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Kinetics of Hindered Rotation about Carbon-Nitrogen Single Bonds in Some *N,N*-Diisopropyldithiocarbamates[1]

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The metal *N,N*-diisopropyldithiocarbamate complexes NaL, NiL_2, CoL_3, AlL_3, InL_3, and ZrL_4 (L = $S_2CN(i\text{-Pr})_2$) have been prepared and characterized by IR and ^1H NMR spectroscopy. Low-temperature ^1H NMR spectra of these compounds exhibit two equally intense isopropyl methyl doublets and two equally intense methine septets, attributed to a ligand conformation in which the methine protons of the inequivalent isopropyl groups are located in the plane of the ligand in environments that may be labeled "inner" or "outer" with respect to the quasi-twofold axis of the ligand. Between −50 and +15 °C the methyl doublets and methine septets coalesce to a single doublet and a single septet, respectively, owing to hindered rotation about the C—N single bonds. Rate constants (s^{-1}) at −10 °C in CH_2Cl_2 solution vary from 1400 for CoL_3 to 8.3 for NaL; E_a = 10-12 kcal/mol and $\Delta S^{\ddagger}$ = −7 to −13 eu. The rates increase with decreasing size, increasing charge, and increasing class b character of the metal ion and with decreasing SCS angle and increasing CNC angle in the analogous *N,N*-diethyldithiocarbamates. These trends can be understood in terms of a metal-induced variation in the amount of steric congestion in the $N(i\text{-Pr})_2$ group. The methyl ester $MeSC(S)N(i\text{-Pr})_2$ exists in CH_2Cl_2 solution as a 0.58:0.42 equilibrium mixture of two conformers that have the "outer" methine proton cis and trans, respectively, to the SMe group. Exchange of isopropyl methyl groups among the four inequivalent sites of the two conformers has been analyzed in terms of hindered rotation about (i) the C—N single bonds and (ii) the $C\overset{\cdots}{-}N$ partial double bond. Kinetic data are also reported for rotation about the $C\overset{\cdots}{-}N$ bond in the diisobutyl derivative $MeSC(S)N(i\text{-Bu})_2$.

Introduction

Low-temperature ^1H NMR spectra of metal *N,N*-diisopropyldithiocarbamates exhibit two equally intense isopropyl methyl doublets and two equally intense methine septets that coalesce to a single doublet and a single septet, respectively, at higher temperatures.[3-5] The low-temperature spectra have been attributed to the ligand conformation shown in Figure 1 in which the methine protons lie in the plane of the ligand and the methyl groups are symmetrically disposed on opposite sides of this plane. In this conformation, the two isopropyl groups are inequivalent; one of the methine protons lies in an "outer" site near a sulfur atom, and the other is located in an "inner" site equidistant from the two methyl groups of the other isopropyl group. This ligand conformation, which apparently minimizes nonbonded repulsions between the isopropyl groups, is evident in X-ray crystallographic studies of metal *N,N*-diisopropyldithiocarbamates.[6-17]

Coalescence of the isopropyl resonances has been interpreted in terms of hindered rotation about the isopropyl-nitrogen (C—N) bonds.[3-5] Originally, a synchronous, gearlike mechanism was suggested[3] (Figure 1). More recently, however, molecular mechanics calculations on *N,N*-diisopropylthioamides[18] and NMR studies of $MeSeC(Se)N(i\text{-Pr})_2$[19] have indicated that a nonsynchronous, stepwise mechanism is more likely. Note (Figure 1) that rotation about the carbon-diisopropylamino ($C\overset{\cdots}{-}N$) bond does not exchange the inequivalent isopropyl groups.

Previous studies of C-N rotation in *N,N*-diisopropyldithiocarbamates are limited to complexes of Ni(II),[3a] Co(III),[3a] Ti(IV),[3b] and Sn(IV).[4,5] Reported activation energies span an unreasonably large range, from 4.6 and 5.0 kcal/mol for $Ni(S_2CN(i\text{-Pr})_2)_2$ and $Co(S_2CN(i\text{-Pr})_2)_3$,[3a] respectively, to 18.3 kcal/mol for $Sn(S_2CN(i\text{-Pr})_2)_2Cl_2$.[5] The purpose of the present work was to study C—N rotation in additional metal *N,N*-diisopropyldithiocarbamates in an effort to relate the kinetics of this process to the size, charge, and electronic properties of the metal ion. Reported herein are kinetic data for the complexes of Na(I), Ni(II), Co(III), Al(III), In(III), and Zr(IV); the last three complexes are new. Also reported in this paper are kinetic data for C—N and $C\overset{\cdots}{-}N$ bond rotation in the methyl ester, $MeSC(S)N(i\text{-Pr})_2$, and data for $C\overset{\cdots}{-}N$ bond rotation in the analogous diisobutyl compound, $MeSC(S)N(i\text{-Bu})_2$.

Experimental Section

Preparation of Compounds. Sodium salts of the *N,N*-dialkyldithiocarbamate ligands, $Na(S_2CNR_2)$ (R = *i*-Pr or *i*-Bu), were prepared in good yield by reaction in aqueous solution (10-15 °C) of equimolar amounts of the appropriate secondary amine, carbon disulfide, and sodium hydroxide.[20] The sodium salts were dried in vacuo over phosphorus(V) oxide, first at room temperature and then at 110 °C, until their infrared spectra showed no water or only traces of water. Solvents (benzene, hexane, dichloromethane, and chloroform) were dried by refluxing for at least 24 h over calcium hydride. In order to avoid possible hydrolysis, the Al(III), In(III), and Zr(IV) complexes were prepared and subsequently handled under a dry nitrogen atmosphere.

Tris(*N,N*-diisopropyldithiocarbamato)aluminum(III). A mixture of sodium *N,N*-diisopropyldithiocarbamate, $Na(S_2CN(i\text{-Pr})_2)$ (3.0

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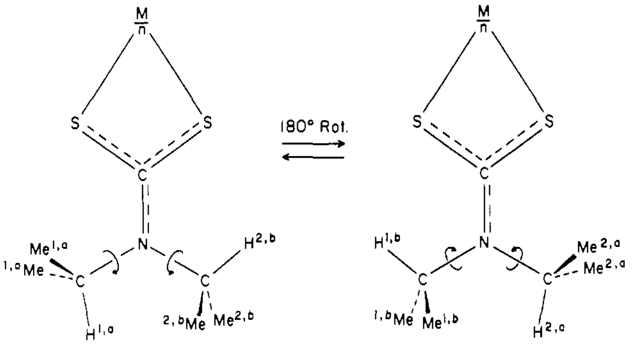

Figure 1. Conformation of the ligand in metal *N*,*N*-diisopropyldithiocarbamate complexes. Also shown is the exchange of inequivalent isopropyl groups via a gearlike rotation (180°) about the C–N single bonds. Numbers label protons and letters label environments.

g, 15 mmol), and anhydrous aluminum(III) chloride (0.60 g, 4.5 mmol) in 75 mL of benzene was allowed to reflux for 12 h. The solution was filtered, and 1.7 g of crude product (68% theoretical yield) was precipitated by addition of hexane. Recrystallization from benzene–hexane afforded white crystals, mp 210–225 °C dec. Anal. Calcd for $Al(C_7H_{14}NS_2)_3$: C, 45.37; H, 7.61; N, 7.56. Found: C, 45.41; H, 8.30; N, 7.76.

Tris(*N*,*N*-diisopropyldithiocarbamato)indium(III). A solution of $Na(S_2CN(i\text{-}Pr)_2)$ (2.0 g, 10 mmol) and anhydrous indium(III) chloride (0.60 g, 2.7 mmol) in 75 mL of absolute ethanol was heated at 40 °C for 12 h, filtered, and then evaporated to dryness. The residue was extracted with dichloromethane, and after the solution was filtered, 0.90 g of product (52% theoretical) was precipitated by addition of hexane. Recrystallization from dichloromethane–hexane afforded white crystals, mp >270 °C. Anal. Calcd for $In(C_7H_{14}NS_2)_3$: C, 39.18; H, 6.58; N, 6.53. Found: C, 38.96; H, 6.51; N, 6.52.

Tetrakis(*N*,*N*-diisopropyldithiocarbamato)zirconium(IV). Triethyl phosphite (1.77 mL, 10.0 mmol) was added to a slurry of zirconium(IV) chloride (1.16 g, 5.0 mmol) in ~80 mL of dichloromethane, and the mixture was stirred for 2 h to dissolve the $ZrCl_4$. The resulting solution was treated with $Na(S_2CN(i\text{-}Pr)_2)$ (4.33 g, 21.7 mmol), and the mixture was allowed to reflux for 12 h. After filtration of the mixture to remove NaCl, the crude product (3.10 g, 78% theoretical) was isolated by reduction of the solution volume and addition of hexane. Recrystallization from dichloromethane–hexane afforded white crystals that decompose above 250 °C. Anal. Calcd for $Zr(C_7H_{14}NS_2)_4$: C, 42.22; H, 7.09; N, 7.03; Zr, 11.45. Found: C, 42.23; H, 6.79; N, 6.96; Zr, 11.67.

Tris(*N*,*N*-diisopropyldithiocarbamato)cobalt(III). A solution of $Na(S_2CN(i\text{-}Pr)_2)$ (4.7 g, 24 mmol) in ~50 mL of water was added to a solution of cobalt(II) chloride hexahydrate (1.8 g, 7.6 mmol) and sodium acetate (3.0 g, 37 mmol) in ~50 mL of water. The dark green solid, which formed immediately, was filtered and dried in vacuo; yield 4.0 g (90% theoretical). The product was purified by chromatography on Florisil followed by recrystallization from dichloromethane–hexane; it decomposes above 260 °C. Anal. Calcd for $Co(C_7H_{14}NS_2)_3$: C, 42.90; H, 7.20; N, 7.15. Found: C, 43.04; H, 7.23; N, 7.18.

Bis(*N*,*N*-diisopropyldithiocarbamato)nickel(II). A solution of $Na(S_2CN(i\text{-}Pr)_2)$ (3.0 g, 15 mmol) in ~50 mL of water was added to a solution of nickel(II) chloride hexahydrate (1.8 g, 7.6 mmol) and sodium acetate (2.0 g, 24 mmol) in ~50 mL of water. The green precipitate, which formed immediately, was filtered and dried in vacuo; yield 2.5 g (81% theoretical). Recrystallization from dichloromethane–hexane afforded green crystals that decompose above 250 °C. Anal. Calcd for $Ni(C_7H_{14}NS_2)_2$: C, 40.88; H, 6.86; N, 6.81. Found: C, 40.83; H, 7.00; N, 6.43.

Methyl *N*,*N*-Diisopropyldithiocarbamate and Methyl *N*,*N*-Diisobutyldithiocarbamate. The methyl esters, $MeSC(S)NR_2$ (R = *i*-Pr, *i*-Bu), were prepared by reaction of the appropriate sodium salt, $Na(S_2CNR_2)$, with an excess of methyl iodide in 95% ethanol. The procedure employed was the same as that reported by Holloway and Gitlitz[21] for preparation of $EtSC(S)NEt_2$. Purification by vacuum distillation afforded clear, colorless liquids in ~60% yield. Anal. Calcd for $C_8H_{17}NS_2$: C, 50.21; H, 8.95; N, 7.32; S, 33.51. Found: C, 50.06; H, 8.85; N, 7.40; S, 33.54. Calcd for $C_{10}H_{21}NS_2$: C, 54.74; H, 9.65; N, 6.38; S, 29.23. Found: C, 54.87; H, 9.64; N, 6.49; S, 29.04.

Table I. Characteristic Infrared Frequencies for Some *N*,*N*-Dialkyldithiocarbamates (cm^{-1})

compd	$\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{N})$	$\nu(NC_2)$	$\nu(\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{S})$	ν(M–S) region
$Co(S_2CN(i\text{-}Pr)_2)_3$	1476	1148	955	366
$Ni(S_2CN(i\text{-}Pr)_2)_2$	1495	1146	941	392
$Zr(S_2CN(i\text{-}Pr)_2)_4$	1478	1143	955	372, 314
$Al(S_2CN(i\text{-}Pr)_2)_3$	1481	1144	945	412, 396, 358
$In(S_2CN(i\text{-}Pr)_2)_3$	1478	1144	944	405, 390, 302
$Na(S_2CN(i\text{-}Pr)_2)$	1475	1145	936	
$MeSC(S)N(i\text{-}Pr)_2$	1477	1143	948	
$MeSC(S)N(i\text{-}Bu)_2$	1480	1145	1005, 958	

Infrared Spectra. Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 521 grating spectrophotometer. Frequencies (±4 cm^{-1}) of characteristic bands are listed in Table I. The metal complexes were studied as Nujol mulls supported between cesium iodide plates; the esters were studied as neat liquids.

Nuclear Magnetic Resonance Spectra. Proton chemical shifts and coupling constants were measured at ambient temperature (~39 °C) in dichloromethane and deuteriochloroform solutions with a Varian A-60A spectrometer. Spectra were recorded in triplicate, and the values reported in Table II are average values; the magnetic field sweep width was calibrated with a standard sample of chloroform and tetramethylsilane in carbon tetrachloride.

Variable-temperature ^1H NMR spectra of degassed dichloromethane solutions were recorded in the temperature range +80 to −90 °C at a sweep width of 50 or 100 Hz (Varian A-60A spectrometer). Van Geet's equations[23] were employed to calculate the probe temperature from the chemical shift between the nonequivalent protons of methanol or 1,2-ethanediol. The procedures used to eliminate or minimize the common sources of error in NMR line-broadening studies[24] are detailed in a previous paper.[25] For all compounds studied, the transverse relaxation times, T_2, are temperature dependent. T_2 values at temperatures in the coalescence region were estimated by plotting log $\Delta_{1/2}$ vs. $1/T$ over a wide temperature range and then extrapolating these plots from the fast- and slow-exchange regions into the intermediate-exchange region; $\Delta_{1/2} = (\pi T_2)^{-1}$ is the full line width at half-maximum amplitude. Errors introduced by uncertainty in the T_2 values should be small because chemical shifts between the resonances of the exchanging protons (Tables III and VI) are quite large. The chemical shifts are temperature independent in the slow-exchange limit.

Spin-decoupling experiments on $MeSC(S)N(i\text{-}Pr)_2$ were carried out at −40 °C with a Bruker HX-90 spectrometer.

Results and Discussion

Metal *N*,*N*-Diisopropyldithiocarbamates. Rate constants for rotation about the C–N bonds (Table III) were determined by analysis of the line shape of the isopropyl methyl resonances. Typical spectra for $In(S_2CN(i\text{-}Pr)_2)_3$ are presented in Figure 2. Spectra of the other complexes are qualitatively similar; chemical shifts in the slow-exchange limit, $\delta\nu$, and the ranges of the transverse relaxation times, T_2, are given in the footnotes to Table III. Theoretical spectra (Figure 2) were calculated with the computer program DNMR 3.[26] Observed and calculated spectra were compared visually and quantitatively (with reference to line widths and peak separations).

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 3) and log (k/T) vs. $1/T$ plots, respectively. The activation parameters are presented in Table IV along with extrapolated values of k at 25 °C and values of k and $\Delta G^‡$ at a common temperature in the coalescence region (−10 °C). Also included in Table IV are kinetic data

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Table II. Proton Chemical Shifts[a] and Coupling Constants[b] for Some *N,N*-Dialkyldithiocarbamates

	dichloromethane			deuteriochloroform		
compd	CH[c]	CH_3[d]	$J(CH_3\text{-}CH)$	CH[c]	CH_3[d]	$J(CH_3\text{-}CH)$
$Co(S_2CN(i\text{-}Pr)_2)_3$	4.62	1.44	6.9	4.65	1.45	6.9
$Ni(S_2CN(i\text{-}Pr)_2)_2$	4.49	1.39	6.8	4.52	1.40	6.8
$Zr(S_2CN(i\text{-}Pr)_2)_4$	4.68	1.43	6.9	4.69	1.41	6.9
$Al(S_2CN(i\text{-}Pr)_2)_3$	4.61	1.44	6.8	4.61	1.46	6.9
$In(S_2CN(i\text{-}Pr)_2)_3$	4.59	1.46	6.7	4.66	1.46	6.8
$[Na(S_2CN(i\text{-}Pr)_2)]_n$	*e*	*e*	*e*	*e*	1.40	6.7
$MeSC(S)N(i\text{-}Pr)_2$[f]	4.81	1.44	7.0	4.82	1.47	7.1
$MeSC(S)N(i\text{-}Bu)_2$[g]	2.43	1.00	6.6	2.39	0.93	6.7

[a] In ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume) at ~39 °C. Concentration of compounds is ~20 g/100 mL of solvent, except for $[Na(S_2CN(i\text{-}Pr)_2)]_n$. [b] In Hz (±0.1) at ~39 °C. [c] Septet for R = *i*-Pr; most intense peak of multiplet for R = *i*-Bu. [d] Doublet. [e] Accurate measurement is precluded by low solubility and exchange broadening at 39 °C. The anhydrous sodium salt is probably an oligomer in solution;[22] its formula is written hereafter as $[Na(S_2CN(i\text{-}Pr)_2)]_n$. [f] In CH_2Cl_2, $\delta(S\text{-}CH_3) = 2.58$; in $CDCl_3$, $\delta(S\text{-}CH_3) = 2.64$. [g] In CH_2Cl_2, $\delta(S\text{-}CH_3) = 2.64$, $\delta(CH_2) = 3.78$, $J(CH_2\text{-}CH) = 7.4$ Hz; in $CDCl_3$, $\delta(S\text{-}CH_3) = 2.60$, $\delta(CH_2) = 3.76$, $J(CH_2\text{-}CH) = 7.4$ Hz.

Table III. Rate Constants for Exchange of Isopropyl Methyl Groups in Metal *N,N*-Diisopropyldithiocarbamates[a,b]

$Co(S_2CN(i\text{-}Pr)_2)_3$[c]		$Ni(S_2CN(i\text{-}Pr)_2)_2$[d]		$Zr(S_2CN(i\text{-}Pr)_2)_4$[e]		$Al(S_2CN(i\text{-}Pr)_2)_3$[f]		$In(S_2CN(i\text{-}Pr)_2)_3$[g]		$[Na(S_2CN(i\text{-}Pr)_2)]_n$[h]	
temp, °C	$10^{-2}k$, s^{-1}	temp, °C	$10^{-2}k$, s^{-1}	temp, °C	$10^{-2}k$, s^{-1}	temp, °C	$10^{-2}k$, s^{-1}	temp, °C	$10^{-2}k$, s^{-1}	temp, °C	$10^{-2}k$, s^{-1}
−11.8	11.9	−6.4	6.3	21.0	6.7	21.7	5.7	21.7	2.92	62.3	9.9
−15.1	8.4	−11.8	4.1	16.0	4.6	12.2	3.4	17.1	2.12	52.5	5.6
−21.6	5.9	−15.1	2.9	11.1	3.7	6.6	2.3	12.2	1.56	48.1	4.9
−24.9	4.2	−21.6	1.79	7.7	2.9	−0.4	1.41	8.5	1.20	41.9	3.2
−28.7	3.6	−24.9	1.38	4.9	2.4	−3.7	1.06	6.6	0.99	37.7	2.4
−32.6	2.4	−28.7	0.99	3.0	1.89	−4.3	0.99	−0.4	0.54	33.2	1.95
−34.7	1.8	−32.6	0.59	0.6	1.72	−8.0	0.62	−3.7	0.43	31.0	1.63
−38.3	1.4	−34.7	0.55	−2.1	1.29	−10.6	0.58	−4.3	0.40	27.8	1.37
−42.8	0.87	−38.3	0.38	−4.9	1.05	−14.6	0.40	−8.0	0.29	23.8	1.00
−46.6	0.57	−42.8	0.25	−8.8	0.81	−17.8	0.30	−10.6	0.26	21.7	0.88
−48.9	0.43	−46.6	0.18	−12.4	0.65	−22.3	0.24	−14.6	0.18	17.8	0.66
−54.9	0.27	−48.9	0.14	−16.2	0.40	−25.2	0.18	−17.8	0.14	14.5	0.54
				−21.3	0.27	−29.7	0.126	−22.3	0.095	10.9	0.43
				−25.0	0.20	−34.9	0.076			8.1	0.36
										2.9	0.23

[a] In dichloromethane solution, except for $[Na(S_2CN(i\text{-}Pr)_2)]_n$. The data for the sodium salt refer to a saturated solution (~0.06 M) in $CDCl_3$. This compound gives essentially identical spectra in CH_2Cl_2 and in $CDCl_3$, but because of higher solubility in the latter solvent, the data for the $CDCl_3$ solution are considered to be more reliable. [b] The probable uncertainty in the rate constants is ~10%. [c] 0.17 M; $\delta\nu = 25.7$ Hz; $J = 6.9$ Hz; $T_2 = 0.19\text{–}0.094$ s. [d] 0.12 M; $\delta\nu = 22.5$ Hz; $J = 6.8$ Hz; $T_2 = 0.27\text{–}0.16$ s. [e] 0.19 M; $\delta\nu = 24.8$ Hz; $J = 6.9$ Hz; $T_2 = 0.32\text{–}0.17$ s. [f] 0.27 M; $\delta\nu = 21.1$ Hz; $J = 7.0, 6.6$ Hz (low-field doublet listed first); $T_2 = 0.29\text{–}0.135$ s. [g] 0.29 M; $\delta\nu = 20.8$ Hz; $J = 6.8, 6.6$ Hz; $T_2 = 0.30\text{–}0.165$ s. [h] ~0.06 M in $CDCl_3$; $\delta\nu = 29.9$ Hz; $J = 6.7$ Hz; $T_2 = 0.38\text{–}0.21$ s.

Table IV. Kinetic Data for C–N Bond Rotation in *N,N*-Diisopropyldithiocarbamates and $C\underset{\cdot\cdot}{-}N$ Bond Rotation in Methyl *N,N*-Diisobutyldithiocarbamate[a]

compd	$10^{-2}k$-(25 °C), s^{-1}	$10^{-2}k$-(−10 °C), s^{-1}	$\Delta G^{\ddagger}$(−10 °C), kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	log *A*
$Co(S_2CN(i\text{-}Pr)_2)_3$	136	14	11.55 ± 0.08[b]	9.7 ± 0.4	−7.1 ± 1.8	10.2 ± 0.4	11.58 ± 0.39
$Ni(S_2CN(i\text{-}Pr)_2)_2$	49	4.5	12.14 ± 0.06	10.1 ± 0.3	−7.7 ± 1.3	10.6 ± 0.3	11.47 ± 0.29
$Ti(S_2CN(i\text{-}Pr)_2)_3Cl$[c]	21	2.3	12.49 ± 0.05	9.3 ± 0.2	−12.1 ± 0.9	9.8 ± 0.2	10.52 ± 0.19
$Ti(S_2CN(i\text{-}Pr)_2)_2Cl_2$[c]	17	1.7	12.64 ± 0.05	9.6 ± 0.2	−11.6 ± 0.7	10.1 ± 0.2	10.64 ± 0.14
$Ti(S_2CN(i\text{-}Pr)_2)_4$[c]	16	1.7	12.64 ± 0.05	9.3 ± 0.2	−12.6 ± 0.8	9.8 ± 0.2	10.42 ± 0.17
$Zr(S_2CN(i\text{-}Pr)_2)_4$	8.9	0.72	13.10 ± 0.05	10.7 ± 0.3	−9.3 ± 1.2	11.2 ± 0.3	11.16 ± 0.26
$Al(S_2CN(i\text{-}Pr)_2)_3$	7.2	0.63	13.17 ± 0.08	10.3 ± 0.4	−10.9 ± 1.6	10.8 ± 0.4	10.80 ± 0.35
$In(S_2CN(i\text{-}Pr)_2)_3$	3.6	0.26	13.63 ± 0.05	11.1 ± 0.3	−9.6 ± 1.3	11.6 ± 0.3	11.08 ± 0.28
$[Na(S_2CN(i\text{-}Pr)_2)]_n$[d]	1.1	0.083	14.23 ± 0.04	11.0 ± 0.2	−12.3 ± 0.8	11.6 ± 0.2	10.55 ± 0.17
$MeSC(S)N(i\text{-}Pr)_2$[e]	8.3	0.51	13.28 ± 0.05	11.9 ± 0.6	−5.3 ± 2.2	12.4 ± 0.6	12.01 ± 0.49
$MeSC(S)N(i\text{-}Bu)_2$[f]	0.36	0.012	15.23 ± 0.04	14.4 ± 0.4	−3.0 ± 1.4	15.0 ± 0.4	12.55 ± 0.31

[a] In dichloromethane solution, except for $[Na(S_2CN(i\text{-}Pr)_2)]_n$. [b] The uncertainties in the activation parameters are random errors estimated at the 95% confidence level. [c] Reference 3b. [d] In $CDCl_3$ solution. [e] Data refer to the C–N bond rotation that converts the trans conformer to the cis conformer (see Figure 7). [f] Data refer to $C\underset{\cdot\cdot}{-}N$ bond rotation.

for the Ti(IV) complexes $Ti(S_2CN(i\text{-}Pr)_2)_nCl_{4-n}$ (n = 2–4), which we have studied previously.[3b] The rate constants at −10 °C decrease from 1400 to 8.3 s^{-1} and the activation energies increase from ~10 to ~12 kcal/mol as the metal varies in the order Co(III), Ni(II), Ti(IV), Zr(IV), Al(III), In(III), and Na(I). Activation entropies are in the range −7 to −13 eu.

Our results for the Co(III) and Ni(II) complexes do not agree with the unusually low activation energies of ~5 kcal/mol reported by Golding et al.[3a] in a study of the isopropyl methine resonances of $Co(S_2CN(i\text{-}Pr)_2)_3$ and $Ni(S_2CN(i\text{-}Pr)_2)_2$. Our study of the methine resonances afforded rate constants and activation parameters similar to those obtained from study of the methyl resonances. However, because the

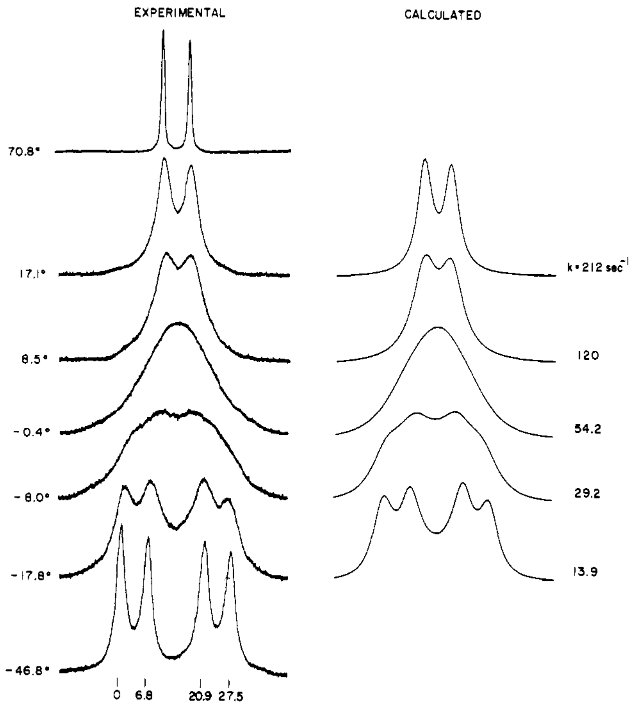

Figure 2. Observed and calculated ^{1}H NMR line shapes for the isopropyl methyl resonances of $In(S_2CN(i\text{-}Pr)_2)_3$, 0.29 M in dichloromethane solution, at 60 MHz.

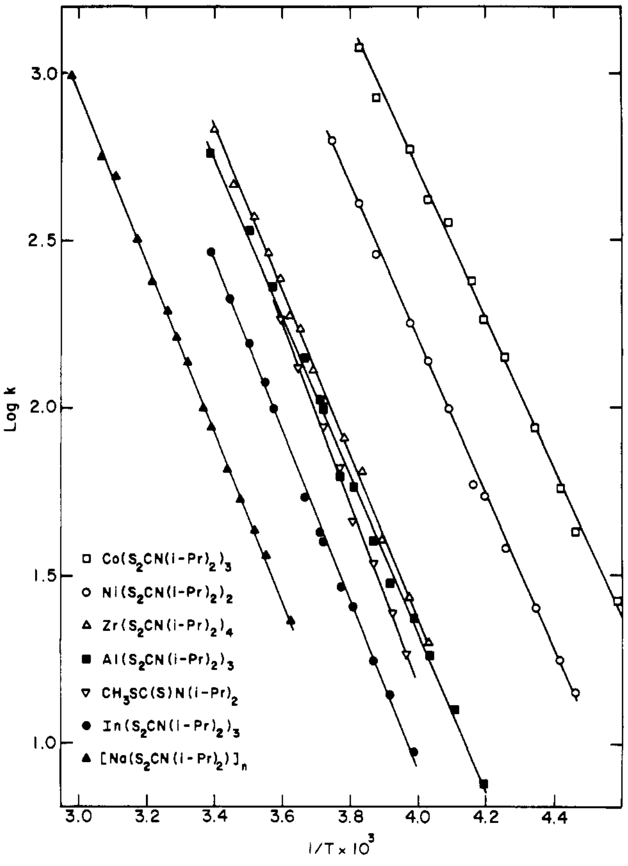

Figure 3. Arrhenius plots for exchange of isopropyl methyl groups in some *N,N*-diisopropyldithiocarbamates.

methyl resonances are more intense and better resolved, we consider kinetic data derived from the methyl resonances to be more reliable.

Table V. Metal Ion Radii, Bond Angles in Metal *N,N*-Diethyldithiocarbamates, and Rate Constants for C-N Bond Rotation in Metal *N,N*-Diisopropyldithiocarbamates

metal ion	ionic radius, Å^a	SCS angle, deg	CNC angle, deg	$k(-10\ °C)$,^{b} s^{-1}
Co(III)	0.63	109.5 (4)^c	119.1 (8)^c	1400
Ni(II)	0.72	110.6 (6)^d	116.9 (12)^d	450
Ti(IV)	0.68	113 (1)^e	118 (2)^e	170
Zr(IV)	0.80	115.1 (3)^f	116.4 (5)^f	72
Al(III)	0.50			63
In(III)	0.81	118.4 (3)^g	116.2 (5)^g	26
Na(I)	0.95	120.4 (4)^h	114.3 (5)^h	8.3

^{a} Reference 34. ^{b} Rate constants for the compounds listed in Table IV. ^{c} For $Co(S_2CNEt_2)_3$.[27,28] ^{d} For $Ni(S_2CNEt_2)_2$.[29] For $Ni(S_2CN(i\text{-}Pr)_2)_2$, the SCS and CNC angles are 109.4 (7) and 117.4 (12)°, respectively.[6] ^{e} For $Ti(S_2CNEt_2)_4$.[30] ^{f} For $(\eta^5\text{-}C_5H_5)Zr(S_2CNMe_2)_3$.[33] ^{g} For $In(S_2CNEt_2)_3$.[31] ^{h} For $Na(S_2CNEt_2)\cdot 3H_2O$.[32]

The values of $\Delta G^‡$ at 25 °C reported by Takeda et al.[5] for $Sn(S_2CN(i\text{-}Pr)_2)_2Cl_2$ (13.3 kcal/mol) and $Me_2Sn(S_2CN(i\text{-}Pr)_2)_2$ (13.8 kcal/mol) lie within the range found in this work, but their activation energies (18.3 and 16.4 kcal/mol, respectively) are considerably larger than the values in Table IV. The differences are probably due to systematic errors in the line-shape analysis rather than a real difference between the Sn(IV) complexes and complexes of the other metals.

The barrier to C—N bond rotation involves clashing of isopropyl methyl groups in the region of the quasi-twofold axis of the ligand (see Figure 1). Consequently, the rate of the exchange process should be affected by factors that alter the amount of steric crowding in the diisopropylamino part of the ligand. In particular, factors that increase the CNC bond angle should increase the rate of rotation about the C—N bonds. The CNC angle will depend in turn on the SCS angle, which will be a function of the size, charge, and electronic properties of the metal ion.

Table V compares rate constants for C—N bond rotation in the *N,N*-diisopropyldithiocarbamates with CNC and SCS bond angles in the corresponding *N,N*-diethyldithiocarbamates[27–32] (and, in one case, an *N,N*-dimethyldithiocarbamate[33]). For the *N,N*-diisopropyl derivatives that we have studied, structural data are available only for $Ni(S_2CN(i\text{-}Pr)_2)_2$.[6] However, the CNC and SCS angles in $Ni(S_2CN(i\text{-}Pr)_2)_2$[6] and $Ni(S_2CNEt_2)_2$ are rather similar (see Table V), and therefore, structural data for the *N,N*-diethyl derivatives should provide a rough idea of the relative amount of steric crowding in the *N,N*-diisopropyl derivatives. Table V suggests that the CNC and SCS angles are inversely related, as expected. These angles vary by a considerable amount on going from the Co(III) complex to the Na(I) compound. Also, as expected, the rates of C—N rotation increase as the CNC angle increases and the SCS angle decreases.

These structural and rate changes can be understood qualitatively in terms of the size, charge, and electronic properties of the central metal ion. For complexes of ions having electronic configuration d^0 or d^{10}, the metal–sulfur bond strength should increase and the SCS angle should decrease with decreasing size and increasing charge of the metal ion. Thus, the rate of C—N rotation is faster in the Ti(IV) com-

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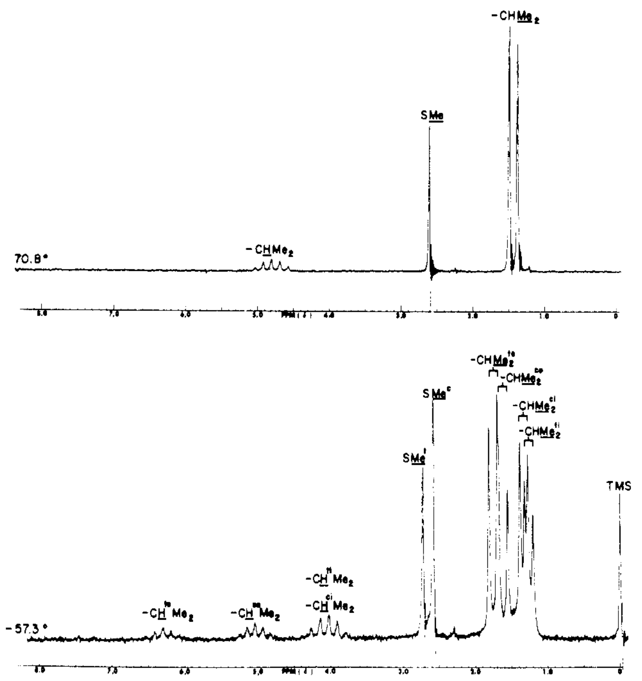

Figure 4. ^{1}H NMR spectra at 60 MHz and peak assignments for MeSC(S)N(i-Pr)$_2$ in deuteriochloroform solution at 70.8 and −57.3 °C. The symbols to, co, etc. are defined in the text and in Figure 7.

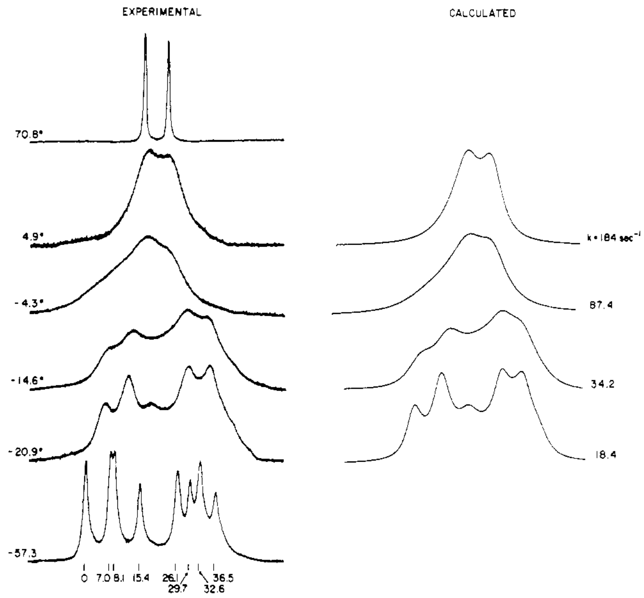

Figure 5. Observed and calculated ^{1}H NMR line shapes for the isopropyl methyl resonances of MeSC(S)N(i-Pr)$_2$, 0.79 M in dichloromethane, at 60 MHz.

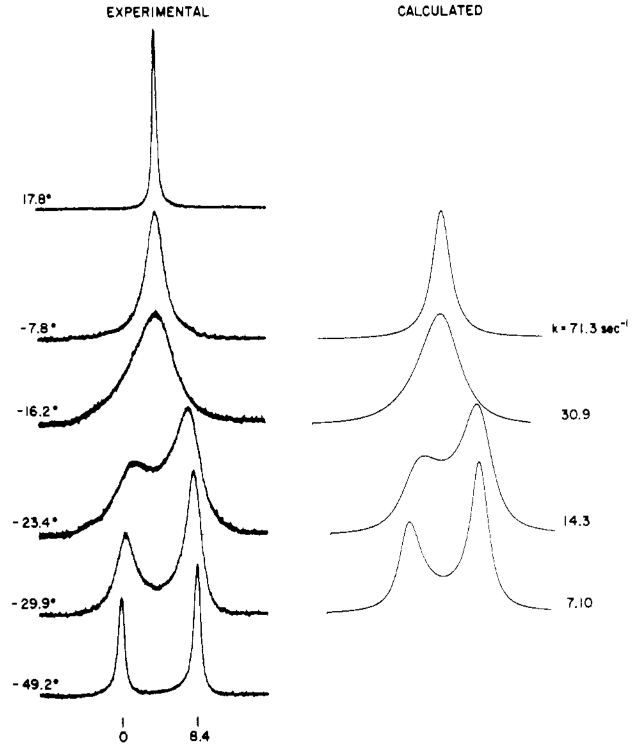

Figure 6. Observed and calculated ^{1}H NMR line shapes for the S-methyl resonances of MeSC(S)N(i-Pr)$_2$, 0.79 M in dichloromethane, at 60 MHz.

plexes than in the Zr(IV) complex and faster in the Al(III) complex than in In(III) compound. Comparing complexes of ions that have similar size but different charge, e.g. In(III) and Zr(IV), one sees (Table V) that C—N rotation is faster in the complex of the more highly charged Zr(IV) ion. For complexes of the later transition metals, one might expect especially strong metal–sulfur bonds and small SCS angles since sulfur is a class b (soft) donor atom.[35] Thus, the rates of C—N rotation are faster in the Ni(II) and Co(III) complexes than in the early-transition-metal Ti(IV) and Zr(IV) complexes. In conclusion, it is evident that the properties of the metal ion influence the amount of steric congestion in the N(i-Pr)$_2$ group and thereby have a substantial effect on the rates of rotation about the C–N bond.

Methyl *N*,*N*-Diisopropyldithiocarbamate. ^{1}H NMR spectra of MeSC(S)N(i-Pr)$_2$ in deuteriochloroform solution at 70.8 and −57.3 °C are presented in Figure 4; spectra in dichloromethane solution are essentially identical. The isopropyl methyl and S-methyl regions of the spectra (in dichloromethane) are shown in more detail in Figures 5 and 6. The high-temperature spectra exhibit a single S-methyl resonance, a single isopropyl methyl doublet, and a single methine septet, indicative of rapid rotation about the C—N single bonds and the C$\overset{\cdots}{-}$N partial double bond. The low-temperature spectra display two S-methyl resonances, four isopropyl methyl doublets, and four methine multiplets, two of which overlap. The relative intensities of these resonances, in order of increasing field, are as follows: 0.42 and 0.58 (S-methyl); 0.29, 0.21, 0.29, and 0.21 (isopropyl methyl); 0.21, 0.29, and 0.50 (methine). In the temperature range −30 to −57 °C, the relative intensities are temperature independent.

We interpret the low-temperature spectra in terms of a 0.58:0.42 equilibrium mixture of the two conformers (Figure 7) that have the isopropyl groups oriented as in metal *N*,*N*-diisopropyldithiocarbamates. The conformer with the "outer" methine proton adjacent to the SMe group is labeled cis, and the conformer with the "outer" methine proton trans to the SMe group is labeled trans. The four inequivalent isopropyl methyl groups and the four inequivalent methine protons are designated co ("cis-outer"), to ("trans-outer"), ci ("cis-inner"), or ti ("trans-inner"), depending on their cis or trans location with respect to the SMe group and their "inner" or "outer" location with respect to the C$\overset{\cdots}{-}$N bond axis.

The methine proton resonances (Figure 4) are assigned on the basis of the well-known magnetic anisotropy of the C$\overset{\cdots}{-}$S group.[36] The lowest field septet is assigned to H$^{\mathrm{to}}$ (Figure 7), the proton adjacent to the C$\overset{\cdots}{-}$S bond. The next lowest field septet is attributed to H$^{\mathrm{co}}$, the proton adjacent to the C—SMe

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Table VI. Rate Constants for Bond Rotation in Methyl *N,N*-Dialkyldithiocarbamates[a]

MeSC(S)N(*i*-Pr)$_2$[b]					MeSC(S)N(*i*-Bu)$_2$[c]	
temp, °C	approx *k*(C=N),[d] s^{-1}	*k*(C—N),[d] s^{-1}	temp, °C	*k*(C—N) + *k*(C=N),[e] s^{-1}	temp, °C	*k*(C=N),[f] s^{-1}
4.9	21 ± 11	184	−3.3	105	34.9	77
1.1	18 ± 9	131	−7.8	71	31.2	56
−4.3	10.5 ± 4.5	87	−10.0	56	25.0	35
−7.8	7.5 ± 3.5	66	−11.4	49	21.5	28
−10.4	5.5 ± 2.5	46	−14.2	39	19.4	22.5
−14.6	4.2 ± 1.8	34	−16.2	31	16.7	17.6
−18.0	2.0 ± 1.0	24	−19.0	26	14.1	13.7
−20.9	1.3 ± 0.7	18	−21.3	20	11.4	10.7
			−23.4	14.3	8.2	8.0
			−24.4	11.9	3.6	4.9
			−27.1	9.5	−3.3	2.4
			−28.8	8.2		
			−29.9	7.1		

[a] In dichloromethane solution. The probable uncertainty in the rate constants is ~10%. [b] 0.79 M. [c] 0.60 M. [d] Obtained from the isopropyl methyl region of the spectrum. Chemical shifts (Hz), relative to Me^{to}, and coupling constants (Hz): Me^{to}, $\delta\nu = 0.0$, $J = 7.0$; Me^{ci}, $\delta\nu = 25.8$, $J = 6.5$; Me^{co}, $\delta\nu = 8.2$, $J = 7.3$; Me^{ti}, $\delta\nu = 29.6$, $J = 6.8$; $T_2 = 0.38\text{–}0.32$ s. Rate constants refer to trans → cis conversion (see Figure 7); rate constants for cis → trans conversion are smaller by a factor of [trans]/[cis] = 0.42:0.58. [e] Obtained from the *S*-methyl region of the spectrum; $\delta\nu = 8.4$ Hz; $T_2 = 0.59\text{–}0.45$ s. Rate constants refer to trans → cis conversion. [f] Obtained from the methylene region of the spectrum; $\delta\nu = 17.0$ Hz; $J = 7.4$ Hz; $T_2 = 0.36\text{–}0.24$ s.

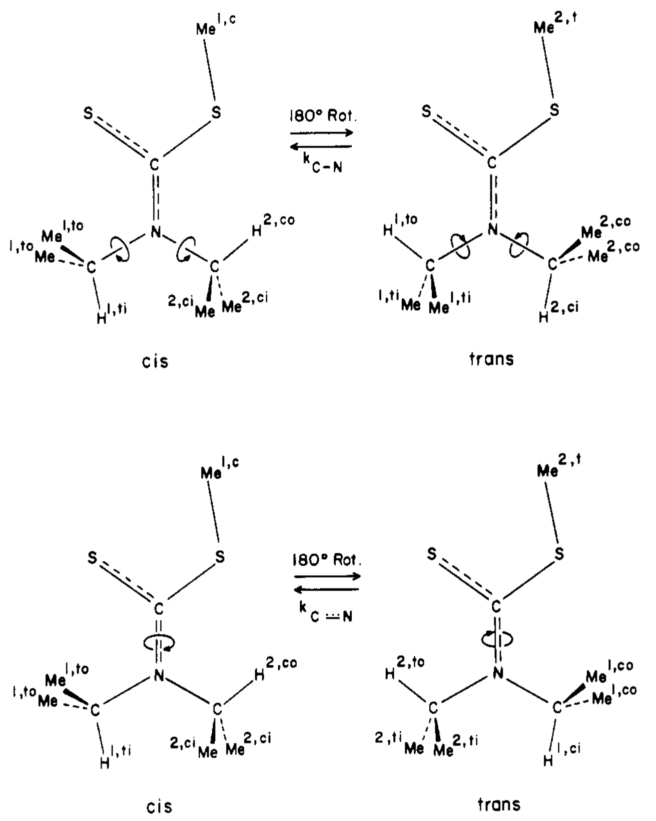

Figure 7. Conformation of the isopropyl groups in the "cis" and "trans" conformers of methyl *N,N*-diisopropyldithiocarbamate. Numbers label protons and letters label environments. Also shown is the exchange of inequivalent protons via rotation about the C—N single bonds and the C=N partial double bond. The C—N rotation is shown as a synchronous process; however, rotation about the two C—N bonds may occur by a stepwise mechanism.[19]

bond, while the overlapping septets at highest field are assigned to H^{ci} and H^{ti}, the two protons more distant from the C=S and C—SMe bonds. These assignments and the relative intensities identify the major conformer as cis and the minor conformer as trans. The trans conformer may be destabilized by steric interactions between the SMe group and the Me^{co} groups. Assignments for the isopropyl methyl resonances and the methine resonances were linked on the basis of relative intensities and spin-decoupling experiments. All of the assignments are indicated in Figure 4, and chemical shifts for the methyl groups are included in the footnotes to Table VI.

Susequent to the completion of this work, ^{1}H NMR spectra of MeSC(S)N(i-Pr)$_2$ in three other solvents have been reported.[4,18,37] In each of these solvents, the cis and trans conformers (Figure 7) were found, with the cis conformer being present in larger concentration; however, a third conformer was detected below −45 °C in small concentrations. Mole ratios of the three conformers are 71:27:2 in carbon disulfide,[37] 59:37:4 in dichlorofluoromethane,[18] and 75:22:3 in dimethyl-d_6 ether.[18] We did not detect the third conformer in dichloromethane (cf. Figures 5 and 6) at temperatures down to −57 °C.

The effects of rotation about the C—N single bonds and the C=N partial double bond are outlined in Figure 7. Both C—N and C=N rotation interconvert the cis and trans conformers, thus exchanging the inequivalent *S*-methyl groups. However, the two rotation processes effect different site exchanges for the isopropyl methyl groups (and for the methine protons). C—N rotation exchanges isopropyl methyl groups between "inner" and "outer" sites (Me^{ci} $\rightleftarrows$ Me^{co} and Me^{to} $\rightleftarrows$ Me^{ti}), while C=N rotation exchanges these groups between cis and trans sites (Me^{ci} $\rightleftarrows$ Me^{ti} and Me^{to} $\rightleftarrows$ Me^{co}). It is evident from the coalescence of all four isopropyl methyl doublets (Figure 5) that both C—N and C=N bond rotation are fast on the NMR time scale at 70.8 °C.

Rate constants for C—N and C=N rotation (Table VI) were determined by comparing observed and calculated line shapes for the isopropyl methyl resonances (Figure 5). Theoretical line shapes were calculated as a function of *k*(C—N) for several ratios of *k*(C—N)/*k*(C=N) by using the computer program PZDMFX;[38] the exchange was treated as a four-site exchange process, with spin coupling to a fifth, nonexchanging, site (methine proton). Because the line-shape changes are dominated by the C—N rotation process, only *k*(C—N) could be accurately determined. The values of *k*(C=N) are approximate because (i) C—N rotation is appreciably faster than C=N rotation ($8 \lesssim k(\mathrm{C{-}N})/k(\mathrm{C{=}N}) \lesssim 14$) and (ii) the chemical shifts between isopropyl methyl groups exchanged by C—N rotation (17.6 and 29.6 Hz) are substantially larger than the chemical shifts between isopropyl methyl groups

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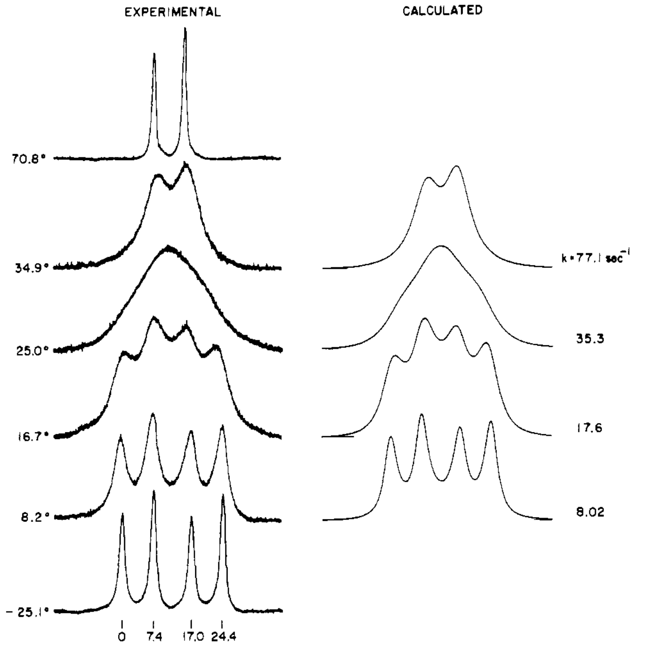

Figure 8. Observed and calculated ^{1}H NMR line shapes for the isobutyl methylene resonances of MeSC(S)N(*i*-Bu)$_2$, 0.60 M in dichloromethane solution, at 60 MHz.

exchanged by C=N rotation (3.8 and 8.2 Hz). As a check on the values of *k*(C—N) and *k*(C=N) obtained from the isopropyl methyl region of the spectrum, rate constants for exchange of *S*-methyl groups, *k*(C—N) + *k*(C=N), were determined from the line shape of the *S*-methyl resonances (Figure 6). The values of *k*(C—N) + *k*(C=N) (Table VI) are in good agreement with the values obtained by summing the individual rate constants determined from the isopropyl methyl region.

A least-squares plot of log *k*(C—N) vs. 1/*T* for MeSC(S)N(*i*-Pr)$_2$ is included in Figure 3, and activation parameters are given in Table IV. The rate of rotation about the C—N bond in the ester, $k = 51$ s^{-1} at −10 °C (for the rotation that converts the trans conformer to the cis conformer), is at the low end, and the activation energy, 12.4 ± 0.6 kcal/mol, is at the high end of the ranges found for the metal complexes (cf. Table IV). These results are consistent with a model in which steric congestion in the diisopropylamino group is relieved by formation of strong metal–sulfur bonds. The only piece of kinetic data for MeSC(S)N(*i*-Pr)$_2$ in the literature with which we can compare our results is a value of $\Delta G^{\ddagger}$ = 13.6 ± 0.1 kcal/mol for cis-to-trans conversion at −8 °C in dichlorofluoromethane solution.[19] Our value of $\Delta G^{\ddagger}$ for the C—N rotation that converts the cis to the trans conformer at −8 °C in dichloromethane is 13.34 ± 0.05 kcal/mol.

Since the rate constants for C=N rotation in MeSC(S)N(*i*-Pr)$_2$ are not sufficiently accurate for determination of activation parameters, we studied the C=N rotation process in the corresponding diisobutyl derivative, MeSC(S)N(*i*-Bu)$_2$, where the NMR spectra are not complicated by hindered rotation about the C—N bonds. Rate constants for rotation about the C=N bond in MeSC(S)N(*i*-Bu)$_2$ (Table VI) were determined by comparison of observed and calculated NMR line shapes for the isobutyl methylene proton resonances (Figure 8). Activation parameters are included in Table IV. The activation energy for C=N rotation in MeSC(S)N(*i*-Bu)$_2$, 15.0 ± 0.4 kcal/mol, should be a fairly good estimate[39] of the activation energy for C=N rotation in MeSC(S)N(*i*-Pr)$_2$; rate constants for the two esters are similar (*k*(C=N) at −10 °C is 1.2 s^{-1} for MeSC(S)N(*i*-Bu)$_2$ and ~6 ± 3 s^{-1} for MeSC(S)N(*i*-Pr)$_2$). The barrier to rotation about the C=N partial double bond is 2.6 ± 0.7 kcal/mol higher than the barrier to rotation about the C–N single bonds.

Acknowledgment. The support of this research by National Science Foundation Grants GP-30691X and MPS7424297 is gratefully acknowledged. We thank John R. Weir for synthesis of Zr(S$_2$CN(*i*-Pr)$_2$)$_4$.

Registry No. Co(S$_2$CN(*i*-Pr)$_2$)$_3$, 24412-36-0; Ni(S$_2$CN(*i*-Pr)$_2$)$_2$, 15694-55-0; Zr(S$_2$CN(*i*-Pr)$_2$)$_4$, 85883-31-4; Al(S$_2$CN(*i*-Pr)$_2$)$_3$, 85883-32-5; In(S$_2$CN(*i*-Pr)$_2$)$_3$, 85883-33-6; Na(S$_2$CN(*i*-Pr)$_2$), 4092-82-4; MeSC(S)N(*i*-Pr)$_2$, 28248-88-6; MeSC(S)N(*i*-Bu)$_2$, 70785-27-2.

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(39) Steric crowding may cause a slight increase in the barrier for MeSC(S)N(*i*-Pr)$_2$. Activation energies in the range 10–13 kcal/mol have been reported for MeSC(S)NR$_2$ (R = Me or Et).[21,40]

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Mutual Labilization of Dimethyl Sulfoxide in the Bis(dimethyl sulfoxide)(1,2-diaminoethane)platinum(II) Cation

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Received October 19, 1982

The kinetics of the reactions [Pt(en)(Me$_2$SO)(L)]$^{2+}$ + Y^{n-} → [Pt(en)(Me$_2$SO)Y]$^{(2-n)+}$ + L (L = Me$_2$SO, Y^{n-} = NO$_2^-$, N$_3^-$, Cl$^-$, Br$^-$, I$^-$, SCN$^-$, SC(NH$_2$)$_2$ in MeOH at 30 °C; L = H$_2$O, Y^{n-} = Cl$^-$, Br$^-$, I$^-$, SCN$^-$, SC(NH$_2$)$_2$ in H$_2$O at 30 °C) have been studied. In all cases the simple second-order rate law is obeyed. The reactivity of the bis(dimethyl sulfoxide) complex is always greater than that of the aquo–dimethyl sulfoxide complex, and a comparison of the rate constants (corrected to zero ionic strength) for the two systems shows that the substrate where L = Me$_2$SO has a significantly greater nucleophilic discrimination ability than that where L = H$_2$O. A mechanism is suggested for the mutual labilization.

Introduction

Sulfoxides as ligands offer many problems and apparent contradictions in their various roles in the substitution reactions of platinum(II) and other four-coordinate planar d^8 metal complexes. For example, dimethyl sulfoxide can exert a moderately strong trans effect[1] while having a negligible trans influence.[2] It is also a poor nucleophile.[3] In these respects

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