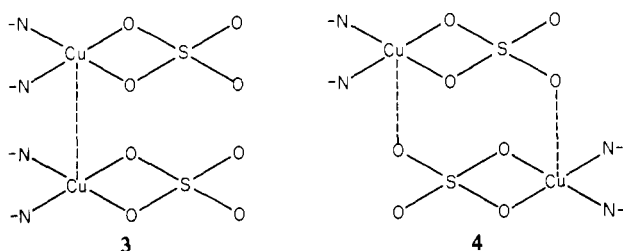


Figure 3. X-Band (9.15 GHz) ESR spectrum of $(dpe)Pt(3,5-Me_2pz)_2CuSO_4$ in CH_2Cl_2 at room temperature.

powdered samples indicate a large Cu-Cu distance among the dimeric unities.

The ESR data are consistent either with a structure of type 2 or with a system where a pair of neighboring molecules of type 1 are interacting, e.g., as in 3 or 4.



When the complex is dissolved in dichloromethane, a glassy ESR spectrum is obtained, typical of a magnetically diluted copper(II) complex with axial symmetry ($g_{\parallel} = 2.304$, $g_{\perp} = 2.051$, $A_{\parallel} = 482.7$ MHz). The room-temperature ESR spectrum (Figure 3) displays, in addition, five well-resolved shf lines, indicating the presence of two nitrogen atoms in the chromophore. The electronic spectrum shows a noticeable shift of the maximum to 17240 cm^{-1} , suggesting a more planar geometry at the copper ion.

Thus it seems that, upon dissolution, not only the magnetic exchange is lost but also the chromophore attains a different geometry. This observation is more consistent with the hypothesis that, in the solid state, a structure of type 2 or 4 is present, the sulfato bridge inducing a pseudotetrahedral distortion or a pentacoordination at the copper atom. Faced type 1 molecules (e.g., 3), on the contrary, would likely interact axially; in this case the copper(II) ions, at a distance of ca. 7 \AA , would be in a planar configuration even in the solid state, so that, upon dissolution, only minor changes in the electronic spectrum should be expected.

In conclusion the spectroscopic data point to the existence, in the solid state, of a structure where the copper atoms are bridged by sulfato groups.

Experimental Section

The synthesis of the complex has been described previously.²

Spectroscopic Measurements. ESR spectra were recorded down to 4 K in either X or Q band (≈ 9.1 and 34.9 GHz, respectively) on a Varian E9 spectrometer. Electronic spectra were obtained by using a Beckman Acta M IV spectrophotometer equipped with an integrating sphere for solid samples. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were obtained as Nujol mulls on a Perkin-Elmer 683 spectrophotometer.

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Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Characterization of the Gas-Phase Components in Equilibrium with the Ionic Compound Ammonium Trimethylsilyl Sulfite: A New Silanol Source

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In previous work we proposed a reaction scheme for the oxygen atom transfer reaction between sulfur dioxide and hexamethyldisilazane.² One of the products of this reaction is $NH_4(CH_3)_3SiOSO_2$ (1), a new ionic solid with an extraordinarily high volatility. Consistent with the proposed mechanism, this product was postulated to be in equilibrium with NH_3 , SO_2 , and $(CH_3)_3SiOH$, the gas-phase components from which it is formed in the reaction.²

There are several examples of ammonium salts that are in equilibrium with two or more molecular species in the gas phase.³ Most have very small equilibrium constants and consequently low vapor pressures for this type of dissociative process, e.g., NH_4Cl and NH_4NO_3 .³ Ammonium sulfites and bisulfites, however, are characterized by considerably higher volatility and dissociate into three molecular components, NH_3 , SO_2 , and H_2O .^{4,5} Equilibria of this type are rather rare, offering a challenging dynamical problem with respect to how they can occur at all. Since initial work in this laboratory with the new salt, 1, indirectly indicated that a facile equilibrium existed with three molecular components² and the heat of sublimation of 1 was measured to be only 15 kcal/mol ,^{2a} we felt it important to seek direct evidence for the molecular species postulated to be in equilibrium with the solid. Additional motivation for this study derived from the earlier mechanistic suggestion that one of the molecular components was silanol.² Thus, the new sulfite was considered to be a candidate for a solid-state source of this reactive silyl alcohol.

The solid sulfite, $NH_4(CH_3)_3SiOSO_2$, was prepared with the method described previously^{2b} by condensing dry SO_2 over a frozen, dried, and degassed sample of $((CH_3)_3Si)_2NH$. Upon warming, the reaction proceeds rapidly, giving the white solid product and the liquid coproducts $(CH_3)_3SiNSO$ and $((CH_3)_3Si)_2O$. Separation of products to yield the sulfite was carried out by using vacuum and Schlenk techniques as described earlier. Fourier transform infrared spectra of the vapor above the solid were obtained on a Nicolet 7199A spectrometer. Infrared spectra of solid films of the sulfite were collected on a Beckman IR-20 instrument. Mass spectral data were obtained with a Varian 112S mass spectrometer by using electron impact ionization at 60 V.

To verify the existence of the postulated equilibrium, we have measured the Fourier transform infrared spectrum of the vapor phase over 1. The solid was introduced into a small well in a gas IR cell with a 10-cm path length, which was then evacuated, leaving solid 1 and its vapor-phase components. Figure 1A is an FT IR spectrum of the vapor in this cell. By inspection the spectrum was found to contain absorptions from several distinct substances: unassigned materials, NH_3 (lit.⁶ 935 and 970 cm^{-1}), SO_2 (lit.⁶ 1340 and 1380 cm^{-1}), and

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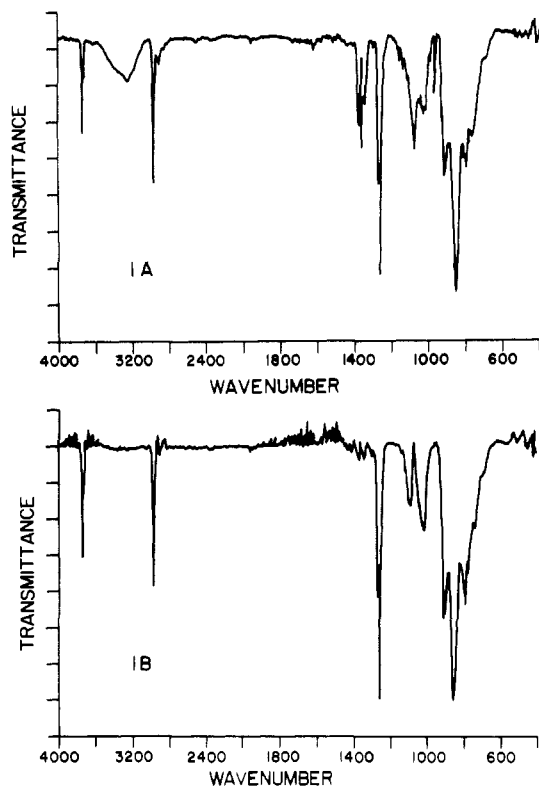


Figure 1. (A) FT IR spectrum of the vapor sublimed over $\text{NH}_4(\text{CH}_3)_3\text{SiOSO}_2$. (B) Above spectrum after instrument subtraction of signals from NH_3 , SO_2 , and $((\text{CH}_3)_3\text{Si})_2\text{O}$.

$((\text{CH}_3)_3\text{Si})_2\text{O}$ (lit.⁶ 750, 830, 1050, 1250, and 2950 cm^{-1}). Spectra of authentic samples of the three known compounds were independently recorded in the spectrometer memory file so that they could be deleted from the FT IR spectrum of the vapor over **1** by software subtraction. The residual spectrum is shown in Figure 1B. The remaining peaks can be assigned to silanol on the basis of the published gas-phase spectra⁷ (principal peaks at 762, 780, 851, 906, 914, 1258, 1266, 2968, and 3735 cm^{-1}). This result indicates that there are at least four components in the vapor phase over $\text{NH}_4(\text{CH}_3)_3\text{SiOSO}_2$.

Mass spectral data verify the existence of SO_2 , $(\text{CH}_3)_3\text{SiOH}$, and $((\text{CH}_3)_3\text{Si})_2\text{O}$. Major peaks were observed at m/e 64 (31%) for SO_2^+ , m/e 75⁸ (100%) for $(\text{CH}_3)_2\text{SiOH}^+$, and m/e 147⁸ (6%) for $(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3^+$. The mass peak corresponding to NH_3^+ was below the mass range of the instrument and was not observed.

Separation of the vapor-phase components was attempted in a preliminary experiment on the vacuum line via fractional condensation into two cold traps in a series. The results indicated that even in a trap as warm as 0 °C the solid preferentially re-formed on the walls, making this separation procedure ineffective. While a more carefully executed vacuum-separation process may very well isolate the silanol, this result suggests that the best way to utilize the silanol released from the solid may be in direct reaction without separation. Indeed, since pure silanol tends to undergo condensation reactions rather rapidly, limiting its shelf life, its use directly from the solid sulfite precursor is an advantage provided the ammonia and sulfur dioxide byproducts can be tolerated.

The presence of $((\text{CH}_3)_3\text{Si})_2\text{O}$ is consistent with the fact that silanol condenses slowly to form hexamethyldisiloxane and water.⁹ This phenomenon was confirmed to occur in the

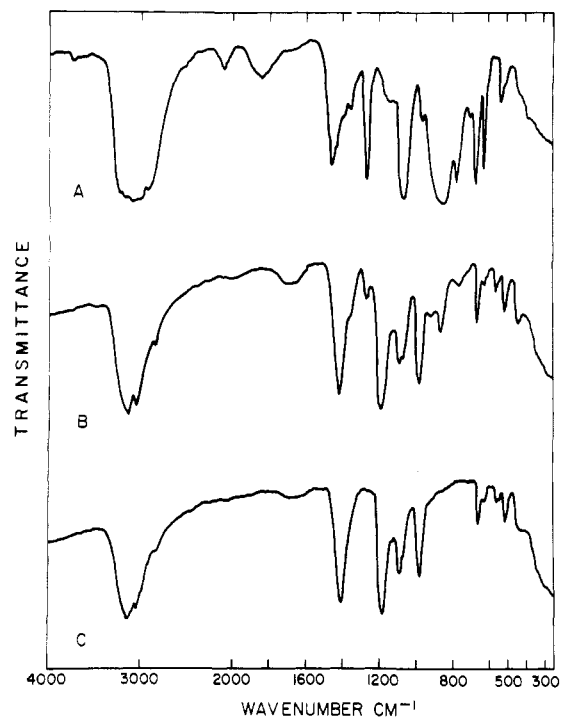
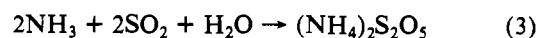
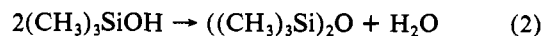
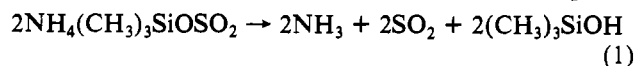


Figure 2. (A) Infrared spectrum of a freshly prepared $\text{NH}_4(\text{CH}_3)_3\text{SiOSO}_2$ solid film on a KBr window. (B) Above spectrum after ca. 12-h exposure to the atmosphere. (C) Above spectrum after 3-day exposure to the atmosphere.

vapor phase above **1** by a totally unexpected experimental result. A small amount of solid **1** was transferred into a U-trap on the vacuum line by vacuum sublimation and isolated in the evacuated trap for several weeks. After this period small crystals were observed to adhere to the walls, apparently having been formed spontaneously from vapor within the trap. One of the crystals was lifted from the wall under dry nitrogen with a glass fiber and quickly transferred to a Lindemann glass capillary tube. The tube was sealed, and the X-ray structural data were collected. Surprisingly, the crystalline material was identified as ammonium pyrosulfite, $(\text{NH}_4)_2\text{S}_2\text{O}_5$, rather than the original $\text{NH}_4(\text{CH}_3)_3\text{SiOSO}_2$ as expected.¹⁰ $(\text{NH}_4)_2\text{S}_2\text{O}_5$ is reported to form from NH_3 and SO_2 in the presence of limited amounts of water.^{4,5} The formation of H_2O from silanol condensation was verified by identifying the other product of the reaction, hexamethyldisiloxane, from the infrared spectrum obtained with a small amount of volatile liquid taken from the trap in which the $(\text{NH}_4)_2\text{S}_2\text{O}_5$ crystal had formed.

Thus **1** decomposes to form hexamethyldisiloxane and ammonium pyrosulfite via the mechanism shown in eq 1–3.



These reactions proceed very slowly at room temperature under vacuum as evidenced by both the spectrum and the powder pattern of the bulk material (**1**), which remain virtually unchanged over periods of months.

The decomposition of **1** is enhanced markedly if the solid is exposed to the atmosphere. Figure 2A shows an infrared spectrum of a thin film of **1** sublimed on a KBr window in vacuo in a gas IR cell.¹¹ Figure 2B shows a spectrum of the

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(10) The structural data will be published in a later paper. See also: Baggio, S. *Acta Crystallogr., Sect. B* **1971**, *B27*, 517.

film after the stopcock had been opened to the atmosphere for ca. 12 h, followed by a rapid evacuation of the cell. Figure 2C is a spectrum of the film after 3 days of exposure to the atmosphere through the 2-mm bore in the stopcock plug. The disappearance of the $\nu(\text{C-H})$ peak at 2190 cm^{-1} and $\nu(\text{Si-O})$ at 1065 cm^{-1} and the appearance of new absorptions that correspond to the spectrum of $(\text{NH}_4)_2\text{S}_2\text{O}_5$ ⁴ are readily seen.

This study clearly demonstrates that the solid ammonium trimethylsilyl sulfite exists in equilibrium with the vapor-phase components ammonia, sulfur dioxide, and silanol and that it slowly decomposes via silanol condensation to form hexamethyldisiloxane and ammonium pyrosulfite, a reaction enhanced by exposure to the atmosphere. Further these results suggest that the new solid 1 can be used as a solid-state source of silanol, a useful, highly reactive reagent.

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(11) See ref 2a for spectral assignments.

Contribution from the Department of Chemistry,
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Ligation Modes for Nicotinic Acid Binding to the Chromium(III) salen Complex

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The nutritional role of chromium(III) has been well established for maintenance of normal glucose metabolism.¹⁻³ The exact nature of biologically active chromium is unknown, but nicotinic acid (3-carboxypyridine) has been suggested as a structural component of the low-molecular-weight complex.²⁻⁴ No synthetic monomeric nicotinic acid complexes of chromium(III) with well-defined structure are available for evaluation of possible ligation modes as well as thermodynamic and kinetic stability. Accordingly, we have examined the aqueous solution equilibria and solid-state ligation mode for a simple-model nicotinic acid complex. The chromium(III) species under investigation is diaqua[*N,N'*-ethylenebis(salicylideneamino)]chromium(III) chloride, $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$. Equilibrium quotients for the binding of various 3-substituted pyridine bases have been measured spectrophotometrically at nearly neutral pH. Adducts have been isolated in the solid state in favorable cases and have been structurally characterized by infrared spectroscopy.

Results and Discussion

The complex $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$ was prepared by standard methods.⁵ The $[\text{Cr}(\text{salen})(\text{nicotinate})(\text{H}_2\text{O})]$ and $[\text{Cr}(\text{salen})(\text{benzoate})(\text{H}_2\text{O})]$ species were prepared by mixing aqueous solutions of the diaquachromium complex with excess ligand solutions at pH 6.5. Solid microcrystalline products formed over a period of 24 h. Products were collected by filtration and washed with water before being dried under vacuum at 40°C . Analytical results⁶ are consistent with

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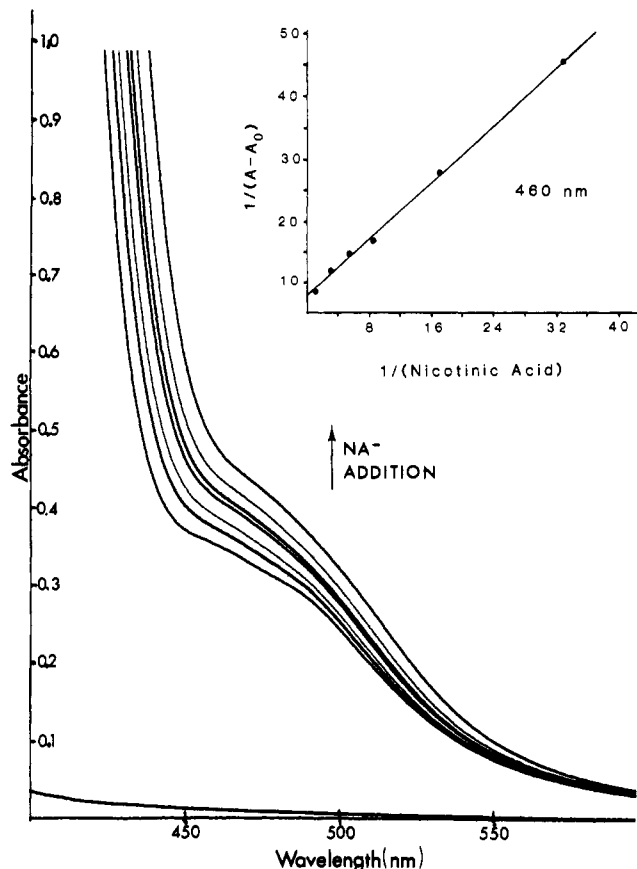


Figure 1. Visible spectra indicating the absorbance changes in the addition of nicotinic acid to $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$ in aqueous solution. The experimental conditions are pH 6.5, 25°C , ionic strength 1.2 (NaNO_3), 0.001 M Cr(III) complex, and $[\text{nicotinic acid}] = 0.030\text{--}1.002\text{ M}$. The curve near the base line is for a stock 1.5 M solution of nicotinic acid at pH 6.5 (adjusted with NaOH). The small ligand absorbance was taken into account in subsequent calculations.

monoligation by the carboxylate species and association of at least one water molecule per molecule of Cr(salen) complex. Attempts to grow crystals suitable for X-ray structural analysis were unsuccessful.

Changes in absorbance for the overall reaction of $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]^+$ and the pyridine bases were measured in aqueous solution at pH 6.5 and 25°C . Concentration ranges of the bases were $[\text{nicotinic acid}] = 0.030\text{--}1.002\text{ M}$, $[\text{pyridine}] = 0.013\text{--}0.520\text{ M}$, $[\text{nicotinamide}] = 0.052\text{--}0.520\text{ M}$, and $[\text{nicotinic acid methyl ester}] = 0.011\text{--}0.110\text{ M}$. Sodium nitrate was used to control the ionic strength at 1.20 and 0.27 for nicotinic acid and benzoic acid equilibrium measurements, respectively. Equilibrium was achieved upon mixing of $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]^+$ and pyridine base solutions, as no subsequent spectral changes were observed. A typical set of visible spectra employed for an equilibrium calculation is given in Figure 1. Calculation of the equilibrium quotient, Q , is possible by using eq 1.⁷ The concentration of deprotonated nicotinic acid ($\text{p}K_a$

$$\frac{1}{A - A_0} = \frac{1}{A_\infty - A_0} + \frac{1}{A_\infty - A_0} \frac{1}{Q[\text{NA}^-]} \quad (1)$$

- (6) Anal. Calcd for $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]\text{Cl}$: C, 49.3; H, 4.65; N, 7.19; Cr, 13.3. Found: C, 49.3; H, 4.81; N, 7.14; Cr, 13.4. Calcd for $[\text{Cr}(\text{salen})(\text{nicotinate})(\text{H}_2\text{O})]$: C, 57.6; H, 4.40; N, 9.17; Cr, 11.34. Calcd for $[\text{Cr}(\text{salen})(\text{nicotinate})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$: C, 55.5; H, 4.65; N, 8.82; Cr, 10.91. Found: C, 55.0; H, 4.58; N, 8.67; Cr, 11.2. Calcd for $[\text{Cr}(\text{salen})(\text{benzoate})(\text{H}_2\text{O})]$: C, 60.4; H, 4.63; N, 6.12; Cr, 11.37. Calcd for $[\text{Cr}(\text{salen})(\text{benzoate})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$: C, 58.1; H, 4.88; N, 5.89; Cr, 10.94. Found: C, 59.3; H, 4.65; N, 5.94; Cr, 11.2. These results indicate that a water molecule of hydration or fractional water of hydration may be present.