4330	−0.0236	−0.9011	4.9256

Atoms and Their Displacements from Planes, A

1 S_{a2}, 0.083; S_{b1}, 0.005; S_{b2}, −0.057; S_{c1}, 0.054; S_{c2}, −0.086; Ti, −0.599
2 Ti, 0.003; S_{a1}, −0.001; S_{a2}, 0.000; Cent Cp, −0.002
3 S_{a1}, 0.000; S_{a2}, 0.011; C_a, −0.006; N_a, −0.026; C_{a1}, 0.017; C_{a2}, 0.004; Ti, 0.047
4 S_{b1}, 0.042; S_{b2}, −0.021; C_b, −0.023; N_b, −0.020; C_{b1}, −0.025; C_{b2}, 0.046; Ti, −0.008
5 S_{c1}, −0.010; S_{c2}, −0.005; C_c, 0.017; N_c, 0.013; C_{c1}, −0.005; C_{c2}, −0.010; Ti, −0.060
6 C_1, −0.001; C_2, 0.002; C_3, −0.002; C_4, 0.001; C_5, 0.000
7 C_6, −0.011; C_7, 0.005; C_8, 0.005; C_9, −0.009; C_{10}, 0.003; C_{11}, 0.007

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

axis (Figure 3) by 2.0° in the direction of S_{a2} (1.9° in the Zr compound), and the Ti–S_{a1} bond is rotated off the quasi-fivefold axis by 6.6° (8.9° in the Zr compound). The bond from the metal to the axial sulfur atom lies closer to the quasi-fivefold axis in the Ti compound because the shorter metal–sulfur bonds in the Ti case permit dithiocarbamate ligand a to subtend a larger angle at Ti (68.0°) than at Zr (66.1°).

Of primary interest in this structure is the crowding among sulfur atoms in the equatorial plane and the effect of this crowding on the Ti–S bond distances. The average of the interligand $S_{eq}\cdots S_{eq}$ contacts (S_{eq} refers to an equatorial sulfur atom) of 3.10 Å for $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ is similar to the corresponding average of 3.05 Å for $Ti[S_2CN(CH_3)_2]_3Cl$[11] and is significantly less than the average of 3.22 Å for $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$.[1] All three averages are appreciably less than the van der Waals diameter for sulfur (3.45 Å[19]). Thus, the equatorial plane is more crowded in $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ than in the Zr analogue, as expected. However, it was also anticipated that substitution of a cyclopentadienyl ligand for a chlorine atom might lead to more severe crowding among the equatorial sulfur atoms in $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ than in $Ti[S_2CN(CH_3)_2]_3Cl$. Such is not the case. In fact, the $S_{eq}\cdots S_{eq}$ contacts are slightly longer in the cyclopentadienyl complex. The longer $S_{eq}\cdots S_{eq}$ contacts are possible because of a marked (0.10 Å) expansion of the averaged Ti–S bond length from 2.512 Å in $Ti[S_2CN(CH_3)_2]_3Cl$[11] to 2.611 Å in $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$. Thus, the increased steric requirements of the cyclopentadienyl ligand compared to a chlorine atom result in longer Ti–S bonds rather than shorter $S_{eq}\cdots S_{eq}$ contacts.

It seems likely that repulsive interactions among the equatorial sulfur atoms[27] and repulsive interactions between the equatorial sulfur atoms and the axial ligands both contribute to the lengthening of the Ti–S bonds. In $Ti[S_2CN(CH_3)_2]_3Cl$ and in $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$, the averaged distances between the equatorial and axial ligands are not signicantly less than the sum of the van der Waals radii.[18] However, in $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ all of the $S_{a1}\cdots S_{eq}$ and $C\cdots S_{eq}$ distances (Table III) are less than the van der Waals contact, and the averaged interligand $S_{a1}\cdots S_{eq}$ and $C\cdots S_{eq}$ contacts are less than the van der Waals contacts by 0.13 and 0.22 Å, respectively. If repulsive interactions between the equatorial and axial ligands in $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ were not important, one might have expected shorter Ti–S distances and shorter $S_{eq}\cdots S_{eq}$ contacts; an averaged interligand $S_{eq}\cdots S_{eq}$ contact as short as 2.92 Å has been observed in $Ru[S_2CN(CH_3)_2]_3I$.[13]

The individual Ti–S bond lengths in $(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$ follow a very interesting pattern. The Ti–S bonds to the two equatorial dithiocarbamate ligands (2.609–2.666 Å, av 2.633 Å) are significantly longer than the Ti–S bonds to the ligand which spans axial and equatorial sites (2.565 and 2.570 Å). The average increase in the Ti–S bond lengths on going from $Ti[S_2CN(CH_3)_2]_3Cl$ to $(\eta^5\text{-}C_5H_5)Ti[S_2CN\text{-}$

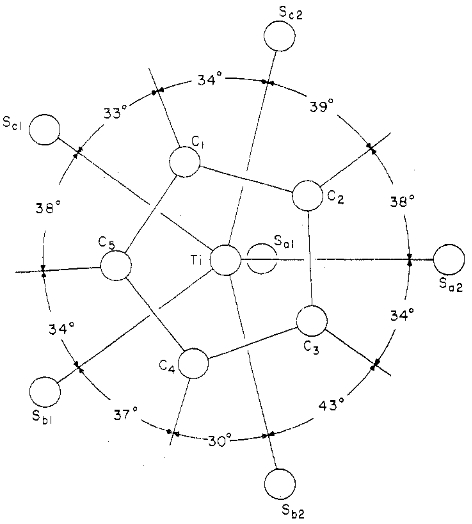

Figure 4. Projection of the TiS_6C_5 coordination group of (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$ on the plane of the η^5-cyclopentadienyl ligand.

$(CH_3)_2]_3$ is 0.13 Å for the equatorial ligands, but only 0.04 Å for the spanning ligand. Thus, the increased steric requirements of the η^5-C_5H_5 ligand result primarily in an expansion and, presumably, a weakening of the Ti–S bonds to the equatorial ligands. It seems likely that the low-temperature kinetic process in (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$,[3] which involves exchange of dithiocarbamate methyl groups between the two inequivalent sites in the equatorial ligands, becomes important because of the weaker Ti–S_{eq} bonds. The low-temperature process is not observed in (η^5-C_5H_5)Zr[$S_2CN(CH_3)_2$]$_3$ where the lengths of the Zr–S bonds to the equatorial ligands (2.683–2.717 Å, av 2.701 Å) exceed the lengths of the bonds to the spanning ligand (2.681 and 2.655 Å) by a much smaller amount. In (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$, as in the Zr analogue, the two Ti–S bonds to each equatorial ligand are not equal but vary in accord with the quasi-mirror symmetry in the coordination group. The Ti–S_{b2} and Ti–S_{c2} bonds are longer than Ti–S_{b1} and Ti–S_{c1} (by ~0.04 Å) presumably because of the off-axis positioning of sulfur atom S_{a1} and the C_5H_5 ligand (cf. Figure 3); the $S_{a1}\cdots S_{eq}$ and $C\cdots S_{eq}$ contacts are ~0.12 Å shorter for S_{b2} and S_{c2} than for S_{b1} and S_{c1}.

The Ti–C bond lengths are remarkably uniform with all five Ti–C distances lying in the range 2.420–2.425 Å (av 2.422 Å; cf. Table III). The mean Ti–C bond length for a large number of four-coordinate Ti complexes containing η^5-C_5H_5 ligands varies from 2.31 to 2.43 Å with a majority between 2.35 and 2.38 Å.[30-40] The Ti–C distances in (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$ are at the upper limit of this range, as expected for the more crowded seven-coordinate complex. The distance from the Ti atom to the centroid of the C_5H_5 ring (2.103 Å) exceeds the mean Ti–Cent Cp distance for four-coordinate Ti complexes (2.06 Å[30-38,41]) by ~0.04 Å. The increase in the Ti–Cent Cp distance on changing the coordination number from 4 to 7 is small in view of the 0.10-Å increase in the averaged Ti–S bond length on going from Ti[$S_2CN(CH_3)_2$]$_3$Cl to (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$, both seven-coordinate complexes. The Ti–C_5H_5 bond appears to be fairly strong and its length rather invariant; consequently, most of the strain in (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$ is relieved by expansion of the Ti–S bonds.

Carbon–carbon bond distances within the cyclopentadienyl ligand are quite uniform (1.403–1.429 Å; cf. Table V), and the mean C–C distance (1.412 Å) is in good agreement with the expected value[42] of ~1.42 Å and with the average C–C bond length in other cyclopentadienyl–titanium complexes (1.34–1.44 Å[30-40]). The C–C–C bond angles in the cyclopentadienyl ring (107.4–108.3°, cf. Table V) average to 108.0°, the internal angle for a regular pentagon. The cyclopentadienyl ring adopts a staggered configuration with respect to the five sulfur atoms of the pentagonal girdle (see Figure 4); the ring is rotated only ~2° from the exactly staggered configuration.

Bond lengths and angles within the dithiocarbamate ligands (Table IV) are consistent with those found in other dithiocarbamate structures.[1,11-17,43-58] The dimensions of the three dithiocarbamate ligands are essentially identical except that ligand a, which spans the axial and an equatorial position, has a slightly larger bite (by 0.032 Å), a larger S–C–S bite angle (by 0.9°), and correspondingly smaller C–S–Ti angles than ligands b and c. The averaged bite of the three dithiocarbamate ligands in (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$ (2.851 Å) is nearly identical with the averaged bite in Ti[$S_2CN(CH_3)_2$]$_3$Cl (2.859 Å)[11] and ~0.04 Å shorter than the averaged bite in (η^5-C_5H_5)Zr[$S_2CN(CH_3)_2$]$_3$ (2.892 Å).[1] The six atoms of each S_2CNC_2 dithiocarbamate skeleton are nearly coplanar (Table VI), the average displacement of the 18 atoms of the three ligands from their respective mean planes being 0.017 Å (maximum displacement 0.046 Å). Displacements of the Ti atom from the mean planes of the ligands are small: 0.047, 0.008, and 0.060 Å for ligands a, b, and c, respectively.

The benzene solvate molecule is planar (Table VI), and the six C–C bond distances (Table V) are equal within experimental uncertainty. The mean C–C bond length of 1.385 Å is in excellent agreement with literature values of 1.397 Å[59] for gaseous benzene and 1.392 Å[60] for crystalline benzene.

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Registry No. (η^5-C_5H_5)$_2$TiCl$_2$, 1271-19-8; (η^5-C_5H_5)Ti[$S_2CN(CH_3)_2$]$_3$·C_6H_6, 67891-23-0.

Supplementary Material Available: A listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Stereochemically Nonrigid Pentacoordinate Nickel(II) Complexes. X-ray Structure of Bromotetrakis(trimethylphosphine)nickel(II) Tetrafluoroborate and Solution Study of $[NiX(PMe_3)_4]BF_4$ (X = Cl, Br, I)[1]

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New cationic Ni(II) complexes $[NiX(PMe_3)_4]BF_4$ have been isolated and studied thoroughly in the solid state and in dichloromethane solution, using the X-ray diffraction technique, variable-temperature electronic spectroscopy, and $^{31}P\{^1H\}$ Fourier mode NMR. The crystal and molecular structure of bromotetrakis(trimethylphosphine)nickel(II) tetrafluoroborate has been determined from the three-dimensional X-ray data collected by counter methods. Full-matrix least-squares refinement of the structure has led to a final conventional *R* factor on *F* of 0.072. The crystals have orthorhombic symmetry, space group *Pbca*, with eight molecules per unit cell of dimensions $a = 16.029\ (4)$ Å, $b = 25.179\ (4)$ Å, and $c = 11.413\ (2)$ Å. The crystallographically derived density is 1.527 g cm^{-3}. The crystal chemical unit consists of separate cationic $[NiX(PMe_3)_4]^+$ and anionic BF_4^- entities. The geometry around the Ni atom is a somewhat distorted version of a trigonal bipyramid of C_{2v} symmetry with the bromine atom in an equatorial position. The two axial Ni–P bond distances are 2.247 (4) and 2.244 (4) Å while the slightly longer equatorial Ni–P lengths are 2.257 (5) and 2.290 (5) Å. The Ni–Br bond distance is 2.515 (2) Å and the P_{ax}–Ni–P_{ax} bond angle is 167.1 (2) Å. Solid-state and solution electronic spectra of $[NiX(PMe_3)_4]BF_4$ (X = Cl, Br, I) have been measured at 295, 180, and 77 K and the results compared to those of the variable-temperature $^{31}P\{^1H\}$ Fourier mode NMR spectra. The three complexes have the C_{2v} structure in the solid state and in solution, at room and low temperature, provided an excess of PMe_3 is present to prevent dissociation. They are stereochemically nonrigid at 295 K on the NMR time scale. Phosphorus exchange has been shown to occur through an intramolecular rearrangement following the Berry pseudorotation process. The rate of this rearrangement is in the order $k_{Cl} > k_{Br} > k_I$. The measured free energies of activation are $\Delta G^* = 6.6 \pm 0.2$ (Cl), 7.8 ± 0.2 (Br), and 8.2 ± 0.2 (I) kcal mol^{-1} at 169 K.

I. Introduction

Although the existence of low-spin molecular NiX_2L_3 and cationic $[NiL_5]^{2+}$ complexes is now well established with monodentate phosphine, phosphite, arsine, and stibine ligands,[3,4] only few cationic $[NiXL_4]^+$ complexes have been reported: $[NiH(PMe_3)_4]^+$,[5] $[Ni(CH_3)(PMe_3)_4]^+$,[6] $[NiX(PHEt)_4]^+$,[7] $[NiBr(P(OMe)_3)_4]^+$.[8]

Recently,[9] we have communicated the first NMR evidence that when X = halide, the pentacoordinate NiX_2L_3 and $(NiXL_4)X$ species are closely related in dichloromethane solution by the equilibrium

$$NiX_2(PMe_3)_3 + PMe_3 \underset{295\ K}{\overset{180\ K}{\rightleftharpoons}} [NiX(PMe_3)_4]^+X^- \quad (1)$$

As a continuing part of this investigation, initiated to obtain quantitative information on how different factors (nature of X and L, solvent, temperature) influenced the existence and the stereochemistry of each species, we have prepared the