

Articles

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Stereochemistry of Eight-Coordinate Dodecahedral Complexes of the Type MX_4Y_4 . 3. Kinetics of Metal-Centered Rearrangement and $\text{C}=\text{N}$ Bond Rotation in Titanium(IV) and Zirconium(IV) N,N -Dialkylthiocarbamates

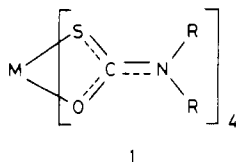
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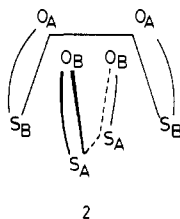
The kinetics of metal-centered rearrangement and rotation about the $\text{C}=\text{N}$ bonds in N,N -dimethylmonothiocarbamate ligands of the eight-coordinate dodecahedral complexes $[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$) have been studied by total line-shape analysis of variable-temperature ^1H NMR spectra. The barriers ΔG^\ddagger to metal-centered rearrangement are 9–12 kcal/mol; ΔG^\ddagger values for $\text{C}=\text{N}$ rotation are ~ 17 –20 kcal/mol. The $[\text{M}(\text{Me}_2\text{mtc})_4]$ complexes rearrange much more slowly than analogous dithiocarbamates $[\text{M}(\text{R}_2\text{dtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$; $\text{R} = \text{Et}, n\text{-Pr}$), which are still nonrigid on the NMR time scale at -140°C . This difference in the behavior of the mtc and dtc complexes points to a polytopal rearrangement mechanism. Also reported are kinetic data for exchange of inequivalent isopropyl methyl groups in $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$: $\Delta G^\ddagger(25^\circ\text{C}) = 18.4 \pm 0.1$ kcal/mol; $\Delta H^\ddagger = 16.4 \pm 0.3$ kcal/mol; $\Delta S^\ddagger = -6.7 \pm 0.7$ eu. The latter process involves rotation about the isopropyl–nitrogen ($\text{C}-\text{N}$) single bonds and rotation about the $\text{C}=\text{N}$ partial double bond.

Introduction

Previous papers from this laboratory have described the preparation, characterization, and structure of eight-coordinate titanium(IV) and zirconium(IV) N,N -dialkylmonothiocarbamate complexes, $[\text{M}(\text{R}_2\text{mtc})_4]$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}$) (**1**).¹⁻³



X-ray diffraction studies³ have established that the N,N -diethyl derivatives, $[\text{M}(\text{Et}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$), exist in the solid state as the dodecahedral stereoisomer that has an $mmmm$ ligand wrapping pattern⁴ and a C_{2v} arrangement of the sulfur and oxygen donor atoms. Two of the sulfur atoms occupy dodecahedral A sites and two occupy B sites so as to give an all-cis arrangement with the four sulfur atoms clustered on one side of the coordination polyhedron and the four oxygen atoms on the other side. This stereoisomer, of C_{2v} symmetry, is represented schematically in **2**. It is the most polar of the



six dodecahedral stereoisomers that have the $mmmm$ ligand wrapping pattern.⁵ The dipole moments of $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ (4.49 ± 0.11 D) and $[\text{Zr}(\text{Et}_2\text{mtc})_4]$ (3.61 ± 0.16 D) in benzene solution are relatively large, indicating that the C_{2v} stereo-

isomer is the predominant species in solution as well.² Low-temperature ^1H NMR spectra of the N,N -dimethyl derivatives, $[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$), can also be interpreted in terms of the C_{2v} stereoisomer. Variable-temperature ^1H NMR spectra exhibit evidence of two distinct kinetic processes: (i) metal-centered rearrangement and (ii) rotation about the $\text{C}=\text{N}$ partial double bond in the monothiocarbamate (mtc) ligand. Kinetic data for these processes are reported in this paper, and the relative stereochemical rigidity of the mtc complexes is discussed in relation to the nonrigidity of analogous dithiocarbamates, $[\text{M}(\text{R}_2\text{dtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$).⁶⁻⁹ Also reported herein are kinetic data for exchange of inequivalent isopropyl methyl groups in the N,N -diisopropylmonothiocarbamate $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$.

Experimental Section

$[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$) and $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$ were prepared as described previously.²

S-Methyl N,N -dimethylthiocarbamate, $\text{MeSC}(\text{O})\text{NMe}_2$, was synthesized in dry acetonitrile by reaction of stoichiometric amounts of sodium N,N -dimethylthiocarbamate² and iodomethane that had been dried over and freshly distilled from phosphorus(V) oxide. After a reaction time of 1.5 h, the acetonitrile was pumped off and the product was extracted with dry dichloromethane, which was subsequently pumped off. Vacuum distillation at 37 – 39°C ($\sim 10^{-2}$ torr) afforded a 42% yield of a colorless liquid (lit.¹⁰ bp 55°C (5 torr)). Anal. Calcd for $\text{C}_4\text{H}_9\text{NOS}$: C, 40.31; H, 7.61; N, 11.75. Found: C, 39.92; H, 7.39; N, 11.74. ^1H NMR (CDCl_3 solution, 7.3 g/100 mL, 37°C): 2.25 (SMe) and 2.92 ppm (NMe_2) downfield from an internal reference of tetramethylsilane (3% by volume). IR (neat liquid) $\nu(\text{C}=\text{O})$ 1637 cm^{-1} .

Diphenylmethane was purified by fractional crystallization, vacuum distilled from calcium hydride, and stored over sodium hydride for at least 24 h prior to use. All other solvents were dried by refluxing over calcium hydride for at least 24 h.

^1H NMR Spectra of $[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}, \text{Zr}$). ^1H NMR spectra of a degassed 0.0267 M solution of $[\text{Ti}(\text{Me}_2\text{mtc})_4]$ in dichloromethane were recorded in triplicate in the temperature range -109 to $+44^\circ\text{C}$

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Table I. Rate Constants for Metal-Centered Rearrangement and C-N Bond Rotation in Metal *N,N*-Dimethylmonothiocarbamate Complexes

[Ti(Me ₂ mtc) ₄] ^a		[Zr(Me ₂ mtc) ₄] ^b	
temp, °C	k, s ⁻¹	temp, °C	k, s ⁻¹
A. Metal-Centered Rearrangement			
-100.8	0.80	-84.0	0.80
-96.8	1.60	-79.6	1.30
-93.2	3.00	-75.0	2.50
-91.4	4.5	-69.0	5.30
-89.8	6.9	-62.7	10.5
-86.8	10.6	-58.3	19.0
-84.2	16.3	-53.5	31.0
-81.2	25.5	-47.5	55.0
-78.0	39.4	-38.2	120
-75.1	61		
-72.5	82		
-65.5	206		
-45.5	2060		
B. C-N Bond Rotation			
-3.0	0.22	62.4	0.63
8.1	0.65	65.8	1.00
12.2	0.83	68.5	1.41
14.8	1.06	71.0	1.79
17.0	1.49	73.7	2.78
19.2	2.01	78.2	3.84
21.6	2.38	81.3	5.00
24.3	3.15	84.2	6.33
25.6	3.53	87.0	8.93
26.4	3.80	90.0	10.9
27.8	4.9	97.7	22.4
29.9	5.8		
31.6	6.2		
33.4	7.0		
35.5	8.8		
39.7	12.8		
43.9	18.2		

^a For LTP, 0.0267 M in CH₂Cl₂, relative chemical shifts (Hz at 90 MHz) and transverse relaxation times for peaks 1-4 in order of increasing field are as follows: $\nu_1 = 0.00$ Hz, $T_2 = 0.13$ -0.28 s; $\nu_2 = 1.92$ Hz, $T_2 = 0.12$ -0.25 s; $\nu_3 = 8.75$ Hz, $T_2 = 0.11$ -0.28 s; $\nu_4 = 11.64$ Hz, $T_2 = 0.11$ -0.25 s. For HTP, 0.0267 M in CH₂Cl₂, relative chemical shifts and T_2 values for the two time-averaged peaks are as follows: $\nu_{1,3} = 0.00$ Hz, $T_2 = 0.56$ -0.90 s; $\nu_{2,4} = 2.41$ Hz, $T_2 = 0.46$ -0.60 s. ^b For LTP, 0.0343 M in CD₂Cl₂: $\nu_1 = 0.00$ Hz, $T_2 = 0.11$ -0.26 s; $\nu_2 = 2.00$ -0.85 Hz, $T_2 = 0.10$ -0.26 s; $\nu_3 = 4.95$ -3.80 Hz, $T_2 = 0.07$ -0.24 s; $\nu_4 = 10.60$ -7.70 Hz, $T_2 = 0.09$ -0.24 s. For HTP, 0.0527 M in 1,1,2,2-tetrachloroethane: $\nu_{1,3} = 0.00$ Hz, $T_2 = 0.31$ s; $\nu_{2,4} = 2.40$ Hz, $T_2 = 0.31$ s.

with a Varian EM-390 90-MHz spectrometer that was locked on the methylene proton resonance of the solvent. ¹H NMR spectra of [Zr(Me₂mtc)₄] were recorded similarly in the temperature range -90 to +105 °C. In the high-temperature range (40-105 °C), 1,1,2,2-tetrachloroethane was used as the solvent. In the low-temperature range (-90 to +4 °C), higher quality spectra of [Zr(Me₂mtc)₄] were obtained by using a Bruker HX-90 spectrometer operating in the Fourier-transform mode; the solvent was dichloromethane-d₂, and the spectrometer was locked on the deuterium resonance. Probe temperatures, estimated to be accurate to ±0.5 °C, were measured by using a copper-constantan thermocouple (Bruker HX-90) or were determined from the temperature-dependent chemical shift between the inequivalent protons of methanol or 1,2-ethanediol¹¹ (Varian EM-390). In recording of the variable-temperature spectra, care was taken to minimize the common sources of error in NMR line-broadening studies,¹² as previously described.¹³

Spectra were analyzed with the line-shape program PZDMFX obtained from P. Meakin of E. I. du Pont de Nemours and Co., Inc. Calculated spectra were evaluated by qualitative comparison with

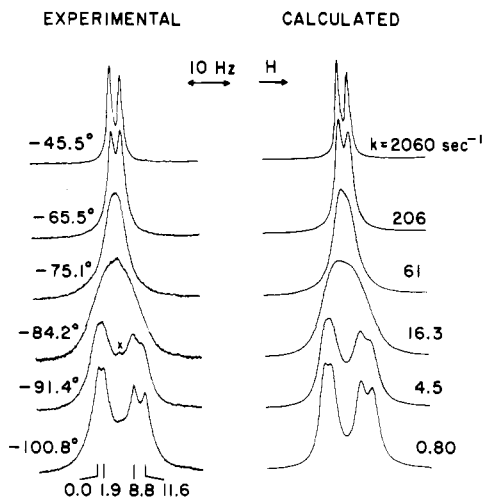


Figure 1. Observed and calculated line shapes for the methyl proton resonances of [Ti(Me₂mtc)₄], 0.0267 M in dichloromethane, at 90 MHz (low-temperature region). The peak marked with an X is due to an impurity.

observed spectra, one being overlaid on the other, supplemented by comparison of measured parameters (peak separations, relative heights of maxima and minima, and peak widths at one-fourth, half, and three-fourths maximum amplitude). The temperature-dependent transverse relaxation times, T_2 , used to generate calculated spectra of the CH₂Cl₂ and CD₂Cl₂ solutions were based on 90-MHz variable-temperature spectra of a 0.616 M solution of MeSC(O)NMe₂ in CD₂Cl₂. This compound exhibits broadening of the *N*-methyl resonance at low temperatures due to increasing solvent viscosity but no line broadening due to kinetic exchange; rotation about the C-N bond is fast on the NMR time scale,^{10,14} even at -90 °C. The following line widths (in Hz, with temperatures in parentheses in °C) observed for the *N*-methyl resonance of MeSC(O)NMe₂ were used as a basis for calculation of T_2 values for the metal complexes: 0.66 (-7.1); 0.82 (-23.8); 1.11 (-34.7); 1.39 (-53.5); 1.51 (-62.7); 1.78 (-75.0); 2.36 (-89.7). Small adjustments in the resulting T_2 values were made, subject to the constraint that the T_2 values be a smooth function of temperature, in order to optimize the fit between the calculated and observed spectra. For the high-temperature spectra of [Zr(Me₂mtc)₄] in 1,1,2,2-tetrachloroethane, T_2 is temperature independent. Chemical shifts are also temperature independent, except for low-temperature spectra of [Zr(Me₂mtc)₄], where the chemical shifts were allowed to vary in optimizing the fit between calculated and observed spectra. The final chemical shifts and T_2 values are given in the footnotes to Table I.

¹H NMR Spectra of [Ti(*i*-Pr₂mtc)₄]. ¹H NMR spectra of a degassed 0.0846 M solution of [Ti(*i*-Pr₂mtc)₄] in diphenylmethane were recorded in quadruplicate in the temperature range 31-162 °C with a Bruker HX-90 spectrometer operating in the continuous-wave mode. Rate constants for exchange of inequivalent isopropyl methyl groups were determined by comparison of observed spectra with theoretical spectra calculated by using the Binsch DNMR 3 program.¹⁵ In the slow-exchange region (31-79 °C), the chemical shift ($\delta\nu$ in Hz) exhibits a substantial, linear dependence on temperature (t in °C): $\delta\nu = 77.42 - 0.1931t$. Chemical shifts in the coalescence region were determined by extrapolation of this relation to the temperature region 80-162 °C. T_2 values were varied to optimize the fit between calculated and observed spectra; however, because the chemical shifts are relatively large, the calculated line shapes are rather insensitive to the choice of T_2 . Final T_2 values are included in the footnotes to Table III.

Results and Discussion

Metal-Centered Rearrangement and C-N Bond Rotation in [M(Me₂mtc)₄] Complexes. Variable-temperature ¹H NMR spectra of [Ti(Me₂mtc)₄] are presented in Figures 1 and 2. At -100.8 °C, this compound exhibits four methyl resonances

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Table II. Kinetic Data for Metal-Centered Rearrangement and C \rightarrow N Bond Rotation in Metal *N,N*-Dimethylmonothiocarbamate Complexes

	metal-centered rearrangement			C \rightarrow N bond rotation	
	[Ti(Me ₂ mtc) ₃ Cl] ^{a,b}	[Ti(Me ₂ mtc) ₄] ^c	[Zr(Me ₂ mtc) ₄] ^a	[Ti(Me ₂ mtc) ₄] ^c	[Zr(Me ₂ mtc) ₄] ^d
<i>T</i> _c , °C	-58.2	-84.2	-53.5	29.9	78.2
Δ <i>G</i> [‡] (<i>T</i> _c), kcal/mol	10.78 ± 0.10 ^e	9.88 ± 0.08	11.25 ± 0.05	16.75 ± 0.11	19.77 ± 0.12
Δ <i>H</i> [‡] , kcal/mol	11.2 ± 0.3	10.7 ± 0.3	9.5 ± 0.3	15.9 ± 0.6	23.7 ± 1.3
Δ <i>S</i> [‡] , eu	2.0 ± 1.6	4.5 ± 1.6	-8.2 ± 1.3	-2.7 ± 2.2	11.3 ± 3.6
Δ <i>G</i> [‡] (25 °C), kcal/mol	10.62 ± 0.14	9.39 ± 0.12	11.89 ± 0.07	16.73 ± 0.11	20.37 ± 0.10
<i>k</i> (25 °C), s ⁻¹	9.8 × 10 ⁴	7.6 × 10 ⁵	1.1 × 10 ⁴	3.4	7.1 × 10 ⁻³
<i>E</i> _a , kcal/mol	11.6 ± 0.3	11.1 ± 0.3	9.9 ± 0.3	16.5 ± 0.6	24.4 ± 1.3
log A	13.5 ± 0.3	14.0 ± 0.3	11.3 ± 0.3	12.6 ± 0.5	15.8 ± 0.8

^a In CD₂Cl₂. ^b Reference 16. ^c In CH₂Cl₂. ^d In 1,1,2,2-tetrachloroethane. ^e The uncertainties in the activation parameters are random errors estimated at the 95% confidence level.

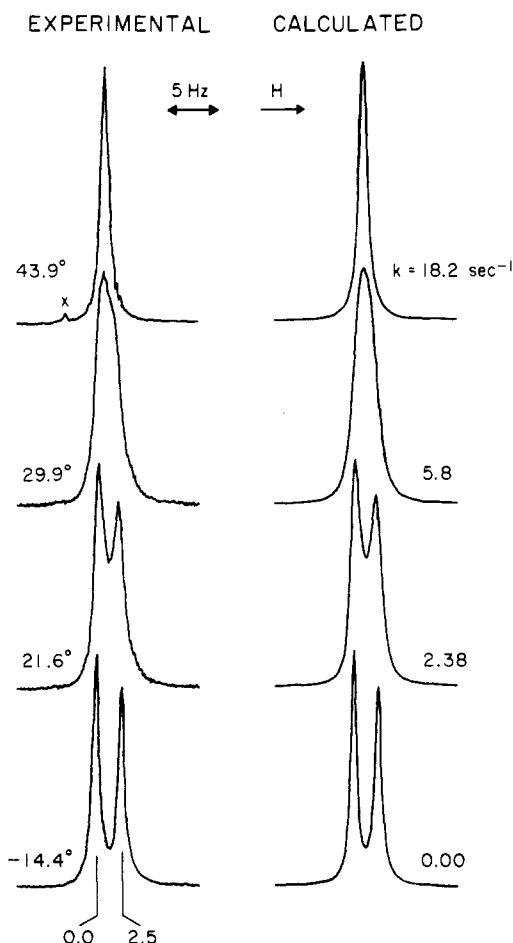


Figure 2. Observed and calculated line shapes for the methyl proton resonances of [Ti(Me₂mtc)₄], 0.0267 M in dichloromethane, at 90 MHz (high-temperature region). The peak marked with an X is due to an impurity.

of equal intensity, consistent with dodecahedral stereoisomer **2** of C_{2v} symmetry. The four resonances are assigned to the methyl protons adjacent to O_A, O_B, S_A, and S_B in **2**. The variable-temperature spectra exhibit evidence of two distinct kinetic processes: (i) a low-temperature process (LTP) in which the four methyl resonances collapse in a pairwise fashion to give two time-averaged resonances in the fast-exchange limit (Figure 1) and (ii) a high-temperature process (HTP) in which the two time-averaged resonances merge to give a single time-averaged resonance (Figure 2). Coalescence temperatures for the LTP and HTP are -84.2 and +29.9 °C, respectively. Below -84 °C, both metal-centered rearrangement and rotation about the C \rightarrow N bond in the mtc ligand must be slow on the NMR time scale.

The LTP could be due to metal-centered rearrangement or C \rightarrow N bond rotation. Metal-centered rearrangement would

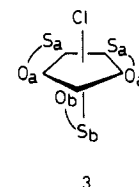
Table III. Kinetic Data for Exchange of Isopropyl Methyl Groups in [Ti(*i*-Pr₂mtc)₄]^a

Rate Data			
temp, °C	<i>k</i> , s ⁻¹	temp, °C	<i>k</i> , s ⁻¹
42.1	1.03	109.5	113
52.0	2.26	117.2	168
63.0	5.1	124.8	256
70.7	9.2	131.6	375
78.9	16.8	138.7	600
86.5	27.8	145.4	900
94.4	43	153.4	1330
101.9	72	161.5	1790

Activation Parameters ^b			
<i>T</i> _c , °C	109.5	Δ <i>G</i> [‡] (25 °C), kcal/mol	18.40 ± 0.08
Δ <i>G</i> [‡] (<i>T</i> _c), kcal/mol	18.97 ± 0.10	<i>k</i> (25 °C), s ⁻¹	0.20
Δ <i>H</i> [‡] , kcal/mol	16.4 ± 0.3	<i>E</i> _a , kcal/mol	17.1 ± 0.3
Δ <i>S</i> [‡] , eu	-6.7 ± 0.7	log A	11.9 ± 0.2

^a Concentration 0.0846 M in diphenylmethane. The chemical shift between the isopropyl methyl resonances is a linear function of temperature: $\delta\nu = 77.42 - 0.1931t$, where $\delta\nu$ is in Hz and t is in °C. *T*₂ values are 0.157 (42.1 °C), 0.209 (52.0 °C), 0.285 (63.0 °C), and 0.395 s above 70 °C. ^b The uncertainties in the activation parameters are random errors estimated at the 95% confidence level.

exchange the two inequivalent ligands, thus exchanging methyl groups in a pairwise fashion between sites adjacent to S_A and S_B and between sites adjacent to O_A and O_B. Rotation about the C \rightarrow N bond would exchange methyl groups between sites adjacent to sulfur and oxygen within a given ligand, but it would maintain the inequivalence of the two types of mtc ligands. Thus, both processes involve pairwise exchange of methyl groups, and each would produce coalescence of four resonances to give two in the fast-exchange limit. We assign the LTP to metal-centered rearrangement because the LTP in the closely related pentagonal-bipyramidal [Ti(Me₂mtc)₃Cl] complex **3** results in coalescence of four methyl resonances of



relative intensity 1:2:2:1 to give two time-averaged resonances of equal intensity in the fast-exchange limit.¹⁶ This is consistent only with metal-centered rearrangement; rotation about the C \rightarrow N bonds would give two time-averaged resonances of relative intensity 2:1.

The HTP, then, must be due to C \rightarrow N bond rotation. In the [M(Me₂mtc)₄] complexes, the HTP exchanges the methyl

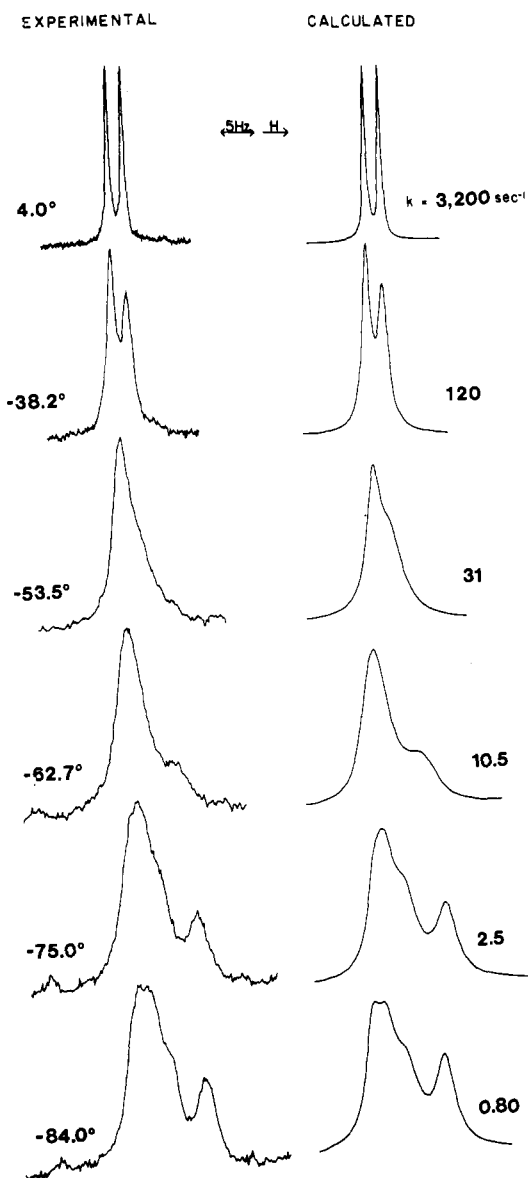


Figure 3. Observed and calculated line shapes for the methyl proton resonances of $[\text{Zr}(\text{Me}_2\text{mtc})_4]$, 0.0343 M in dichloromethane- d_2 , at 90 MHz (low-temperature region).

groups between sites adjacent to sulfur and oxygen within inequivalent ligands that are already undergoing rapid exchange on the NMR time scale owing to metal-centered rearrangement. It is interesting to note that the *O*-methyl ester, $\text{MeOC}(\text{S})\text{NMe}_2$, exhibits a similar $\text{C}=\text{N}$ rotation process with a coalescence temperature of 74.5 °C.^{14,17}

Variable-temperature ^1H NMR spectra of $[\text{Zr}(\text{Me}_2\text{mtc})_4]$ (Figures 3 and 4) are qualitatively similar to spectra of $[\text{Ti}(\text{Me}_2\text{mtc})_4]$. However, in the slow-exchange limit (Figure 3), the three lower field resonances are badly overlapped, and the integrated intensity of these three signals relative to that of the resonance at higher field is 4.25:1 rather than 3:1 as expected for the C_{2v} stereoisomer. This discrepancy is probably due to the presence in solution of small amounts of one or more of the other dodecahedral stereoisomers that have the *mmmm* ligand wrapping pattern.⁵ Since the other stereoisomers are less polar than the C_{2v} isomer, their presence in solutions of $[\text{Zr}(\text{Et}_2\text{mtc})_4]$ would help to explain why the dipole moment of $[\text{Zr}(\text{Et}_2\text{mtc})_4]$ (3.61 ± 0.16 D in benzene solution) is less than that of $[\text{Ti}(\text{Et}_2\text{mtc})_4]$ (4.49 ± 0.11 D).² Coalescence temperatures for $[\text{Zr}(\text{Me}_2\text{mtc})_4]$, -53.5 °C for the LTP and

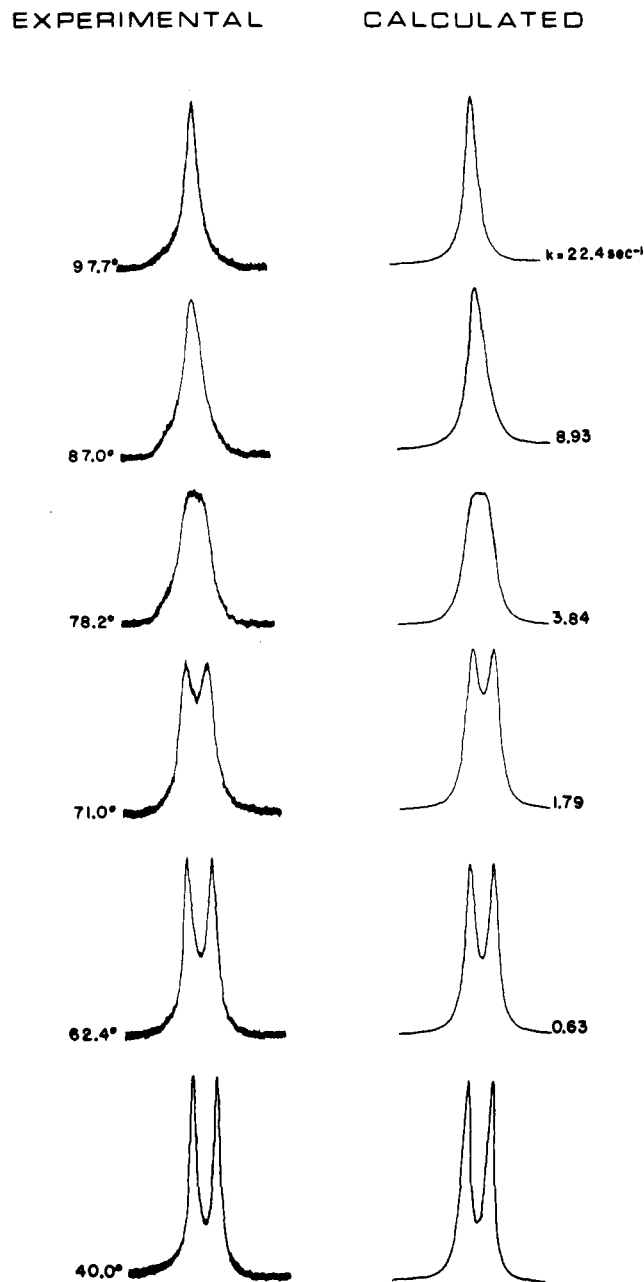


Figure 4. Observed and calculated line shapes for the methyl proton resonances of $[\text{Zr}(\text{Me}_2\text{mtc})_4]$, 0.0527 M in 1,1,2,2-tetrachloroethane, at 90 MHz (high-temperature region).

78.2 °C for the HTP, are substantially higher than for $[\text{Ti}(\text{Me}_2\text{mtc})_4]$.

Rate constants for the LTP and HTP were determined by total line-shape analysis using the procedures described in the Experimental Section. For the LTP (metal-centered rearrangement), theoretical spectra were calculated as a function of a single rate constant $k = k_{13} = k_{24} = k_{31} = k_{42}$, where 1, 2, 3, and 4 label the methyl sites associated with the four resonance lines in Figure 1 and 3, in order of increasing field. The agreement between experimental and calculated spectra is illustrated in Figures 1–4. Rate constants are listed in Table I; included in the footnotes to Table I are the final ranges of chemical shifts and T_2 values required for best agreement between the observed and calculated spectra. Arrhenius and Eyring activation parameters were obtained in the usual way from the least-squares straight lines of $\log k$ vs. $1/T$ plots (Figure 5) and $\log(k/T)$ vs. $1/T$ plots, respectively. Activation parameters are listed in Table II along with coalescence temperatures and extrapolated values of k at 25 °C. Included

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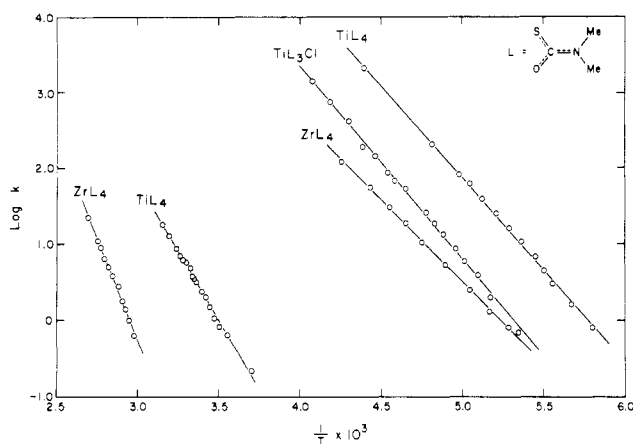


Figure 5. Arrhenius plots for the low-temperature process (metal-centered rearrangement) and the high-temperature process ($C\rightarrow N$ bond rotation).

in Figure 5 and Table II, for comparison, are kinetic data for metal-centered rearrangement in the seven-coordinate $[Ti(Me_2mtc)_3Cl]$ complex.¹⁶

It is evident from Table II that metal-centered rearrangement is $\sim 10^5$ – 10^6 times faster than $C\rightarrow N$ rotation. The barriers ΔG^\ddagger to metal-centered rearrangement are 9–12 kcal/mol; ΔG^\ddagger values for $C\rightarrow N$ rotation are ~ 17 – 20 kcal/mol, similar to the value of $\Delta G^\ddagger(25^\circ C) = 17.4$ kcal/mol found for the *O*-methyl ester, $MeOC(S)NMe_2$.¹⁴ The high barriers to $C\rightarrow N$ rotation are in accord with the high frequencies of the IR band assigned to $C\rightarrow N$ and $C\rightarrow O$ stretching (1543 cm^{-1} for $[Ti(Me_2mtc)_4]$; 1550 cm^{-1} for $[Zr(Me_2mtc)_4]$).² The rather large (~ 3 kcal/mol) difference in ΔG^\ddagger for the titanium and zirconium compounds is somewhat surprising; we do not think that this difference can be attributed to a variation in the solvent (dichloromethane for $[Ti(Me_2mtc)_4]$; 1,1,2,2-tetrachloroethane for $[Zr(Me_2mtc)_4]$).¹⁸

The rate of metal-centered rearrangement is ~ 10 times faster in the eight-coordinate $[Ti(Me_2mtc)_4]$ than in the seven-coordinate $[Ti(Me_2mtc)_3Cl]$. This is in agreement with the longer, and presumably weaker, metal–ligand bonds in the eight-coordinate complex.^{3,16} More surprising is the fact that $[Ti(Me_2mtc)_4]$ rearranges faster than $[Zr(Me_2mtc)_4]$. Ordinarily, the rates of rearrangement of d^0 metal complexes increase with increasing size of the metal atom, as is illustrated by the acetylacetonate complexes $[M(acac)_2X_2]$ ($M = Ti, Zr; X = Cl, Br$).^{19,20}

The most significant aspect of our results is the greater rigidity of the monothiocarbamate complexes $[M(Me_2mtc)_4]$ ($M = Ti, Zr$) in comparison with that of analogous dithiocarbamates.^{6–9} $[M(Et_2dtc)_4]$ and $[M(n\text{-}Pr_2dtc)_4]$ ($M = Ti, Zr$) are still nonrigid on the NMR time scale at $-140^\circ C$.⁷

Mechanism of Metal-Centered Rearrangement. Three classes of mechanisms may be considered for metal-centered rearrangement of $[M(Me_2mtc)_4]$ complexes: (i) intermolecular mechanisms involving complete dissociation of a bidentate ligand or ligand exchange via a bimolecular process; (ii) one-bond rupture or “arm off” mechanisms involving

formation of a seven-coordinate intermediate, followed by intramolecular rearrangement of the intermediate and subsequent ring closure to regenerate the tetrakis chelate; (iii) polytopal rearrangement mechanisms,^{7,21–28} which effect rearrangement without rupture of any metal–ligand bonds.

Intermolecular mechanisms can be ruled out on the basis of the following experimental evidence: (i) rate constants for metal-centered rearrangement of 0.0267 and 0.0723 M $[Ti(Me_2mtc)_4]$ in dichloromethane are independent of concentration; (ii) 1H NMR spectra at $35^\circ C$ of mixtures of $[M(Me_2mtc)_4]$ ($M = Ti, Zr$) and $[Me_2NH_2][Me_2mtc]$ or $Na(Me_2mtc)$ in CH_2Cl_2 or $CH_2Cl_2\text{-}CD_3CN$ exhibit separate resonances for the complex and the excess ligand. This last result indicates that intermolecular exchange of *mtc* ligands is slow on the NMR time scale at temperatures where metal-centered rearrangement is fast.

Since the Ti–S bond lengths in $[Ti(Et_2mtc)_4]$ ($Ti\text{-}S_A = 2.609(1)\text{ \AA}$; $Ti\text{-}S_B = 2.533(1)\text{ \AA}$)³ and $[Ti(Et_2dtc)_4]$ ($Ti\text{-}S_{A(av)} = 2.606(8)\text{ \AA}$; $Ti\text{-}S_{B(av)} = 2.522(8)\text{ \AA}$)²⁹ are nearly identical, the much greater rigidity of the monothiocarbamate complexes in comparison with that of the dithiocarbamate analogues is not consistent with a rearrangement mechanism involving metal–sulfur bond rupture. Consequently, we have been considering polytopal rearrangement mechanisms.

A particularly attractive mechanism is the Hoard–Silverton rearrangement,⁴ which interconverts the two most common eight-coordination polyhedra, the D_{2d} dodecahedron (DD) and the D_{4d} square antiprism (SAP), in one step. The DD is converted to the SAP by a motion that involves expansion of a pair of opposite dodecahedral *b* edges, while the DD is formed from the SAP by a motion involving compression along one diagonal of each square face of the antiprism and simultaneous elongation along the other diagonal of each square face.^{7,28} Figure 6 shows how a series of Hoard–Silverton rearrangements exchanges ligand donor atoms between the A and B sites of the *mmmm* dodecahedral stereoisomer of a tetrakis(bidentate chelate) complex. The reaction path traverses the SAP *ssss*, DD *gggg*, and SAP *llll* stereoisomers. Applied to the $[M(Me_2mtc)_4]$ complexes, this mechanism has the virtue that it exchanges donor atoms (and monothiocarbamate methyl groups) between the inequivalent A and B sites of the observed *mmmm*- C_{2v} stereoisomer. Thus, if one begins with the C_{2v} isomer with the sulfur atoms clustered in positions 1, 3, 6, and 8 (Figure 6), the product is the same C_{2v} isomer, but with sulfur atoms 1 and 6 shifted from B sites to A sites and sulfur atoms 3 and 8 shifted from A sites to B sites. Moreover, this mechanism has the advantage that it maintains the clustering of sulfur atoms throughout the rearrangement; sulfur atoms 1, 3, 6, and 8 remain in all-cis positions in the *ssss*, *gggg*, and *llll* stereoisomers, as in the ground-state *mmmm* isomer.

A conceptually simpler route for polytopal rearrangement is illustrated in the upper part of Figure 7. Motion of the four chelate rings in their own planes so as to elongate the dodecahedral *a* edges generates a cubic transition state, which can collapse to the same C_{2v} stereoisomer but with exchange of donor atoms between the A and B sites. However, as shown

- (18) Attempts to study the HTP of titanium and zirconium complexes in the same solvent were unsuccessful. Dichloromethane could not be used for $[Zr(Me_2mtc)_4]$ because of the high coalescence temperature of this compound. 1,1,2,2-Tetrachloroethane was unsuitable for $[Ti(Me_2mtc)_4]$ because the two time-averaged resonances were unresolved. An attempt to study $[Zr(Me_2mtc)_4]$ in dibromomethane was unsuccessful because the complex decomposed in this solvent at elevated temperatures. However, a coalescence temperature near $90^\circ C$ in dibromomethane (cf. $78.2^\circ C$ in 1,1,2,2-tetrachloroethane) suggests that solvent effects on $C\rightarrow N$ rotation are small.
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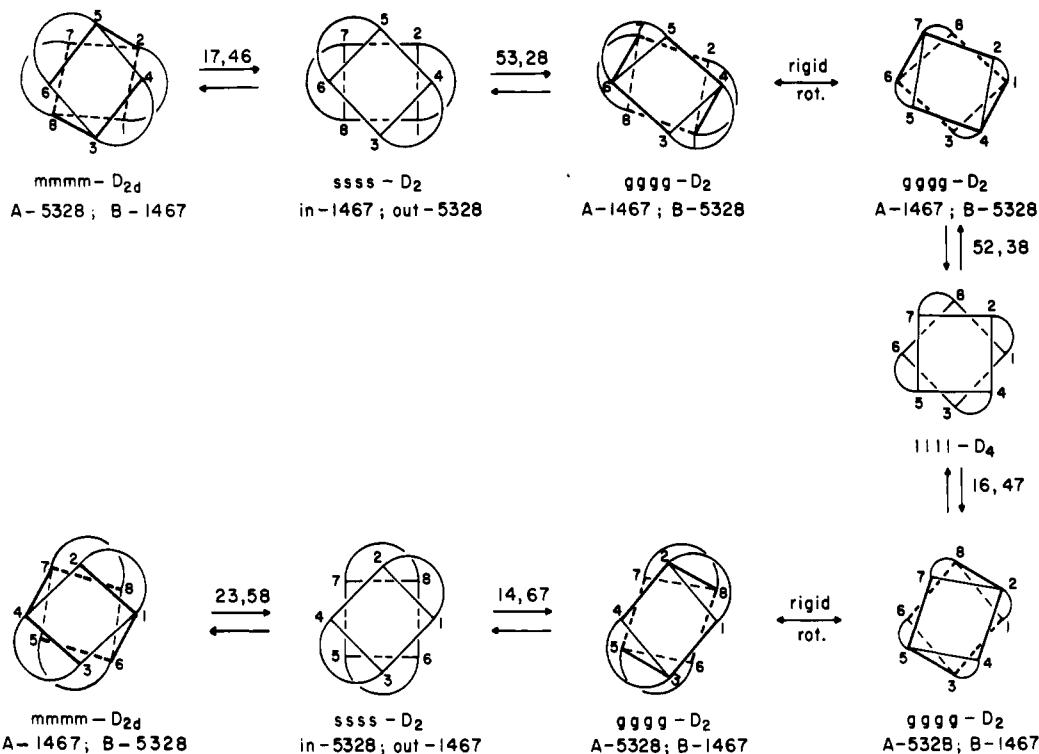


Figure 6. Exchange of ligand donor atoms between the A and B sites of the dodecahedral *mmmm* stereoisomer of a tetrakis(bidentate chelate) complex by a series of Hoard-Silverton rearrangements. The DD stereoisomers are viewed along a twofold axis so as to emphasize the relation between the square faces of the SAP and the "diamond faces" of the DD. The BAAB trapezoids of the DD are outlined by thicker lines; the two thick lines connecting the two "diamond faces" represent dodecahedral *a* edges. Numbers represent ligand donor atoms, and numbers above the arrows specify which *b* edges are elongated on going from the DD to the SAP or which face diagonals are compressed on going from the SAP to the DD. Point group notations apply to a complex containing symmetrical bidentate ligands.

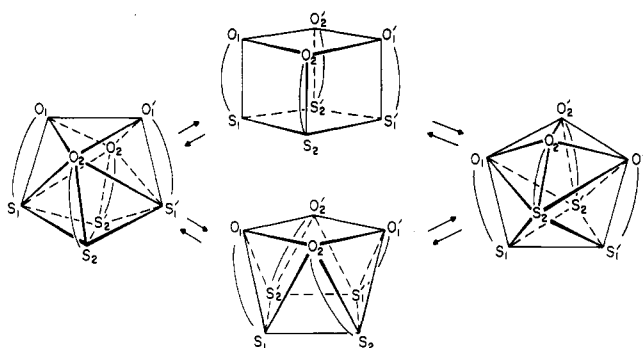


Figure 7. Polytopal rearrangement of an $[M(\text{Me}_2\text{mtc})_4]$ complex via a cubic transition state (upper) or a square-antiprismatic transition state (lower).

in the lower part of Figure 7, some distortion of the cubic transition state in the direction of the SAP pinwheel (*IIII*) stereoisomer is likely to occur in order to reduce nonbonded repulsions in the coordination group. Note that both cubic and SAP transition states maintain an all-cis arrangement of the sulfur atoms. The lower reaction path of Figure 7 is closely related to the Hoard-Silverton mechanism shown in Figure 6; both mechanisms involve the same SAP *IIII* transition state.

The difference in rearrangement rates for the monothiocarbamate and dithiocarbamate complexes could be due to a difference in ligand bites. Molecular mechanics calculations³⁰ indicate that the SAP *ssss*, DD *gggg*, and SAP *IIII* stereoisomers become increasingly stable relative to the DD *mmmm* stereoisomer as the normalized bite *b* of the ligand increases. Thus the energy difference between the DD *mmmm* ground state and the SAP *IIII* transition state should be less for $[\text{Ti}(\text{dte})_4]$ complexes ($b = 1.11$)²⁹ than for the $[\text{Ti}(\text{mtc})_4]$

analogues ($b = 1.09$).³ The effect of ligand bite on the barrier to polytopal rearrangement also explains why $[\text{Zr}(\text{Me}_2\text{mtc})_4]$ ($b = 1.05$)³ is more rigid than $[\text{Ti}(\text{Me}_2\text{mtc})_4]$.

Another factor that may increase the rigidity of the $[\text{M}(\text{mtc})_4]$ complexes relative to that of the $[\text{M}(\text{dte})_4]$ analogues is a requirement that the sulfur atoms in the *mtc* complexes remain clustered in all-cis positions on going to the transition state. We have seen that the Hoard-Silverton rearrangement outlined in Figure 6 maintains the clustering of sulfur atoms. However, there is another Hoard-Silverton pathway, viz. $mmmm \rightarrow ssss \rightarrow mmgg \rightarrow llss \rightarrow gggg \rightarrow llss \rightarrow mmgg \rightarrow ssss \rightarrow mmmm$,²⁸ which does not maintain the clustering of sulfur atoms. For the $[\text{M}(\text{dte})_4]$ complexes, where clustering of sulfur is unimportant, the latter rearrangement path may be of lower energy than that of Figure 6 because it does not require all four ligands to span the *l* edges of an SAP; the *l* edges are among the longer of the DD and SAP edges, and the *dte* and *mtc* ligands are relatively short-bite ligands. For the $[\text{M}(\text{mtc})_4]$ complexes, this lower energy pathway may not be available if the sulfur atoms must remain clustered on going to the transition state.

Exchange of Isopropyl Methyl Groups in $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$. The ¹H NMR spectrum of $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$ in CDCl_3 at ambient temperature exhibits two sets of isopropyl resonances.² However, the chemical shifts (~ 0.3 ppm between the two methyl doublets and ~ 1.1 ppm between the two methine septets) are a great deal larger than the shifts observed in the spectra of the $[\text{M}(\text{Me}_2\text{mtc})_4]$ ($\text{M} = \text{Ti}$ or Zr) complexes (Figures 1–4). The chemical shifts for $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$ are comparable in magnitude to those observed for the corresponding dithiocarbamate complex, $[\text{Ti}(i\text{-Pr}_2\text{dte})_4]$,⁹ suggesting that the two sets of isopropyl resonances arise from "inner" and "outer" sites rather than from adjacency to sulfur or oxygen. The probable conformations of the isopropyl groups, based on X-ray crystallographic studies of metal *N,N*-diiso-

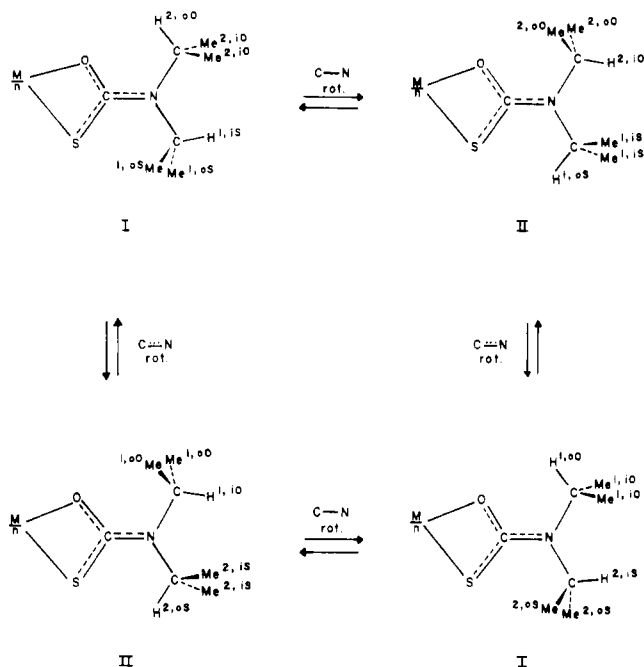


Figure 8. Probable ligand conformations in metal *N,N*-diisopropylmonothiocarbamate complexes. Numbers label protons and letters label the four inequivalent environments: inner near sulfur (iS), outer near sulfur (oS), inner near oxygen (iO), and outer near oxygen (oO). Exchange of protons between inner and outer sites can occur by rotation about the C—N single bonds. Exchange of protons between the oxygen side and the sulfur side of the ligand can occur by rotation about the C=S partial double bond.

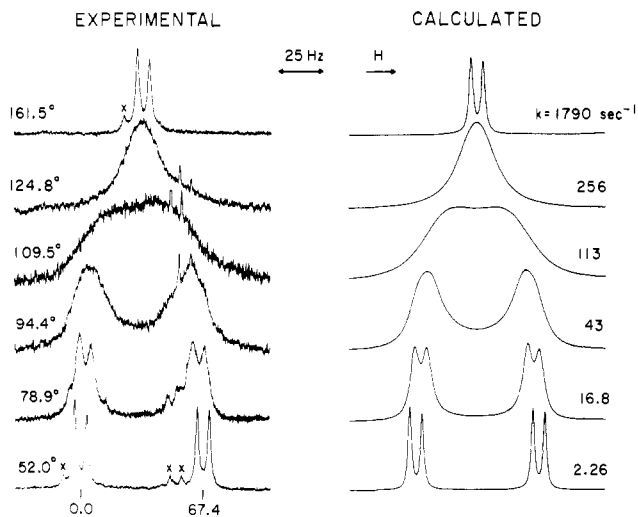
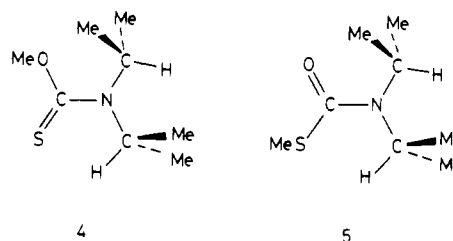


Figure 9. Observed and calculated line shapes for the isopropyl methyl resonances of $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$, 0.0846 M in diphenylmethane, at 90 MHz. Peaks marked with an \times are due to a hydrolysis product.

propyldithiocarbamates,³¹ are shown in Figure 8. The methine protons lie in the plane of the ligand in "inner" sites, near the

quasi-twofold axis of the ligand, and in "outer" sites, away from this axis. Similarly, the methyl groups occupy equally populated inner and outer sites. Since the monothiocarbamate ligand is unsymmetrical, there are two possible ligand conformations (I and II in Figure 8) and four inequivalent sites; methyl groups and methine protons may be in inner or outer sites adjacent to sulfur or oxygen.

It appears, however, that only one ligand conformation is present in solution since only two equally intense and widely separated isopropyl resonances are observed. Conformation II, which locates the outer methyl groups near the oxygen atom, should be more stable than conformation I, which places the outer methyl groups adjacent to the more bulky sulfur atom. This conclusion is suggested by NMR studies of *N,N*-diisopropylmonothiocarbamate esters,^{32,33} which have established conformations 4 and 5 for $\text{MeOC}(\text{S})\text{N}(i\text{-Pr})_2$ and $\text{MeSC}(\text{O})\text{N}(i\text{-Pr})_2$, respectively.



Variable-temperature ^1H NMR spectra of diphenylmethane solutions of $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$ (Figure 9) exhibit coalescence of the two isopropyl methyl doublets at $\sim 110^\circ\text{C}$ to give a single time-averaged doublet in the fast-exchange limit. The spectra are qualitatively similar to variable-temperature spectra of the dithiocarbamate complexes $[\text{Ti}(i\text{-Pr}_2\text{dtc})_n\text{Cl}_{4-n}]$ ($n = 2, 3, 4$),⁹ except that coalescence temperatures for the latter group of compounds are around -25°C . Rate constants for exchange of the inequivalent isopropyl methyl groups (Table III) were determined by total line-shape analysis (see Experimental Section), and activation parameters (Table III) were obtained from the least-squares straight lines of nicely linear plots of $\log k$ vs. $1/T$ and $\log(k/T)$ vs. $1/T$. The agreement between observed and calculated spectra is illustrated in Figure 9.

The barrier, $\Delta G^\ddagger(25^\circ\text{C})$, to exchange of isopropyl methyl groups in $[\text{Ti}(i\text{-Pr}_2\text{mtc})_4]$ (18.4 kcal/mol) is a great deal higher than in the dithiocarbamate complexes $[\text{Ti}(i\text{-Pr}_2\text{dtc})_n\text{Cl}_{4-n}]$ ⁹ (~ 13 kcal/mol); the rate of exchange at 25°C is $\sim 10^4$ times greater in the *i*-Pr₂mtc complexes than in the *i*-Pr₂dtc complex. In *i*-Pr₂dtc complexes, exchange of isopropyl methyl groups is effected not by rotation about the C=N partial double bond but by rotation about the two isopropyl-nitrogen (C—N) single bonds.^{9,34–37} Originally, rotation about the C—N bonds was thought to occur by a synchronous, gearlike mechanism,^{9,34} but more recent work^{32,33} has shown that a nonsynchronous, stepwise process is more likely. It is evident from Figure 8 that in *i*-Pr₂mtc complexes rotation about the C—N single bonds does not suffice to exchange isopropyl methyl groups between the two inequivalent sites of a particular ligand conformer. While either C—N or C=S rotation interconverts conformers I and II, both C—N and C=S rotation are required to exchange isopropyl methyl groups between the two inequivalent sites of the more stable conformer II. Rotation about the

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C \rightarrow N bond should be appreciably slower than rotation about the C—N single bonds, which accounts for the substantially higher barrier to isopropyl methyl group exchange in the *i*-Pr₂mtc complex. Finally, it is pleasing to see that the activation parameters for isopropyl methyl group exchange in [Ti(*i*-Pr₂mtc)₄] (Table III) are similar to those for rotation about the C \rightarrow N bond in [Ti(Me₂mtc)₄] (Table II).

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Registry No. Ti(Me₂mtc)₄, 66791-67-1; Zr(Me₂mtc)₄, 66791-68-2; Ti(*i*-Pr₂mtc)₄, 66758-38-1.

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Crystal and Molecular Structures of C₇H₈(S₃N)₂: Substituent Effects on the S₃N Chromophore

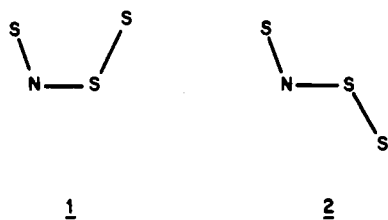
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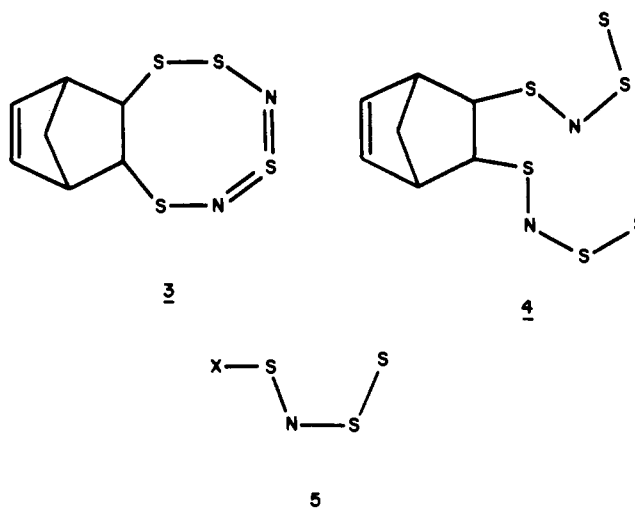
The isolation of C₇H₈(S₃N)₂ from the reaction of tetrasulfur dinitride with norbornadiene is reported. The crystal and molecular structures of the compound have been determined by X-ray crystallography; the crystals are monoclinic, space group *P*2₁/*c*, with *a* = 9.216 (1) Å, *b* = 14.318 (2) Å, *c* = 10.229 (1) Å, β = 104.57 (1)°, *V* = 1306.3 (5) Å³, and *Z* = 4. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares procedures to give a final *R* = 0.037 and *R*_w = 0.053 for 1627 observed reflections. The molecule consists of a norbornenyl unit with two S₃N groups attached in an *exo* fashion at the 2,3-positions. Both S₃N groups possess a *cis* formation with the following mean bond lengths: *d*(S—S) = 1.903 Å, *d*(SS—N) = 1.572 Å, *d*(CS—N) = 1.641 Å. The molecule exhibits a pair of strong visible absorptions at 433 and 408 nm, which are assigned to the excitonically coupled π* → π* transitions of the two S₃N chromophores. The effect of different substituents on the π* → π* transition energy of X—S₃N derivatives is described; π-donor ligands induce a large bathochromic shift.

Introduction

The preparation of the S₃N⁻ anion has recently been reported.² While the connectivity of the atoms, i.e. S—N—S—S, has been confirmed by the characterization of several metal complexes,³ the conformation of the four-atom sequence in the free ion has not been unequivocally established. *Ab initio* Hartree-Fock-Slater (HFS) molecular orbital calculations have indicated a slight preference for the *cis* geometry **1** relative to the *trans* form **2**,² but our attempts to confirm this prediction by crystallographic methods have been unsuccessful.⁴



During our study of the reaction of tetrasulfur dinitride, S₄N₂, with norbornadiene, which yields C₇H₈S₄N₂ (**3**) as the major product,⁵ we were able to isolate in trace quantities a second compound with the elemental composition, C₇H₈S₆N₂. The crystal and molecular structures of this material, which we report herein, reveal that it is an S-ester of the hypothetical



acid HS₃N with two S₃N units per molecule, i.e. **4**. In addition to providing evidence in favor of the *cis* geometry for the S₃N⁻ anion itself, the compound **4** allows a comparison of the effects of inductive and conjugative interactions between the substituent and the S₃N chromophore in molecules of the type X—S₃N, e.g. **5**.⁶⁻⁸ The effects of excitonic coupling between the two S₃N units of **4** are also reported.

Experimental Section

Materials and General Procedures. Tetrasulfur dinitride was prepared as recently described.⁹ UV-vis spectra were recorded on

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