$$\mathrm{Co^{III}(NH_3)_5O_2CH^{2+} + OH \rightarrow [Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+} + H_2O} \quad (1)$$

$$\mathrm{Co^{III}(NH_3)_5O_2CH^{2+} + H \rightarrow [Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+} + H_2} \quad (2)$$

$$\mathrm{[Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+} \rightarrow [Co^{II}(NH_3)_5O_2C]^{2+}\ (low\ spin)} \quad (3)$$

$$\mathrm{[Co^{II}(NH_3)_5O_2C]^{2+}\ (low\ spin) \rightarrow [Co^{II}(NH_3)_5O_2C]^{2+}\ (high\ spin)} \quad (4)$$

$$\mathrm{[Co^{II}(NH_3)_5O_2C]^{2+}\ (high\ spin) \rightarrow Co^{II}(NH_3)_3{}^{2+} + CO_2 + 2NH_3} \quad (5)$$

$$\mathrm{Co^{II}(NH_3)_3{}^{2+} \xrightarrow{t_{1/2} = 8\ \mu s} Co^{II}(NH_3)_2{}^{2+} \xrightarrow{t_{1/2} = 80\ \mu s} Co^{II}(NH_3)^{2+} \xrightarrow{t_{1/2} = 500\ \mu s} Co^{2+}(aq)} \quad (6)$$

$$\mathrm{NH_3 + H_3O^+ \rightarrow NH_4{}^+ + H_2O} \quad (7)$$

with $k_1 \sim 2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 \sim 10^7\ \mathrm{M^{-1}\ s^{-1}}$,[16] $k_4 > 10^6\ \mathrm{s^{-1}}$,[17] $k_5 \geq 10^6\ \mathrm{s^{-1}}$, and $k_7 = 4.3 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$.[18] We estimate $k_3 \geq 10^6\ \mathrm{s^{-1}}$, with the lifetime of $\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+}}$ toward intramolecular electron transfer $\leq 10^{-6}$ s. This conclusion is very resonable in light of what we know about the powerful reducing ability of $\mathrm{\cdot CO_2{}^-}$ toward Co(III) complexes[19] and the lifetimes of ligand radicals coordinated to Co(III) centers.[20]

In continuously radiolyzed $\mathrm{O_2}$-saturated solution containing 5.0×10^{-4} M $\mathrm{Co(NH_3)_5O_2CH^{2+}}$ and 0.5 M $\mathrm{NaHCO_2}$ at pH 6, $G(\mathrm{Co^{2+}(aq)}) = 1.3$ which corresponds entirely to the direct reaction of $\mathrm{e_{aq}{}^-}$, which escape scavenging by $\mathrm{O_2}$, with the complex with $k_8 \sim 5 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$; $\mathrm{\cdot CO_2{}^-}$ reacts preferentially with $\mathrm{O_2}$ than with $\mathrm{Co(NH_3)_5O_2CH^{2+}}$ ($k \sim 1 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$).[19] This result establishes that

$$\mathrm{Co(NH_3)_5O_2CH^{2+} + e_{aq}{}^- \rightarrow Co^{2+}(aq) + 5NH_3 + {}^-O_2CH} \quad (8)$$

$\mathrm{O_2{}^-}$ radicals do not reduce $\mathrm{Co(NH_3)_5O_2CH^{2+}}$. With this result, we can interpret the $G(\mathrm{Co^{2+}(aq)})$ values obtained for the continuous radiolysis of $\mathrm{O_2}$-saturated solutions containing 5.0×10^{-4} M $\mathrm{Co(NH_3)_5O_2CH^{2+}}$; $G(\mathrm{Co^{2+}(aq)}) = 2.8$, 3.1, and 3.8 at pH 1.0, 3.1, and 6.8, respectively. The results are in complete accord with reactions 1, 2, and 8 leading to $\mathrm{Co^{2+}(aq)}$ and with $\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+}}$ not being quenched by $\mathrm{O_2}$ in competition with reaction 3. If reaction 9 occurred to any

$$\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+} + O_2 \rightarrow [Co(NH_3)_5O_2C]^{3+} + O_2{}^-} \quad (9)$$

significant extent, a diminution in the yield of $\mathrm{Co^{2+}(aq)}$ and the formation of $\mathrm{Co(NH_3)_5OH_2{}^{3+}}$ would be expected; these effects were not observed. It can be concluded that k_9 has a value of $\sim 10^9\ \mathrm{M^{-1}\ s^{-1}}$ as an upper limit.

According to the mechanism of Candlin and Halpern,[2] reaction 3 would be in competition with reaction 10 with k_{10}/k_3

$$\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+} + MnO_4{}^- \xrightarrow{H_2O} Co(NH_3)_5OH_2{}^{3+} + CO_2 + MnO_4{}^{2-}} \quad (10)$$

$= 3 \times 10^2\ \mathrm{M^{-1}}$. From our estimate of k_3, a value of $k_{10} \geq 3 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ is obtained. However, the possibility remains that reaction of $\mathrm{MnO_4{}^-}$ with $\mathrm{Co(NH_3)_5O_2CH^{2+}}$ occurs via attachment.[21]

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Registry No. $\mathrm{[Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+}}$, 71214-99-8.

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Temperature-Dependent Optical Spectra of Manganese Acetate: Intratrimer Exchange

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The magnetic structure of manganous acetate tetrahydrate $\mathrm{[Mn(OAc)_2]}$ has been the subject of study for over 15 years. The quasi-two-dimensional lattice configuration, in which the intraplanar exchange field is about 8000 G and the interplane exchange field is some 1000 G, had been recognized early in the history of these studies.[1-4] Furthermore, the strength of these exchange fields is nearly independent of temperature in the liquid helium to room-temperature range.[5] However, a rather interesting structural feature was revealed in the neutron diffraction and X-ray crystallographic studies of Burlet et al.[6,7] Within the layered structure the Mn(II) ions are grouped into linear trimers. The coupling within the trimer is antiferromagnetic as is the coupling between planes, while the intertrimer exchange coupling is ferromagnetic. As noted above, the latter two interactions have been measured, but the strength of the former exchange interaction can only be qualitatively determined from shifts in the low-temperature EPR resonance field which are observed at temperatures below 30 K[3] and from a slight curvature in the $1/\chi$ vs. T plot in the powder susceptibility measurements.[1]

Two earlier optical studies have been concerned with $\mathrm{Mn(OAc)_2}$. Mehra and Venkateswarlu[8] (MV) have studied the spectrum in the 3000–6000 Å region at 300 and 77 K. There is little doubt but that their classification scheme of the major spectral features is correct. The two lowest energy bands above the $^6\mathrm{A}_1$ ground state labeled A and B by MV are assigned as the transition to the $^4\mathrm{T}_1(\mathrm{G})$ and $^4\mathrm{T}_2(\mathrm{G})$ states. The next band (C) is relatively sharp with some narrow features already present at 77 K and is assigned as the transition to $^4\mathrm{A}_1(\mathrm{G})$ and $^4\mathrm{E}(\mathrm{G})$. It is this spectral region which was studied in detail by Tsujikawa at low temperatures (down to 1.3 K)

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and in moderate magnetic fields (up to about 2.4 T).[2] This superb 1963 study provided convincing early evidence for the magnetic structural behavior of the intertrimer and intersheet magnetic interactions. The next highest spectral regions labeled D and E by MV are also expected to show narrow features at low temperatures since they derive from the ^{4}D free-ion state and are not strongly dependent on crystal field interactions.

A major motivation in undertaking this low-temperature optical study of $Mn(OAc)_2$ was to search for spectral features which might provide a quantitative measurement of the intratrimer coupling. There are various new features which are observed in the optical spectra of exchange-coupled metal ions which are not present when the chromophores are noninteracting.[9] Some of the features are associated with the existence of interactions over many metal ions in one, two, or three dimensions, while others are mainly associated with the effects of small clusters. The latter may be present when small or moderate concentrations of paramagnetic ions are doped into diamagnetic lattices, or they may be observed, in favorable cases, in naturally occurring cluster compounds. Some of these optical features exhibit characteristic temperature dependencies. In this paper we report temperature-dependent optical spectra which provide the basis for quantitative assignment of the strength of the intratrimeric exchange interaction. These occur in the region labeled D by MV and have not been studied at temperatures below 77 K before.

Certain considerations based on coordination geometry, most notably the syn–syn carboxylate bridge and the single oxygen bridge within the trimeric unit,[6,7] would suggest a stronger exchange coupling be present than that via the anti–syn and anti–anti configurations which provide the in-plane coupling between trimers.[10] Thus since the latter two configurations produce a total exchange energy of 8000 G or about 1 K, it would not be unexpected to observe intratrimer-exchange effects at temperatures an order of magnitude higher. For this reason and because of some simplification in experimental arrangement, the bulk of our polarized single-crystal work was concentrated in the 4.2–77 K range. Because of some interesting physical effects which have been observed in the presence of external magnetic fields,[2,3] we also carried out magnetic field measurements of selected spectral features in the 0–5 T range.

Experimental Section

The single crystals were grown by the slow evaporation of a saturated aqueous solution at room temperature. The diamond-shaped crystals have been characterized by several workers. We will use the notation of Bertaut et al.[6] in which the larger plane contains the *b* and *c* axes, while the *a* axis is nearly perpendicular to this. Furthermore, while the edge of the diamond has four larger sides (011), two additional smaller faces (010) are usually present as well. While most samples were smaller than this, crystals up to about 5 mm thick could be grown by this simple technique.

Most spectra were measured by using a McPherson RS10 double-beam spectrophotometer equipped with an Oxford Instruments CF100 continuous-flow helium cryostat. Emphasis was placed on measurements with polarized light incident on the *bc* face, although the spectral bands of interest were measured with polarized light on the *ac* and *a***b* face as well. The *a** axis is defined as being perpendicular to the *bc* plane.

In addition, measurements were performed on the *bc* face at 2 K in zero field and 6.3 K in applied fields (up to 5 T) by using a Thor Cryogenics split-coil superconducting magnet. The latter made use of a 5-mm quartz refractor plate mounted in the monochromator and driven by a General Scanning CCX 102 unit. A scanning range of 4.0 Å was chosen at each of two monochromator settings (3722.5 and 3277 Å) to measure the applied field dependence. Since this method obviates the need to reset the (mechanical) monochromator drive, successive scans may be accurately superimposed. The areas under the temperature-dependent bands centered about 3722 Å were measured with a Du Pont curve analyzer.

Table I. Absorption Constants (cm^{-1}) of Bands in 4.2 K Polarized Spectrum of Manganous Acetate Tetrahydrate

	3671 Å	3675 Å	3720 Å	3725 Å
		bc Face		
E∥*b*	1.89	1.79	1.05	0.84
E∥*c*	0.26	0.16	0.37	0.21
		ac Face		
E∥*a*	0.18	0.18	0.02	0.04
e∥*c*	0.04	0.08	0.18	0.14
		ba Face		
E∥*b*	0.75	0.71	0.59	0.39
E∥*a*	0.24	0.35	0.20	0.14

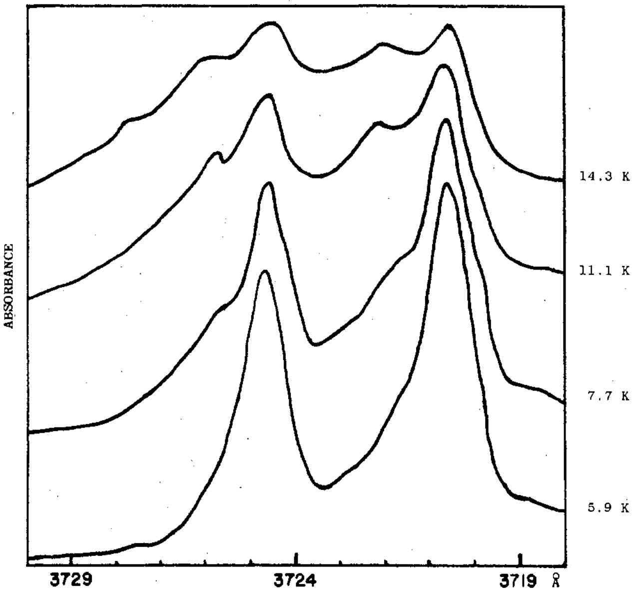

Figure 1. The 3720-Å region of the manganous acetate tetrahydrate spectrum at temperatures between 4 and 15 K.

Polarized spectra were obtained at 4.2 K in the *bc*, *ac*, and *ba** faces. The samples for the latter two studies were obtained by grinding thick crystals with use of wetted emery cloth. The values of the optical density divided by the thickness of the samples appear in Table I for the electric vector parallel to the indicated crystal axes in the three faces studied.

Results

At 4.2 K, in the low-energy side of the ^{4}D spectral region two doublets were observed: one set at 3720 and 3725 Å and the second at 3671 and 3675 Å. The latter set showed some slight broadening as the temperature was increased from 4.2 to 20 K, but, in the same temperature interval, the appearance of the lower energy doublet altered dramatically. Figure 1 shows the development of additional structure on the higher energy side of each of the lines within this doublet. Furthermore, the pattern of intensity shifting within each temperature-dependent submultiplet is the same within experimental uncertainty. The actual amount of broadening of the individual spectral components with increasing temperatures is not great as can be gauged by the slight variation in shape of the high-energy edge of the overall pattern.

This behavior can be associated with the depopulation of the lower excited states of the trimer since this spectral variation occurs at a temperature which is large compared to the intertrimer or intersheet interaction energy expressed in temperature units.

Since the individual Mn(II) ions are spherically symmetrical with a free-ion ground-state term symbol ^{6}S, they normally exhibit no strong angular variation in their magnetic behavior. Furthermore, the interior spin–spin interactions in Mn(II)

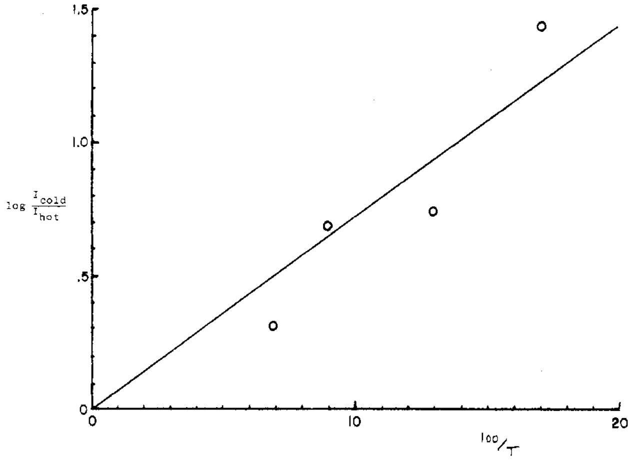

Figure 2. Ratio of the areas *I* of the "hot" and "cold" absorption bands in the 3720-Å region of manganous acetate tetrahydrate as a function of temperature.

compounds can usually be described by a simple Heisenberg Hamiltonian. Therefore, we will take the Hamiltonian in the form

$$\mathcal{H} = -J(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_2\cdot\mathbf{S}_3)$$

where $\mathbf{S}_1$ and $\mathbf{S}_3$ are the spins of the outermost member of the trimer and $\mathbf{S}_2$ is the spin of the central Mn(II) ion. For three ions with spin $^5/_2$ each, the resultant energy level diagram in the absence of a magnetic field consists of 1 level with total spin $^{15}/_2$, 2 with total spin $^{13}/_2$, 3 with total spin $^{11}/_2$, 4 with $^9/_2$, 5 with $^7/_2$, 6 with $^5/_2$, 4 with $^3/_2$, and 2 with $^1/_2$. These 27 macrostates contain a total of 216 microstates. The antiferromagnetic coupling produces a lowest level with $\mathbf{S} = {}^5/_2$. The first and second excited states within this multiplet are an $\mathbf{S} = {}^3/_2$ and $\mathbf{S} = {}^5/_2$ state with energies $5J$ and $7J$ above the ground state. The transitions that are observed in the optical spectrum are assumed to derive from these three (and higher) levels within this ground-state multiplet to multiplets formed by coupling two $\mathbf{S} = {}^5/_2$ ions and one $\mathbf{S} = {}^3/_2$ ion at energy which corresponds approximately to the single-ion $^6A_1$ $(\mathbf{S} = {}^5/_2) \rightarrow {}^4D$ $(\mathbf{S} = {}^3/_2)$ optical transition energy. Depending on the details of the selection rules and the values of the *J*'s in the ground state and excited state, the resultant transitions either may overlap sufficiently so that no strong temperature dependence is observed in the region where $T \leq J/k$ or may be sufficiently resolved to make an estimate of the ground state (J), the excited state (J′), or both. We believe that the higher energy doublet (3671 and 3675 Å) corresponds to the former case while the lower energy doublet (3720 and 3725 Å) provides an example of the latter case.

The ratio of areas under the curve should be proportional to the population of the various submultiplets in the ground state if we assume that the transition moment is governed by a similar mechanism for all these states. The lowest three levels within the ground state are all nondegenerate, and so the separation between them can be calculated by taking the ratios of the areas of the states which grow in intensity on the high-energy side of the 3720- and 3725-Å lines to the area of the lowest level within each set.

Because of the overlapping lines, the slightly asymmetrical shape of the lines at even the lowest temperature, and the large number of lines which start to appear at temperatures above about 15 K, only two ratios could be calculated with any degree of confidence. Even limiting consideration to these levels produced a sufficient range of possibilities on the Du Pont curve analyzer that a range of values for these positions is reported. The second level in the ground multiplet lies at 4.3–5.0 K while the third lies between 7.0 and 7.6 K. The values are consistent with the Heisenberg coupling scheme if the value of *J* is 1.0 ± 0.2 cm^{-1}. A plot of the ratio of the areas vs. $1/T$ is shown in Figure 2.

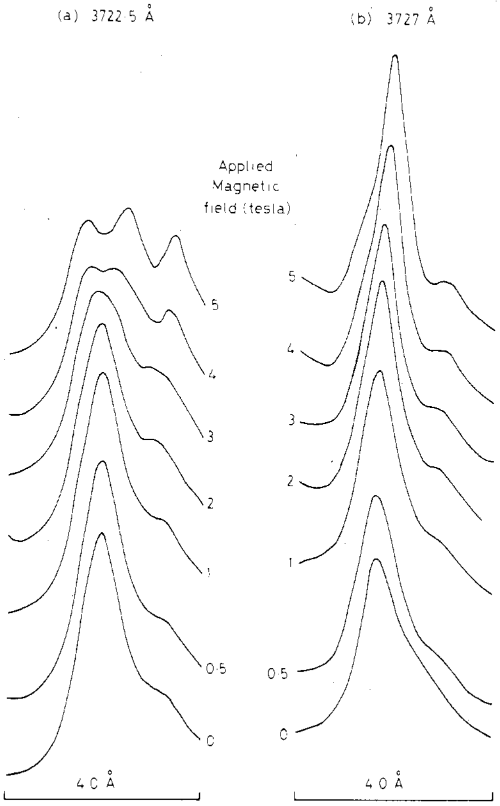

Figure 3. Zeeman measurements on *bc* crystal face of manganous acetate tetrahydrate at 6.3 K; crystal thickness 1.93 mm; *E*‖*b* and *H*‖*b*; monochromator settings (a) 3722.5 ± 0.5 Å and (b) 3727 ± 0.5 Å. Energy increases from right to left.

Thus, the temperature variation of the intensities provide a measurement of the ground-state intertrimer exchange. However, the variation of the intensity of the polarized spectra as shown in Table I clearly indicates that the intensity-producing mechanism is not purely electric dipole. Ferguson[11] has outlined the methods for determining the relative amounts of electric dipole and magnetic dipole parts of the intensity, but such an analysis seems most appropriate in high-symmetry crystals and will not be carried out here.

In an experiment in which the temperature lowered below 3.18 K, the transition temperature, only some small changes in intensity were noted in the higher energy doublet while both members of the lower energy doublet broadened. This suggests the effect of the internal field associated with the development of long-range order, but the intensity was insufficient to resolve any structure. It is worth noting in this connection that the intertrimer-exchange field is about 8000 G, and there is evidence that it is not a strong function of temperature. Indeed room-temperature EPR measurements[5] produce a value for this field in good agreement with the low-temperature results although, of course, at this temperature the field is not static.

The experiments with the refractor plate showed that the two low-energy bands behaved rather differently in high magnetic fields. In Figure 3 the variation of the position and the intensities of the lines in the 3720- and 3725-Å regions are displayed. It is clear that both a shifting of the center of gravity in each portion of the pattern is occurring and some additional structure is developing with increasing magnetic field. However, these effects are not just a simple molecular Zeeman effect as there seems to be a distinct nonlinear dependence to both the shifting and splitting. Indeed at 6.5 K, the temperature at which these studies were carried out, a field of nearly 3 T is needed to clearly show an effect. Since the internal intratrimeric magnetic field is about 0.8 T and the material is a metamagnetic, it is possible that these effects are associated with a Zeeman effect due to both the magnitude and direction of the internal and external fields.

Conclusions

The value of the ground-state exchange parameter J was found to be about 1 cm^{-1}. Since the total spread of this multiplet is $55J$, this value is consistent with the small change in slope of the susceptibility vs. $1/T$ curve at about 20 K[1] and the more pronounced changes in the low-temperature EPR behavior which set in the 20–30 K range.[4] The intensity-producing mechanism contains both electric dipole and magnetic dipole components. Finally, nonlinear Zeeman effects were noted in the low-temperature optical spectra.

Registry No. $Mn(OAc)_2 \cdot 4H_2O$, 6156-78-1.

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Silyl Group Exchange between Chlorosilane and *N*-Methyldisilazane

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A good deal of evidence has been presented in recent years affirming the electron-accepting powers of the silyl (SiH_3) group. In the case where silicon is already bound by a σ bond to another atom, an additional dative bond of the $p\pi$–$d\pi$ type may be formed by utilizing one of the vacant silicon d-orbitals. Where the attached atom is one belonging to group 5 or 6 normally possessing marked electron-donating properties, these properties will be weakened after attachment to a silyl group. This effect explains why the basic properties of the following series of compounds toward Lewis acids increase as shown:[1-3] $(SiH_3)_3N < (SiH_3)_2NCH_3 < SiH_3N(CH_3)_2 < N(CH_3)_3$. Further evidence of the relative basicities of the former two amines is presented as a result of the rapid silyl group exchange between chlorosilane and *N*-methyldisilazane.

Experimental Section

Apparatus and Equipment. All chemical reactions were carried out by using conventional high-vacuum techniques.[4] Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer, Model 137. The samples were confined in a 5-cm gas cell with NaCl windows. Proton NMR spectra were obtained at 60 MHz with a Varian DP60 or Varian A-60A spectrometer equipped with a standard variable-temperature control. Mass spectra were obtained with an MS-10 mass spectrometer.

Reagents. All solvents were reagent grade and were dried by standard methods. Chlorosilane was prepared from silane and hydrogen chloride in the presence of an aluminum chloride catalyst[5,6] and purified by fractional condensation to give a vapor pressure of 50 torr at −78 °C. Chlorosilane-d_3 was synthesized from silane-d_4 and DCl in a similar manner. The preparation of trisilylazane by the ammonolysis of chlorosilane has been described previously.[1,2,7] The vapor pressure of the purified material was 109 torr at 0 °C (lit. 109[7] and 110 torr[2]). *N*-Methyldisilazane was prepared from chlorosilane and methylamine[2,5] and purified to give a vapor pressure of 188 torr at 0 °C (lit. 192[5] and 193 torr[2]).

Exchange Reaction between Chlorosilane and *N*-Methyldisilazane. a. Infrared Studies. In a typical experiment chlorosilane-d_3, 0.45 mmol, and 0.23 mmol of *N*-methyldisilazane were mixed together and allowed to remain in the gas phase in a U-tube for 10 min at room temperature at a total pressure of 0.12 atm. No association could be detected in the gas phase. The gases were separated by passage into a −112 °C trap, and the distillate (chlorosilane fraction) was sampled for an infrared spectrum. All absorbances could be accounted for by assuming a mixture of SiH_3Cl and SiD_3Cl; there was no evidence for the pressure of any mixed species such as SiH_2DCl and $SiHD_2Cl$. (The broad doublet in the 10–15 μm range characteristic of the SiX_3 deformation is uniquely defined in each of the four isotopically different compounds: SiH_3Cl, 950 cm^{-1};[8] SiH_2DCl, 890 cm^{-1}; $SiHD_2Cl$, 845 cm^{-1}; SiD_3Cl, 700 cm^{-1} [9]).

For determination of the extent of silyl group exchange, a calibration curve was constructed wherein the differences between the optical densities of the Si–D and Si–H stretching frequencies were plotted vs. the mole percentage of silyl-d_3 groups in known mixtures of SiD_3Cl and SiH_3Cl. The difference in the optical densities of the two stretching frequencies was chosen as a parameter in preference to that of either frequency alone to minimize the error caused by slight pressure variations in the cell when proceeding from one experiment to the next. The pressure employed in the cell was 40 ± 1 torr. The resulting linear plot was refined by the method of least squares to give $m = 0.0173$, $b = -0.880$, and $\sum r_i^2 = 0.0086$.

The percentage of deuterated silyl groups initially present in the mixture was 49%. By reference to the calibration curve, the percentage found in the chlorosilane fraction after exchange was also 49%, confirming complete equilibration of silyl groups.

b. NMR Studies. It seemed possible that exchange was occurring so rapidly that an NMR spectrum of a mixture of SiH_3Cl and $(SiH_3)_2NCH_3$ might yield only one observable Si–H resonance absorption. The proton resonances (vs. Me_4Si) of each compound were obtained in CS_2: $\delta = -4.66$ for SiH_3Cl; $\delta = -4.38$ (Si–H) and -2.62 (C–H) for $(SiH_3)_2NCH_3$. The observed chemical shifts of a 2:1 molar mixture in CS_2 were identical, showing no tendency toward coalescence. The separations between the two Si–H resonances did not change (within experimental error) as the temperature was raised in 20 °C intervals to 100 °C.

In a second series of experiments SiD_3Cl and $(SiH_3)_2NCH_3$ in a 2:1 molar ratio were separately condensed into an NMR tube, as was CS_2, and the tube was sealed under vacuum. The sample was not allowed to warm above −50 °C; the spectrum was scanned repeatedly at this temperature in an attempt to follow the exchange process. It was expected than an initially small peak at −4.66 ppm would increase as the silyl group exchange occurred and that the peak at −4.38 ppm would decrease. The −4.66 ppm resonance due to SiH_3Cl was unexpectedly intense initially. No changes in relative peak areas occurred as a function of time. Analysis of all three peak areas showed that silyl group scrambling was complete at this temperature in a matter of minutes.

c. Mass Spectral Studies. For determination of whether the liquid phase is required for silyl group exchange, 0.241 mmol of $(SiH_3)_2NCH_3$ and 0.516 mmol of SiD_3Cl were separately sealed into glass tubes joined by a 4-mm stopcock. The two gas phases were allowed to equilibrate, and the mixture sampled for a mass spectrum without condensation. The spectrum was consistent with silyl group exchange, with a strong peak at m/e 97 due to $(SiD_3)_2NCH_3^+$ and minor higher peaks up to 100 due to small amounts of silicon-29 and -30.

Exchange Reaction between Chlorosilane and Trisilazane. In a typical experiment, SiD_3Cl and $(SiH_3)_3N$ in a molar ratio of 3:1 were transferred to an all-glass reaction bulb. After being sealed, the bulb and its contents were immersed in a constant-temperature bath for a given period of time. The bulb was quenched with liquid nitrogen and opened on the vacuum system. The gases were fractionated by a single pass through a −112 °C trap, and the distillate (the chlorosilane

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