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Preparation and Characterization of Some Six-, Seven-, and Eight-Coordinate Titanium(IV) *N,N*-Dialkyldithiocarbamates[1]

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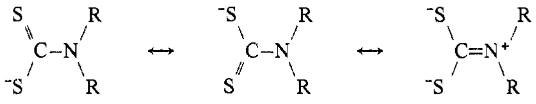
Titanium(IV) *N,N*-dialkyldithiocarbamates of the type $Ti(S_2CNR_2)_nCl_{4-n}$ (n = 2, 3, or 4; R = Me, *i*-Pr, *i*-Bu, or, when n = 3, Et) have been prepared by reaction of titanium(IV) chloride with anhydrous sodium *N,N*-dialkyldithiocarbamates in refluxing dichloromethane (or benzene). Molecular weight, conductance, and infrared data demonstrate that these complexes are monomeric nonelectrolytes in which all of the dithiocarbamate ligands are bidentate. Therefore, the Ti(IV) atom may be assigned coordination numbers 6, 7, and 8 when n = 2, 3, and 4, respectively. The $C\cdots N$, $C\cdots S$, and Ti–Cl stretching frequencies depend systematically on the coordination number. Coordination number 7 has been confirmed for $Ti(S_2CNMe_2)_3Cl$ by X-ray diffraction; the molecule has a pentagonal-bipyramidal structure with the chlorine atom in an axial position. Mass spectra of the monochloro compounds show that monomeric $Ti(S_2CNR_2)_3Cl$ species exist in the gas phase. A cis configuration is indicated for the six-coordinate $Ti(S_2CNR_2)_2Cl_2$ complexes by dipole moments of ~9 D (for R = *i*-Pr or *i*-Bu) in benzene solution. Variable-temperature proton nmr spectra of the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes in dichloromethane (+40 to −90°) indicate that (1) metal-centered rearrangement is fast on the nmr time scale at temperatures above −90° and (2) there is hindered rotation about C–N single bonds in the diisopropyl derivatives. Activation parameters for exchange of isopropyl methyl groups between the two nonequivalent sites are essentially the same for all three $Ti(S_2CN(i\text{-}Pr)_2)_nCl_{4-n}$ complexes (n = 2, 3, or 4): $\Delta H^* = 9.4$ kcal/mol; $\Delta S^* = -12$ eu; $\Delta G^*(-26°) = 12.4$ kcal/mol. A gearlike rotation mechanism is proposed.

Introduction

Although seven- and eight-coordinate complexes of second- and third-row transition metals are now quite common, complexes of first-row transition elements in which the coordination number exceeds 6 are still relatively rare.[3] The first such compound was the *o*-phenylenebis(dimethylarsine) complex $TiCl_4(diars)_2$.[4] Other eight-coordinate titanium(IV) complexes whose structures have been established by X-ray diffraction are $Ti(NO_3)_4$[5] and the tetrakis(*N,N*-diethyldithiocarbamate) $Ti[S_2CN(C_2H_5)_2]_4$.[6] In all three compounds the coordination polyhedron is a D_{2d} dodecahedron.

The existence of seven-coordinate titanium(IV) is less certain since, apart from the oxo-bridged dinuclear peroxodipicolinato complex $[TiO_{1/2}(O_2)(C_7H_3O_4N)(H_2O)]_2^{2-}$,[7] no structures have been established by X-ray diffraction. However, $Ti(tropolonate)_3Cl$,[8] $Ti(oxine)_3Cl$,[9] and certain tetrachlorotriarsine complexes, $TiCl_4(triars)$,[10] have been identified as probable seven-coordinate species on the basis of molecular weight, conductance, and spectroscopic evidence.

By virtue of their low charge and relatively small "bites" (~2.8-2.9 Å), dithiocarbamate ligands, whose molecular and electronic structures are shown in **1a–c**, are especially well suited for stabilization of higher coordination complexes (coordination number >6). We report herein the preparation and characterization of some six-, seven-, and eight-coordinate titanium(IV) dithiocarbamates of the types $Ti(S_2CNR_2)_2Cl_2$, $Ti(S_2CNR_2)_3Cl$, and $Ti(S_2CNR_2)_4$, where R = methyl, isopropyl, isobutyl, and, in one case, ethyl.[11-13]



1a **1b** **1c**

Experimental Section

Reagents and General Techniques. Sodium salts of the *N,N*-dialkyldithiocarbamate ligands, $Na(S_2CNR_2)$ (R = Me, *i*-Pr, *i*-Bu), were prepared in good yield by reaction in aqueous solution (10-15°) of equimolar amounts of the appropriate secondary amine, carbon disulfide, and sodium hydroxide.[14] Sodium and diethylammonium salts of the *N,N*-diethyldithiocarbamate ligand were obtained from Fisher Scientific Co. Because the sodium salts contain water of crystallization, it was necessary to dry them *in vacuo* over phosphorus(V) oxide, first at room temperature and then at 110°, until their infrared spectra showed no water or only traces of water.

Titanium(IV) chloride (Matheson Coleman and Bell) was used as purchased without further purification.

Dichloromethane, cyclohexane, and benzene were dried by refluxing for at least 24 hr over calcium hydride. Nitrobenzene was purified for conductance measurements by the method described earlier.[15] The specific conductance of the purified solvent was $<4 \times 10^{-8}$ ohm^{-1} cm^{-1}.

Because the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes are susceptible to hydrolysis, particularly in solution, all syntheses and subsequent handling of the compounds were conducted under anhydrous conditions in a dry nitrogen atmosphere. Samples and solutions for physical measurements were prepared in a nitrogen-filled glove bag.

Preparation of Complexes. The general procedure employed for preparation of the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes will be presented first, followed by a short description of those details which vary from

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[2] (a) Ford Foundation Faculty Fellow, 1971-1972. (b) Participant in the National Science Foundation Undergraduate Research Participation Program, Summer 1972.

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one preparation to the next. An appropriate quantity of the anhydrous sodium salt of the *N,N*-dialkyldithiocarbamate was added with stirring to a solution of titanium(IV) chloride in 100 ml of dichloromethane. The solution turned red immediately. The mixture was allowed to reflux for 5 hr and was then filtered to remove NaCl and any excess, unreacted $Na(S_2CNR_2)$. The volume of the filtrate was reduced by vacuum distillation, and cyclohexane (or hexane) was added to precipitate the product. In some cases further reduction of the solution volume was required. The solid product was then filtered, dried at room temperature *in vacuo* for 18 hr, and then dried *in vacuo* at 80° until the nmr spectrum of the complex showed that the product was free of cyclohexane. Ordinarily, a drying time of 3 hr at 80° was found to be sufficient.

Dichlorobis(*N,N*-dimethyldithiocarbamato)titanium(IV). This compound was prepared by reaction of 1.1 ml of titanium(IV) chloride (1.9 g, 10 mmol) and 2.86 g (20 mmol) of sodium *N,N*-dimethyldithiocarbamate, $Na(S_2CNMe_2)$. After filtering the reaction mixture, the orange solid (NaCl plus some of the relatively insoluble product) was washed with 200 ml of dichloromethane, which was added to the filtrate. The volume of this solution was reduced to ~50 ml, and ~200 ml of hexane was added to precipitate the red product; yield 2.50 g (70%); mp 220-230° dec. *Anal.* Calcd for $Ti(C_3H_6NS_2)_2Cl_2$: C, 20.06; H, 3.37; N, 7.80; Ti, 13.33. Found: C, 19.89; H, 3.37; N, 7.71; Ti, 13.74.

Chlorotris(*N,N*-dimethyldithiocarbamato)titanium(IV). This complex was prepared by reaction of 1.1 ml of titanium(IV) chloride (1.9 g, 10 mmol) and 4.85 g (34 mmol) of $Na(S_2CNMe_2)$. The red-orange product was isolated in 76% yield (3.35 g) by reduction of the volume of the filtrate from the reaction mixture to ~10 ml followed by addition of 40 ml of cyclohexane. The solid begins to decompose at ~260°; mp >260°. *Anal.* Calcd for $Ti(C_3H_6NS_2)_3Cl$: C, 24.35; H, 4.09; Cl, 7.99; N, 9.46; Ti, 10.79. Found: C, 24.14; H, 4.14; Cl, 8.26; N, 9.31; Ti, 11.11.

Tetrakis(*N,N*-dimethyldithiocarbamato)titanium(IV). This complex was prepared in refluxing benzene by reaction of 1.0 ml of titanium(IV) chloride (1.7 g, 9 mmol) and 6.40 g (45 mmol) of $Na(S_2CNMe_2)$. The reaction time was 48 hr. After filtering, the orange solid was washed with ten 50-ml portions of dichloromethane, which were added to the filtrate. Evaporation of this solution to ~200 ml followed by addition of 400 ml of hexane afforded 1.20 g (25%) of product. An additional 2.0 g (42%) of complex was obtained on further washing of the orange solid with ~1 l. of dichloromethane. The red-orange complex is sparingly soluble in dichloromethane and chloroform and is insoluble in benzene and hexane; mp >280°. *Anal.* Calcd for $Ti(C_3H_6NS_2)_4$: C, 27.26; H, 4.58; N, 10.60; S, 48.51; Ti, 9.06. Found: C, 26.81; H, 4.55; N, 10.20; S, 48.15; Ti, 9.05.

Chlorotris(*N,N*-diethyldithiocarbamato)titanium(IV). This compound was prepared according to the general procedure by reaction of 1.1 ml of titanium(IV) chloride (1.9 g, 10 mmol) and 5.81 g (34 mmol) of sodium *N,N*-diethyldithiocarbamate. The red-orange product was isolated in 62% yield (3.25 g) by reducing the volume of the filtrate from the reaction mixture to ~25 ml followed by adding 150 ml of cyclohexane; mp 193-194°. This complex was also prepared by refluxing for 0.5 hr in benzene solution a 1:3 molar mixture of titanium(IV) chloride and diethylammonium *N,N*-diethyldithiocarbamate. Benzene of crystallization was removed by drying *in vacuo* at 100°. *Anal.* Calcd for $Ti(C_5H_{10}NS_2)_3Cl$: C, 34.11; H, 5.74; Cl, 6.71; N, 7.96; S, 36.42; Ti, 9.07. Found: C, 33.99; H, 5.89; Cl, 6.70; N, 8.12; S, 36.35; Ti, 9.12.

Dichlorobis(*N,N*-diisopropyldithiocarbamato)titanium(IV). This complex was prepared according to the general procedure by reaction of 0.55 ml (5.0 mmol) of titanium(IV) chloride and 2.10 g (10.5 mmol) of sodium *N,N*-diisopropyldithiocarbamate, $Na(S_2CN(i\text{-}Pr)_2)$. After reduction of the volume of the filtrate from the reaction mixture (to ~10 ml) and addition of cyclohexane (100 ml), further reduction of the solution volume (to ~50 ml) was required to precipitate the product. The yield of the red complex was 2.05 g (86%); mp 199-200°. *Anal.* Calcd for $Ti(C_7H_{14}NS_2)_2Cl_2$: C, 35.67; H, 5.99; Cl, 15.04; N, 5.94; Ti, 10.16. Found: C, 35.72; H, 5.80; Cl, 14.87; N, 5.64; Ti, 10.25.

Chlorotris(*N,N*-diisopropyldithiocarbamato)titanium(IV). The procedure for preparation of this red-orange complex was identical with that for preparation of $Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$ except that the quantity of $Na(S_2CN(i\text{-}Pr)_2)$ was 3.13 g (15.7 mmol). The yield was 2.06 g (67%); mp 228-230°. *Anal.* Calcd for $Ti(C_7H_{14}NS_2)_3Cl$: C, 41.19; H, 6.91; Cl, 5.79; N, 6.86; S, 31.41; Ti, 7.82. Found: C, 40.86; H, 6.85; Cl, 6.10; N, 6.77; S, 31.33; Ti, 7.66.

Tetrakis(*N,N*-diisopropyldithiocarbamato)titanium(IV). This compound was prepared according to the general procedure by reaction of 0.55 ml (5.0 mmol) of titanium(IV) chloride and 4.99 g (25 mmol) of $Na(S_2CN(i\text{-}Pr)_2)$. The red product was isolated by reduction of the volume of the filtrate from the reaction mixture to ~5 ml followed by addition of 20 ml of cyclohexane. The complex is very soluble in dichloromethane but sparingly soluble in cyclohexane; yield 3.24 g (86%); mp >265°. *Anal.* Calcd for $Ti(C_7H_{14}NS_2)_4$: C, 44.65; H, 7.49; N, 7.44; S, 34.06; Ti, 6.36. Found: C, 44.53; H, 7.51; N, 7.33; S, 33.50; Ti, 6.67.

Dichlorobis(*N,N*-diisobutyldithiocarbamato)titanium(IV). This red complex was prepared in 74% yield (3.9 g) by reaction of 1.1 ml (10 mmol) of titanium(IV) chloride and 4.66 g (20.6 mmol) of sodium *N,N*-diisobutyldithiocarbamate, $Na(S_2CN(i\text{-}Bu)_2)$. The product was isolated using the procedure employed for $Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$; mp 151-152°. *Anal.* Calcd for $Ti(C_9H_{18}NS_2)_2Cl_2$: C, 40.98; H, 6.87; Cl, 13.41; N, 5.31; S, 24.31; Ti, 9.08. Found: C, 41.09; H, 6.86; Cl, 13.20; N, 5.13; S, 24.16; Ti, 9.08.

Chlorotris(*N,N*-diisobutyldithiocarbamato)titanium(IV). This compound was prepared by reaction of 0.84 ml (7.6 mmol) of titanium(IV) chloride and 5.32 g (23.4 mmol) of $Na(S_2CN(i\text{-}Bu)_2)$. The red-orange product was isolated in 79% yield (4.2 g) using the procedure employed for $Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$; mp 168-169°. *Anal.* Calcd for $Ti(C_9H_{18}NS_2)_3Cl$: C, 46.56; H, 7.81; Cl, 5.09; N, 6.03; S, 27.62; Ti, 6.87. Found: C, 46.66; H, 7.63; Cl, 5.18; N, 5.95; S, 27.76; Ti, 7.02.

Tetrakis(*N,N*-diisobutyldithiocarbamato)titanium(IV). This complex was prepared by reaction of 0.55 ml (5.0 mmol) of titanium(IV) chloride and 5.8 g (25 mmol) of $Na(S_2CN(i\text{-}Bu)_2)$. After reduction of the volume of the filtrate from the reaction mixture (to ~10 ml) and addition of cyclohexane (100 ml), further reduction of the solution volume (to ~20 ml) was required to precipitate the product. The yield of the red complex was 2.75 g (64%); mp 208-210°. *Anal.* Calcd for $Ti(C_9H_{18}NS_2)_4$: C, 49.96; H, 8.38; N, 6.47; S, 29.64; Ti, 5.53. Found: C, 49.80; H, 8.24; N, 6.72; S, 29.44; Ti, 5.46.

Molecular Weight and Conductance Measurements. Molecular weights were determined cryoscopically in benzene solution using the thermistor apparatus described by Knight, *et al.*[16] Conductance measurements were made in nitrobenzene at 25.00 ± 0.05° with an Industrial Instruments Model RC 16B2 conductivity bridge and a Freas-type solution cell with bright platinum electrodes. The bridge frequency was 60 cps, and the cell constant, 0.1832 cm^{-1}.

Mass Spectra. Mass spectra of the $Ti(S_2CNR_2)_3Cl$ complexes were recorded with an Associated Electrical Industries MS 902 mass spectrometer at an ionizing voltage of 70 V and sample temperatures in the range 200-350°. Samples were introduced into the ionization chamber *via* the direct insertion lock. Perfluorokerosene was used as a mass reference.

Infrared Spectra. Infrared spectra were recorded in the region 4000-250 cm^{-1} with a Perkin-Elmer 521 grating spectrophotometer. The complexes were studied as Nujol and hexachlorobutadiene mulls supported between cesium iodide plates and, in some cases, as dichloromethane solutions in 0.1-mm cesium bromide cells. No significant differences between solid-state and solution spectra were noted. (A fivefold frequency scale expansion was employed in recording the bands listed in Table V; reported frequencies should be accurate to about ±3 cm^{-1}.)

Nuclear Magnetic Resonance Spectra. Proton chemical shifts and coupling constants were measured at ambient temperature (~37°) with a Varian A-60A spectrometer. Spectra were recorded in triplicate, and the values reported in Table I are average values; the magnetic field sweep was calibrated with a standard sample of chloroform and tetramethylsilane in carbon tetrachloride.

Variable-temperature spectra of degassed dichloromethane solutions were recorded in the temperature range +40 to −90° at a sweep width of 50-100 Hz (Varian A-60A spectrometer). Van Geet's equation[17] was employed to calculate the probe temperature from the chemical shift between the nonequivalent protons of methanol. The procedures used to eliminate or minimize the common sources of error in nmr line-broadening studies[18] are detailed in a previous paper.[19]

Dipole Moment Measurements. Using a method described previously,[20] dipole moments were determined for $Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$ and $Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$ in dilute benzene solution at 25.0 ± 0.1°.

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Table I. Proton Chemical Shift[a] and Coupling Constant[b] Data

Compd	Dichloromethane				Deuteriochloroform			
	$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\text{-H}^c$	$\text{-CH}_2\text{-}^d$	$\text{-CH}_3{}^e$	J	$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\text{H}^c$	$\text{-CH}_2\text{-}^d$	$\text{-CH}_3{}^e$	J
$Ti(S_2CNMe_2)_2Cl_2$			−206.9				−205.7	
$Ti(S_2CNMe_2)_3Cl$			−201.6				−202.9	
$Ti(S_2CNMe_2)_4$			−198.9				−200.8	
$Ti(S_2CNEt_2)_3Cl$		−229.4	−76.8	7.2		−230.1	−77.2	7.2
$Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$	−278.5		−87.7	6.9	−278.6		−88.2	6.9
$Ti(S_2CN(i\text{-}Pr)_2)_3Cl$	−280.2		−87.3	6.9	−281.4		−87.0	6.9
$Ti(S_2CN(i\text{-}Pr)_2)_4$	−279.3		−83.7	6.8	−281.3		−83.6	6.8
$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$	−133.9	−219.0	−56.9	6.6, 7.6	−134.3	−218.2	−56.6	6.6, 7.5
$Ti(S_2CN(i\text{-}Bu)_2)_3Cl$	−134.9	−218.0	−55.8	6.5, 7.5	−135.8	−217.7	−55.8	6.5, 7.5
$Ti(S_2CN(i\text{-}Bu)_2)_4$	−132.2	−214.8	−52.9	6.5, 7.5	−133.5	−215.5	−52.6	6.6, 7.5

[a] In Hz (±0.3) relative to an internal reference of tetramethylsilane (1% by volume) at 37°. [b] In Hz (±0.1) at 37°. For the isobutyl derivatives the first J value listed is $J(CH_3\text{-}CH)$; the second is $J(CH_2\text{-}CH)$. [c] Septet for R = *i*-Pr; most intense peak of multiplet for R = *i*-Bu. [d] Quartet for R = Et; doublet for R = *i*-Bu. [e] Singlet for R = Me; triplet for R = Et; doublet for R = *i*-Pr or *i*-Bu.

The slopes, α, β, and γ, respectively, of linear plots of the dielectric constant, ϵ_{12}, specific volume, v_{12}, and refractive index, n_{12}, of the solution *vs.* weight fraction of the solute, w_2, were evaluated by least squares analysis. Total molar polarizations, ${}_{\mathrm{T}}P_2$, were obtained from the Halverstadt-Kumler equation,[21] and electronic molar polarizations, ${}_{\mathrm{E}}P_2$, from the modified Halverstadt-Kumler equation.[22] Atomic polarization was ignored. Dipole moments were calculated from the relation $\mu = {}^3/_2[kT_{\mathrm{O}}P_2/\pi N]^{1/2}$ where the orientation molar polarization is given by ${}_{\mathrm{O}}P_2 = {}_{\mathrm{T}}P_2 - {}_{\mathrm{E}}P_2$, and the symbols k, T, and N have their usual significance. Results are presented in Table II.

Table II. Dipole Moment Data

$10^3 w_2$	ϵ_{12}	v_{12}	n_{12}
	$Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$ [a,c]		
1.031	2.2929	1.1448	1.49812
2.035	2.3196	1.1442	1.49825
3.342	2.3396	1.1438	1.49846
3.796	2.3473	1.1434	1.49848
5.693	2.3861	1.1434	1.49856
6.777	2.4148	1.1426	1.49885
7.799	2.4337	1.1421	
	$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$ [b,c]		
3.435	2.3317	1.1435	1.49846
5.030	2.3611	1.1427	1.49868
6.051	2.3763	1.1421	1.49883
7.361	2.4034	1.1415	1.49907
8.836	2.4223	1.1413	1.49919
10.835	2.4606	1.1403	1.49949

[a] $\alpha = 20.54 \pm 1.49$; $\beta = -0.36 \pm 0.10$; $\gamma = 0.11 \pm 0.04$; ${}_{\mathrm{T}}P_2 = 1932 \pm 132$ cm^3; ${}_{\mathrm{E}}P_2 = 138 \pm 18$ cm^3; ${}_{\mathrm{O}}P_2 = 1794 \pm 132$ cm^3; $\mu = 9.37 \pm 0.35$ D. [b] $\alpha = 17.21 \pm 1.16$; $\beta = -0.42 \pm 0.09$; $\gamma = 0.14 \pm 0.02$; ${}_{\mathrm{T}}P_2 = 1822 \pm 116$ cm^3; ${}_{\mathrm{E}}P_2 = 154 \pm 15$ cm^3; ${}_{\mathrm{O}}P_2 = 1668 \pm 115$ cm^3; $\mu = 9.04 \pm 0.31$ D. [c] Errors are estimated at the 95% confidence level.

Table III. Molecular Weight and Conductance Data

Compd	Molarity × 10^2	Mol wt		Conductance data	
		Found[a]	Calcd	Molarity × 10^3	Λ^d
$Ti(S_2CNMe_2)_2Cl_2$		*b*	359	2.76	0.98
$Ti(S_2CNMe_2)_3Cl$		*b*	444	2.46	0.35
$Ti(S_2CNMe_2)_4$		*b*	529	0.39	0.35
$Ti(S_2CNEt_2)_3Cl$	2.71	493[c]	527	1.18	0.39
$Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$		*b*	471	9.6	0.60
$Ti(S_2CN(i\text{-}Pr)_2)_3Cl$	3.20	586	612	14.8	0.11
$Ti(S_2CN(i\text{-}Pr)_2)_4$	3.36	797	753	14.3	0.014
$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$	1.85	517	528	9.1	0.40
$Ti(S_2CN(i\text{-}Bu)_2)_3Cl$	5.79	668	696	2.34	0.093
$Ti(S_2CN(i\text{-}Bu)_2)_4$	6.62	814	865	18.4	<0.007

[a] Determined cryoscopically in benzene. [b] Too insoluble for measurement. [c] 524 in nitrobenzene, 2.0 × 10^{-2} *M* solution. [d] Molar conductance, ohm^{-1} cm^2 mol^{-1}, in nitrobenzene at 25.00 ± 0.05°.

Results and Discussion

Titanium(IV) dithiocarbamates of the type $Ti(S_2CNR_2)_nCl_{4-n}$ (n = 2, 3, or 4; R = Me, *i*-Pr, *i*-Bu, or, when n = 3, Et) have been prepared in high yields by reaction of titanium(IV) chloride with anhydrous sodium *N,N*-dialkyldithiocarbamates in refluxing dichloromethane (or benzene). The product

$$TiCl_4 + nNa(S_2CNR_2) \rightarrow Ti(S_2CNR_2)_nCl_{4-n} + nNaCl$$

depends on the stoichiometry of the reaction mixture, 2:1 and 3:1 molar ratios of $Na(S_2CNR_2)$ to $TiCl_4$ give $Ti(S_2CNR_2)_2Cl_2$ and $Ti(S_2CNR_2)_3Cl$, respectively, while with an excess of $Na(S_2CNR_2)$ (5:1 molar ratio), one obtains $Ti(S_2CNR_2)_4$. The methods used for preparation and isolation of these compounds (see Experimental Section) give materials of good purity as judged by satisfactory elemental analysis and by proton nmr spectra of dichloromethane and deuteriochloroform solutions (Table I). All of the complexes are new compounds except $Ti(S_2CNMe_2)_4$. Bradley and Gitlitz[23] have previously prepared $Ti(S_2CNR_2)_4$ (R = Me, Et, *n*-Pr) by insertion of CS_2 into the Ti-N bond of the corresponding titanium(IV) dialkylamides, $Ti(NR_2)_4$.

All of the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes are brightly colored (red or red-orange). In general, they are soluble in dichloromethane, chloroform, and benzene but are only sparingly soluble in hexanes and cyclohexane; the latter solvents were used to crystallize the compounds. In general, the solubility increases as n increases from 2 to 4, and also as the R group gets bulkier from methyl to isobutyl, so that $Ti(S_2CN(i\text{-}Bu)_2)_4$ has considerable solubility even in cyclohexane, whereas the *N,N*-dimethyl compounds are only slightly soluble in dichloromethane. $Ti(S_2CNMe_2)_4$ is especially insoluble, and when R = Me, the solubility follows the order $Ti(S_2CNMe_2)_4 < Ti(S_2CNMe_2)_2Cl_2 < Ti(S_2CNMe_2)_3Cl$.

The $Ti(S_2CNR_2)_nCl_{4-n}$ complexes are thermally stable, but the solids are slowly hydrolyzed on exposure to air and solutions are hydrolyzed relatively rapidly. The rate of hydrolysis appears to increase as n decreases from 4 to 2.

Molecular weight data are presented in Table III. All of the complexes which are soluble enough to be studied are monomeric in benzene solution. Further, mass spectra of the $Ti(S_2CNR_2)_3Cl$ complexes (Table IV) indicate that these compounds exist as monomeric species in the gas phase as well. The more abundant metal-containing fragments result from

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Table IV. Principal Peaks in the High-Mass Region[a] of Mass Spectra of $Ti(S_2CNR_2)_3Cl$

Ion	*m/e*[b] (rel intens)			
	R = Me	R = Et	R = *i*-Pr	R = *i*-Bu
$(TiL_3Cl)^+$ [c]	443 (2)	527 (2)	611 (3)	695 (2)
$(TiL_3)^+$	408 (8)	492 (41)	576 (86)	660 (30)
$(TiL_3 - (C_2H_4))^+$		464 (12)		
$(TiL_2(CS)Cl)^+$		423 (18)		
$(TiL_2Cl)^+$	323 (100)	379 (100)	435 (100)	491 (100)

[a] Peaks due to ions lighter than $(TiL_2Cl)^+$ are not listed. [b] Based on ^{48}Ti and ^{35}Cl. [c] $L = S_2CNR_2$.

loss of chlorine or one dithiocarbamate ligand, but a weak molecular ion peak is also seen.

Conductance measurements (Table III) show that all of the complexes are essentially nonelectrolytes in nitrobenzene; therefore, the coordination number of the Ti(IV) must be 6, 7, and 8, respectively, for $Ti(S_2CNR_2)_nCl_{4-n}$ ($n = 2, 3,$ and 4) if all of the dithiocarbamate ligands are bidentate. The small amount of dissociation that does occur in nitrobenzene (<4%) probably involves Cl^- ion dissociation predominantly since the molar conductance decreases as n increases from 2 to 4.

Since coordination number 6 for Ti(IV) is common and coordination number 8 has been established by X-ray diffraction,[4-6] the subject of chief interest in the present work is the stereochemistry of the potentially seven-coordinate monochloro complexes, $Ti(S_2CNR_2)_3Cl$. A coordination number of 7 may be assigned if all three dithiocarbamate ligands are bidentate, as in $Mo(NO)(S_2CNR_2)_3$ (R = Me[24] or *n*-Bu[25]); however, the more common coordination number of 6 would result if one of the dithiocarbamate ligands behaves as an S-bonded monodentate ligand, as in $Ru(NO)(S_2CNR_2)_3$ (R = Me[24a] or Et[26]) and $Rh(PPh_3)(S_2CNMe_2)_3$.[24b,27] These two bonding possibilities can be distinguished by infrared spectroscopy since complexes having both monodentate and bidentate dithiocarbamate ligands exhibit additional infrared bands not found for complexes having only bidentate ligands. The more significant of these extra bands are a second $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching band near 1470 cm^{-1} [26,27] and a second $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ stretching band near 1000 cm^{-1}.[28] Thus, $Sn(S_2CNEt_2)_4$, which has been shown by X-ray analysis to be a six-coordinate complex having two monodentate S_2CNEt_2 groups,[29] exhibits two $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bands (1512 and 1471 cm^{-1}) and two $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ bands (1008 and 989 cm^{-1}),[12] while the eight-coordinate $Ti(S_2CNEt_2)_4$[6] displays just one $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ band (1503 cm^{-1}) and one $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ band (1001 cm^{-1}).[12,23]

Characteristic infrared frequencies for the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes are presented in Table V. Except for $Ti(S_2CNMe_2)_3Cl$ and $Ti(S_2CN(i\text{-}Bu)_2)_3Cl$, which show closely spaced doublets (splitting 8-9 cm^{-1}) in the $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ region,[30] all of the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes exhibit just one $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ band and one $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ band. The spectra, therefore, are indicative of bidentate dithiocarbamate attachment and coordination numbers of 6, 7, and 8 for Ti(IV) when $n = 2, 3,$ and 4, respectively.

Further evidence for seven-coordination in the monochloro complexes is provided by the following systematic frequency shifts as n varies from 2 to 3 to 4: (1) a decrease in the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ frequency, (2) an increase in the $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ frequency, and (3) a decrease in the Ti-Cl frequency. These shifts are readily understood if there is a stepwise increase in coordination number from 6 to 7 to 8 on going through the series. We expect that, as the coordination number increases, the Ti-S bonds will become longer and weaker, thus decreasing the relative importance of resonance structure **1c** (see Introduction), which has C=N, and increasing the relative importance of structures **1a** and **1b**, which have C=S. The decrease in the Ti-Cl stretching frequency from 385-397 cm^{-1} in $Ti(S_2CNR_2)_2Cl_2$ to 357-375 cm^{-1} in $Ti(S_2CNR_2)_3Cl$ is also consistent with an increase in coordination number from 6 to 7; similar shifts in ν(M-Cl) have been observed for six-coordinate $M(acac)_2Cl_2$ and seven-coordinate $M(acac)_3Cl$ (M = Zr or Hf; acac = CH_3-CO-CH-CO-CH_3).[31,32] Comparison of the 300-400-cm^{-1} regions of spectra of $Ti(S_2CNR_2)_3Cl$ and $Ti(S_2CNR_2)_4$ indicates that the ν(Ti-Cl) band of the monochloro complexes overlaps a ν(Ti-S) band which occurs in the same region.

On the whole then, the infrared data favor a seven-coordinate structure for the monochloro complexes, despite the presence of two $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ bands for $Ti(S_2CNMe_2)_3Cl$ and $Ti(S_2CN(i\text{-}Bu)_2)_3Cl$. In order to confirm the coordination number and establish the geometry of the coordination polyhedron, we have determined the structure of $Ti(S_2CNMe_2)_3Cl$ by X-ray diffraction. The crystal contains discrete seven-coordinate molecules which have a somewhat distorted pentagonal-bipyramidal structure. The chlorine atom occupies an axial position. Averaged bond distances and angles are entered on Figure 1 which shows a drawing of the molecule in perspective; a full description of the structure, which resembles those of $(\pi\text{-}C_5H_5)Zr(CF_3COCHCOCF_3)_3$,[33] SnT_3X (T = tropolonate; X = Cl or OH),[34] $Zr(acac)_3Cl$,[35] and $Mo(NO)(S_2CN(n\text{-}Bu)_2)_3$,[25] will be published elsewhere.[36] The origin of the splitting of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ band in two of the monochloro complexes is not clear, although it may be relevant to observe that only two of the three dithiocarbamate ligands (b and c in Figure 1) are rendered equivalent by the approximate C_s-m symmetry of the pentagonal-bipyramidal structure. In any case, our results show that a small splitting of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ band does not indicate the presence of monodentate dithiocarbamate.

Concerning the structure of the six-coordinate $Ti(S_2CNR_2)_2Cl_2$ complexes, dipole moments of ~9 D for the isopropyl and isobutyl derivatives (Table II) show that these complexes exist in benzene solution predominantly, if not exclusively, as cis geometrical isomers. This is the expected stereochemistry in view of the cis structures found for related compounds of the type $Ti(chelate)_2Cl_2$.[15,20,37] Since the two metal-halogen stretching frequencies of *cis*-$M(chelate)_2X_2$ complexes are

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[30] This splitting cannot be attributed to a solid-state effect since it is observed in dichloromethane solution spectra as well as in solid-state spectra.

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Table V. Characteristic Infrared Bands of $Ti(S_2CNR_2)_nCl_{4-n}$ Complexes (cm^{-1})

Compd	$\nu(\mathrm{C}\overset{\ldots}{-}\mathrm{N})^a$	$\nu(\mathrm{C}\overset{\ldots}{-}\mathrm{S})^b$	$\nu(\mathrm{Ti–S})^b$	$\nu(\mathrm{Ti–Cl})^b$	Other bands[b,c]
$Ti(S_2CNMe_2)_2Cl_2$	1546 vs[b]	975 m	369 s, 359 s	387 vs	306 vw, ~268 vw
$Ti(S_2CNMe_2)_3Cl$	1526 vs	990 m[d] 981 m	360 s, b	360 s, b	323 w, 270 w
$Ti(S_2CNMe_2)_4$	1521 vs	1002 m	356 s		~260 vw
$Ti(S_2CNEt_2)_3Cl$	1500 vs	1000 m	377 sh, 367 s, 357 s	357 s or 367 s	308 w, 267 w
$Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$	1498 vs	938 w	372 s, 347 m	397 s	299 w
$Ti(S_2CN(i\text{-}Pr)_2)_3Cl$	1489 vs	950 w[f]	375 s, 346 s, 333 m	375 s	300 w
$Ti(S_2CN(i\text{-}Pr)_2)_4$	1479 vs	960 m	369 s, 333 s		295 w, 266 vw
$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$	1505 vs	982 m	371 s, 359 sh	385 s	341 w, 320 w
$Ti(S_2CN(i\text{-}Bu)_2)_3Cl$	1492 vs	997 m[e] 989 m	363 s	363 s	335 vw
$Ti(S_2CN(i\text{-}Bu)_2)_4$	1479 vs	1006 m	362 s		

[a] Unless otherwise indicated, as hexachlorobutadiene mulls between CsI plates; all bands above 1465 cm^{-1} are listed. [b] As Nujol mulls between CsI plates. [c] 400–250-cm^{-1} region; comparison with spectra of $Na(S_2CNR_2)$ salts suggests that these weak bands are ligand bands. [d] Saturated CH_2Cl_2 solution shows a weak doublet at ~994 and ~986 cm^{-1}. [e] CH_2Cl_2 solution (9.6 g/100 ml) shows a medium doublet at 997 and 989 cm^{-1}. [f] $\nu(\mathrm{C}\overset{\ldots}{-}\mathrm{S})$ was given as 1040 cm^{-1} in ref 12. Study of the Na, Ni(II), and Co(III) compounds, as well as the Ti(IV) complexes, for R = *i*-Pr and *i*-Bu indicates that the 950-cm^{-1} band is far more sensitive to the metal and the coordination number than the 1040-cm^{-1} band, hence the revision of this assignment.

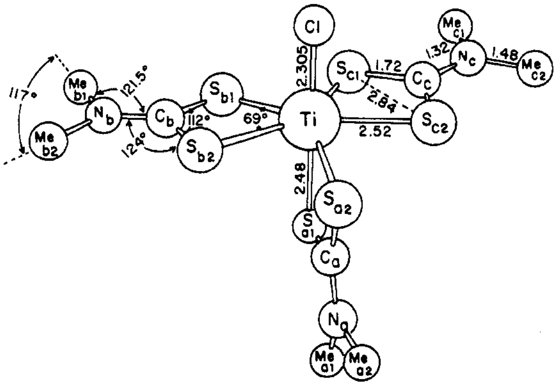

Figure 1. Model of the $Ti(S_2CNMe_2)_3Cl$ molecule in perspective.

often unresolved and since only one ν(Ti–Cl) band is observed for the $Ti(S_2CNR_2)_2Cl_2$ complexes, the far-infrared spectra are not of help in assigning the stereochemistry.

The eight-coordinate $Ti(S_2CNEt_2)_4$ exists in the crystal as the dodecahedral *mmmm* stereoisomer.[6] A similar structure is likely for the $Ti(S_2CNR_2)_4$ complexes prepared in this work.

Stereochemical Nonrigidity. Three kinetic processes have been identified which can affect the line shape in nmr spectra of metal dithiocarbamate complexes: (1) metal-centered rearrangement,[38] (2) $S_2\mathrm{C}\overset{\ldots}{-}\mathrm{N}$ bond rotation,[39] and (3) hindered rotation about C–N single bonds in the NR_2 portion of the S_2CNR_2 ligand.[40] The expected number and relative intensities of R-group resonances for the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes are indicated in Table VI for the following possibilities: (A) metal-centered rearrangement and $S_2\mathrm{C}\overset{\ldots}{-}\mathrm{N}$ bond rotation are both slow on the nmr time scale; (B) $S_2\mathrm{C}\overset{\ldots}{-}\mathrm{N}$ bond rotation is fast, but metal-centered rearrangement is slow; and (C) metal-centered rearrangement is fast ($S_2\mathrm{C}\overset{\ldots}{-}\mathrm{N}$ bond rotation is slow or fast). The analysis assumes that the six-, seven-, and eight-coordinate complexes have cis-octahedral, pentagonal-bipyramidal, and dodecahedral structures, respectively (*vide supra*), and neglects, for the moment, the possibility of hindered rotation about the N–R bonds. The complexes *cis*-$Mo(NO)_2(S_2CNMe_2)_2$ and $Mo(NO)(S_2CNMe_2)_3$, which are stereochemically rigid at 30°, exemplify possibility (A); for the former compound, the two methyl resonances are well separated (by ~0.23 ppm), and for the latter, the four methyl signals span ~0.24 ppm.[24b]

Table VI. Predicted Number (Relative Intensity) of R-Group Resonances for Various Rearrangement Possibilities

Compd	Symmetry	(A)	(B)	(C)
$Ti(S_2CNR_2)_2Cl_2$	C_2-2	2 (1:1)	1	1
$Ti(S_2CNR_2)_3Cl$	C_s-m	4 (2:2:1:1)	2 (2:1)	1
$Ti(S_2CNR_2)_4$	D_{2d}-$\bar{4}2m$	2 (1:1)	1	1

In the case of the $Ti(S_2CNR_2)_nCl_{4-n}$ complexes (n = 2, 3, 4; R = Me, *i*-Bu, or, when n = 3, Et), variable-temperature nmr spectra of dichloromethane solutions show that the R groups remain equivalent over the temperature range +40 to −90°. The dimethyl complexes exhibit a single, time-averaged methyl resonance, which broadens with decreasing temperature but is still relatively narrow at the lower temperatures (~1-2 Hz at −60°; ~1.5-5 Hz at −85°). When R = Et or *i*-Bu, the expected multiplets (Table I) for a single, time-averaged R group are observed above approximately −60°; however, in the range −60 to −90° the lines get broad enough to obscure the spin coupling. It is likely that the line broadening at the lower temperatures is due to solvent viscosity since similar broadening is observed for the corresponding $Ni(S_2CNR_2)_2$ complexes and also for the sodium salt, $Na^+(S_2CN(i\text{-}Bu)_2)^-$.[41] In no case were nonequivalent R groups observed when R = Me, Et, or *i*-Bu; therefore, we may conclude that metal-centered rearrangement in $Ti(S_2CNR_2)_nCl_{4-n}$ complexes is fast on the nmr time scale (possibility (C)) at temperatures above −90°. Possibility (B), rapid $S_2\mathrm{C}\overset{\ldots}{-}\mathrm{N}$ bond rotation but slow metal-centered rearrangement, is precluded by observation of a single, time-averaged R-group resonance for the $Ti(S_2CNR_2)_3Cl$ complexes.

Further evidence for rapid metal-centered rearrangement in these titanium complexes is provided by comparing the CH_2 proton resonances of *cis*-$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$, $Co(S_2CN(i\text{-}Bu)_2)_3$, and $Ni(S_2CN(i\text{-}Bu)_2)_2$. The stereochemically rigid Co(III) complex exhibits an ABX pattern owing to the overall dissymmetry of the molecule.[40,41] The dissymmetric *cis*-$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$, however, like the square-

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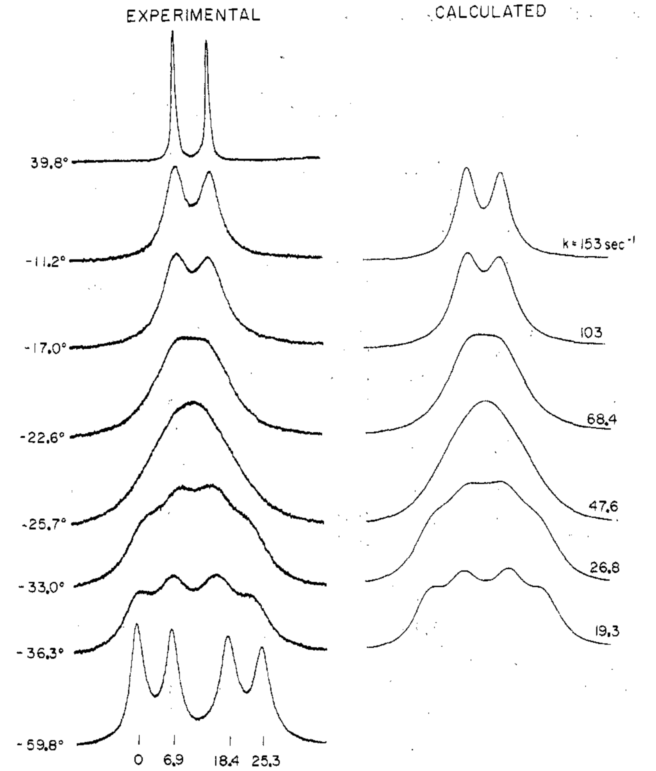

Figure 2. Observed and calculated line shapes for the isopropyl methyl groups of $Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$ in dichloromethane solution at 60 MHz.

planar Ni(II) complex,[40,41] shows only an A_2X pattern (+40 to −60°). Time averaging of the resonances of the diastereotopic CH_2 protons in *cis*-$Ti(S_2CN(i\text{-}Bu)_2)_2Cl_2$ implies that enantiomerization is fast on the nmr time scale. (Note that, whereas enantiomerization averages ABX patterns to A_2X, this averaging is not effected by $S_2C\overset{\cdots}{-}N$ bond rotation because the configuration at the metal center is unaltered.)

We do not know the rate of $S_2C\overset{\cdots}{-}N$ bond rotation in these $Ti(S_2CNR_2)_nCl_{4-n}$ complexes. However, $S_2C\overset{\cdots}{-}N$ rotation in the corresponding methyl esters, MeS_2CNR_2 (R = Me,[42] Et,[42] *i*-Pr,[41] *i*-Bu[41]), is slow on the nmr time scale below about −30°, and comparison of the $C\overset{\cdots}{-}N$ stretching frequencies in the esters (1498,[42] 1489,[42] 1477,[41] and 1480 cm^{-1} [41] for R = Me, Et, *i*-Pr, and *i*-Bu, respectively) with the generally higher values of $\nu(C\overset{\cdots}{-}N)$ in the Ti(IV) complexes (Table V) suggests[39] that $S_2C\overset{\cdots}{-}N$ bond rotation may be even slower in the complexes.

Variable-temperature nmr spectra of the $Ti(S_2CN(i\text{-}Pr)_2)_n$-$Cl_{4-n}$ complexes are qualitatively different from spectra of the Me, Et, and *i*-Bu derivatives in that the spectra reveal the presence of two equally populated *i*-Pr sites at low temperatures. Splitting of the isopropyl methyl doublet below −26° into two doublets of equal intensity is shown for *cis*-$Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$ in Figure 2. Similarly, splitting of the CH septet indicates the presence of two equally populated CH sites at low temperatures.[43] The kinetic process responsible for the line-shape changes (Figure 2) is neither metal-centered rearrangement nor $S_2C\overset{\cdots}{-}N$ bond rotation since (1) we have already shown that metal-centered rearrangement in $Ti(S_2CNR_2)_nCl_{4-n}$ (R = Me, Et, or *i*-Bu) is fast on the nmr time scale at temperatures above −90° and (2) the line-shape changes are essentially independent of the nature and coordination number of the metal. Line-shape changes qualitatively similar to those in Figure 2 are observed for $Ti(S_2CN(i\text{-}Pr)_2)_3Cl$, $Ti(S_2CN(i\text{-}Pr)_2)_4$, $Ni(S_2CN(i\text{-}Pr)_2)_2$, $Co(S_2CN(i\text{-}Pr)_2)_3$, $Zr(S_2CN(i\text{-}Pr)_2)_4$, and also the tetramethylammonium salt, $(NMe_4)^+(S_2CN(i\text{-}Pr)_2)^-$ Golding, *et al.*, [40] who have reported spectra for the Ni(II) and Co(III) complexes, have suggested that the line-shape changes result from hindered rotation about C–N single bonds in the ligand. If the ligand adopts the conformation found in crystalline $Ni(S_2CN(i\text{-}Pr)_2)_2$[44] (Figure 3), there

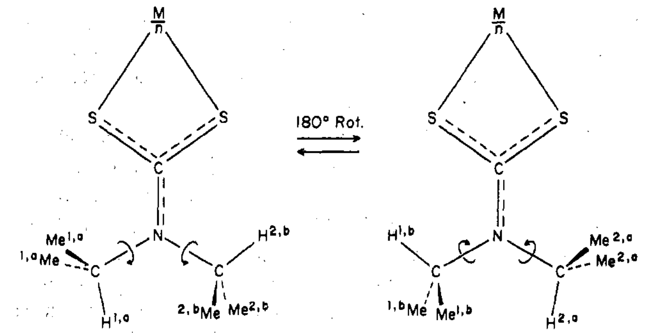

Figure 3. Exchange of *i*-Pr groups in metal *N,N*-diisopropyldithiocarbamates *via* a gearlike rotation (180°) about the C–N single bonds. Numbers label protons and letters label environments. (Note that $S_2C\overset{\cdots}{-}N$ bond rotation does not exchange the *i*-Pr groups.)

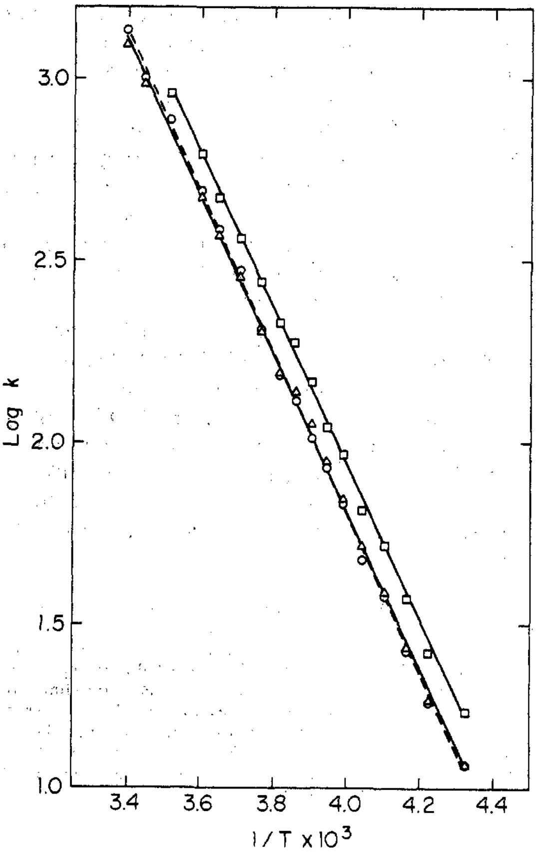

Figure 4. Arrhenius plots for exchange of isopropyl methyl groups in $Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$ (○), $Ti(S_2CN(i\text{-}Pr)_2)_3Cl$ (□), and $Ti(S_2CN(i\text{-}Pr)_2)_4$ (△).

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[42] C. E. Holloway and M. H. Gitlitz, *Can. J. Chem.*, **45**, 2659 (1967).

[43] We have studied the methyl resonances in most detail because of their greater intensity and simplicity.

[44] P. W. G. Newman and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2239 (1972).

are two equally populated *i*-Pr environments, and *i*-Pr groups can be exchanged between these two sites by a synchronous rotation about the two C-N bonds.[40] We propose a gearlike rotation mechanism (Figure 3).

The rate of exchange of isopropyl methyl groups in the $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_nCl_{4-n}}$ complexes was determined by total line-shape analysis. Computer-simulated line shapes were calculated using the Binsch DNMR3 program[45] with $\delta\nu$, the frequency separation between the two isopropyl methyl doublets at the slow-exchange limit, equal to 18.4, 22.4, and 24.0 Hz for $n = 2$, 3, and 4, respectively; in the slow-exchange region these frequency separations are essentially temperature independent. Observed and calculated spectra were compared visually and quantitatively (with reference to line widths and peak separations); examples of best fits are given in Figure 2. Rate constants are presented in Table VII along with values of T_2, the transverse relaxation time, used in calculation of the best fits. The T_2 values were estimated from spectra in the fast- and slow-exchange regions supplemented by examination of line widths over the entire temperature range for the corresponding $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Bu)_2)_nCl_{4-n}}$ complexes.[46] Also presented in Table VII are Arrhenius and Eyring activation parameters, extrapolated values of k at 25°, and ΔG^* near the coalescence temperature (−26°); the Arrhenius and Eyring parameters were obtained in the usual way from the least-squares straight lines of log k *vs.* $1/T$ plots (Figure 4) and log (k/T) *vs.* $1/T$ plots, respectively. Consistent with interpretation in terms of rotation about C-N single bonds in the ligand, the kinetic data are essentially independent of coordination number. Rate constants for the three complexes are nearly the same (~30% larger for $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_3Cl}$), and activation parameters are identical within experimental uncertainty. Our values for E_a (~10.0 kcal/mol) differ significantly from reported values of 4.6 and 5.0 kcal/mol for exchange of CH protons in $\mathrm{Ni(S_2CN(\mathit{i}\text{-}Pr)_2)_2}$ and $\mathrm{Co(S_2CN(\mathit{i}\text{-}Pr)_2)_3}$, respectively.[40]

Table VII. Kinetic Data for Exchange of Isopropyl Methyl Groups in $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_nCl_{4-n}}$ Complexes[a]

	$\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_2Cl_2}$ [b]		$\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_3Cl}$ [c]		$\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_4}$ [d]	
Temp, °C	T_2, sec	$10^{-2}k$, sec^{-1}	T_2, sec	$10^{-2}k$, sec^{-1}	T_2, sec	$10^{-2}k$, sec^{-1}
21.4	0.38	13.7			0.34	12.4
17.2	0.36	10.2			0.34	9.7
11.3	0.36	7.7	0.34	9.2		
4.6	0.34	4.9	0.34	6.2	0.34	4.7
1.0	0.29	3.9	0.27	4.7	0.27	3.7
−3.4	0.29	3.0	0.26	3.65	0.26	2.85
−7.6	0.29	2.04	0.25	2.77	0.24	2.03
−11.2	0.28	1.53	0.24	2.14	0.23	1.55
−13.9	0.27	1.31	0.23	1.89	0.21	1.38
−17.0	0.25	1.03	0.21	1.47	0.18	1.13
−19.7	0.22	0.86	0.18	1.11	0.15	0.89
−22.6	0.20	0.68	0.16	0.93	0.13	0.71
−25.7	0.18	0.48	0.14	0.65	0.11	0.52
−29.5	0.17	0.38	0.12	0.52	0.095	0.39
−33.0	0.15	0.27	0.10	0.38	0.090	0.27
−36.3	0.14	0.19	0.09	0.26	0.082	0.19
−42.0	0.13	0.13	0.085	0.18	0.075	0.13

Activation parameters	$\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_2Cl_2}$	$\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_3Cl}$	$\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_4}$
E_a, kcal/mol	10.1 ± 0.2	9.8 ± 0.2	9.8 ± 0.2
log A	10.64 ± 0.14	10.52 ± 0.19	10.42 ± 0.17
$10^{-3}k_{25°}$, sec^{-1}	1.7 ± 0.3	2.1 ± 0.6	1.6 ± 0.4
ΔH^*, kcal/mol	9.6 ± 0.2	9.3 ± 0.2	9.3 ± 0.2
ΔS^*, eu	−11.6 ± 0.7	−12.1 ± 0.9	−12.6 ± 0.8
$\Delta G^*(-26°)$, kcal/mol	12.45 ± 0.04	12.30 ± 0.05	12.44 ± 0.05

[a] In dichloromethane solution. The probable uncertainty in the rate constants is ~10%. The uncertainties in the activation parameters are random errors estimated at the 95% confidence level. [b] 0.36 *M*. [c] 0.21 *M*. [d] 0.29 *M*.

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Registry No. $\mathrm{Ti(S_2CNMe_2)_2Cl_2}$, 50322-09-3; $\mathrm{Ti(S_2CNMe_2)_3Cl}$, 50322-10-6; $\mathrm{Ti(S_2CNMe_2)_4}$, 32218-45-4; $\mathrm{Ti(S_2CNEt_2)_3Cl}$, 49792-38-3; $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_2Cl_2}$, 49792-39-4; $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_3Cl}$, 49792-40-7; $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_4}$, 50322-11-7; $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Bu)_2)_2Cl_2}$, 49792-41-8; $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Bu)_2)_3Cl}$, 49792-42-9; $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Bu)_2)_4}$, 49792-43-0; $\mathrm{Na(S_2CNMe_2)}$, 128-04-1; $\mathrm{Na(S_2CNEt_2)}$, 148-18-5; $\mathrm{Na(S_2CN(\mathit{i}\text{-}Pr)_2)}$, 4092-82-4; $\mathrm{Na(S_2CN(\mathit{i}\text{-}Bu)_2)}$, 2219-18-3.

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(46) The T_2 values are appreciably temperature dependent owing to viscosity broadening, and therefore the exact value of T_2 at a given temperature in the intermediate exchange region is somewhat uncertain. However, uncertainty in T_2 produces a relatively small error in the rates and activation parameters because of the relatively large values of $\delta\nu$. For example, use of $T_2 = 0.34$ sec for $\mathrm{Ti(S_2CN(\mathit{i}\text{-}Pr)_2)_4}$ throughout the temperature range +21.4 to −42.0° gives errors of 1-14% in k, 0.2 kcal in ΔH^*, and 0.7 eu in ΔS^*.