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 ν(C–H) peak at 2190 cm^{-1} and ν(Si–O) at 1065 cm^{-1} and the appearance of new absorptions that correspond to the spectrum of $(NH_4)_2S_2O_5$[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.

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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(salicylideneaminato)]chromium(III) chloride, [Cr(salen)$(H_2O)_2$]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 [Cr(salen)$(H_2O)_2$]Cl was prepared by standard methods.[5] The [Cr(salen)(nicotinate)H_2O] and [Cr(salen)(benzoate)H_2O] 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 results[6] are consistent with

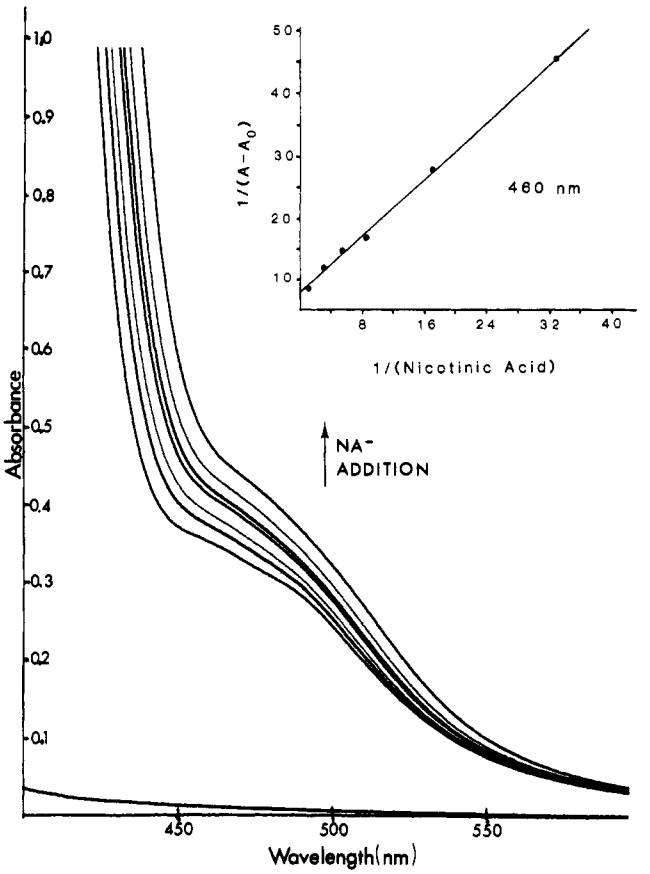

Figure 1. Visible spectra indicating the absorbance changes in the addition of nicotinic acid to [Cr(salen)$(H_2O)_2$]Cl in aqueous solution. The experimental conditions are pH 6.5, 25 °C, ionic strength 1.2 ($NaNO_3$), 0.001 M Cr(III) complex, and [nicotinic acid] = 0.030–1.002 M. The curve near the 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 [Cr(salen)$(H_2O)_2$]$^+$ and the pyridine bases were measured in aqueous solution at pH 6.5 and 25 °C. Concentration ranges of the bases were [nicotinic acid] = 0.030–1.002 M, [pyridine] = 0.013–0.520 M, [nicotinamide] = 0.052–0.520 M, and [nicotinic acid methyl ester] = 0.011–0.110 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 [Cr(salen)$(H_2O)_2$]$^+$ 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 (pK_a

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

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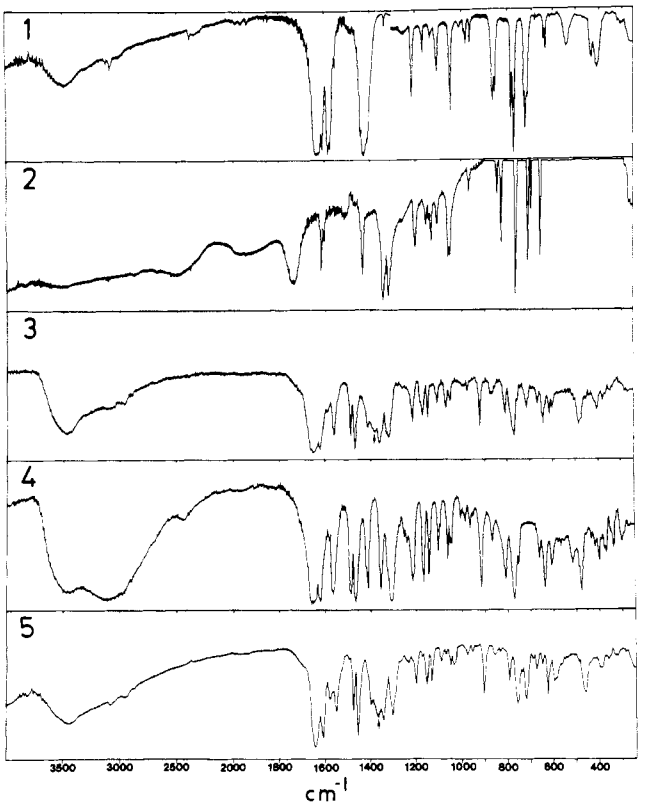

Figure 2. Infrared spectra (Beckman Model IR-20A) obtained from KBr pellets: (1) sodium nicotinate; (2) nicotinic acid; (3) [Cr(salen)(nicotinate)(H_2O)]; (4) [Cr(salen)(H_2O)$_2$]Cl; (5) [Cr(salen)(benzoate)(H_2O)]. Arrows in spectra 3 and 5 locate the appearance of a new peak for these compounds, which is indicative of carboxylate binding.

= 4.85) was employed in the calculation. The insert in Figure 1 presents graphical analysis of results for nicotinic acid coordination. Satisfactory fit to the linear function confirms the 1:1 stoichiometry. (Monosubstitution has also been observed with NCS^- and N_3^- as ligands.[8]) Equilibrium quotients measured at the previously specified conditions are as follows: nicotinic acid, 7.3 M^{-1}; pyridine, 9.6 M^{-1}; nicotinamide, 2.7 M^{-1}; nicotinic acid methyl ester, 5.7 M^{-1}.

Spectral changes for the reaction with benzoic acid at pH 6.5 were not detectable by these methods. The fact that no observable change in absorbance occurred for deprotonated benzoic acid, coupled with the similarity in binding constants for the pyridinium bases, indicates that binding to the ring nitrogen is predominant for nicotinic acid in solution.

Solutions containing either deprotonated nicotinic acid or deprotonated benzoic acid and the [Cr(salen)(H_2O)$_2$]$^+$ complex that were allowed to react overnight formed brown precipitates, which could be separated by filtration, washed with water, and vacuum dried. This behavior is reminiscent of the generally poor solubility observed for neutral chromium(III) complexes and is exemplified by the hydroxo complex of Cr(salen). Absence of precipitates for solutions containing pyridine, nicotinamide, or nicotinic acid methyl ester is suggestive of carboxyl binding to yield a neutral, insoluble nicotinic acid complex. Elemental analyses of isolated nicotinate or benzoate products were consistent with binding by one ligand, although it is unclear how much water of crystallization may be retained in the complex. These solid materials were analyzed by IR spectroscopy, and their spectra are presented in Figure 2. The most striking feature of these spectra is the appearance of an additional peak at 1370 cm^{-1} for the nicotinate and benzoate species. This peak most likely results from the carboxylate group bound to the chromium center. It should be noted that the carbonyl stretching frequency for nicotinic acid is shifted to about 1600 cm^{-1} with formation of the sodium salt (Figure 2). Similar results are reported for the EDTA ligand and its salts.[9] For the salen complexes under investigation it is not possible to identify the extent of shift for the carbonyl band due to overlapping bands from the salen ligand in this region. However, for nicotinic acid the $\nu_s(CO_2^-)$ stretch occurs at 1428 cm^{-1}, and on coordination to a metal center this stretching mode is transformed into a ν(C–O) stretch with a lower frequency near 1400 cm^{-1} as predicted by theory.[10] For the chromium salts of carboxylic acids this shift is even more pronounced. For the [Cr(glycinate)$_3$]·3H_2O complex the shift is from 1399 to 1372 cm^{-1} for the coordinated carboxyl group.[11] Hence, the appearance of a new peak at 1370 cm^{-1} for the nicotinate and benzoate compounds in spectra 3 and 5 is indicative of carboxylate binding in the solid state.[12] This conclusion is contrary to a previous report in the literature for complexes prepared and recrystallized by a somewhat different route.[13]

With respect to the possible involvement of nicotinic acid as a ligand for biological chromium, this study shows that either ligation mode is possible, although nitrogen coordination is preferred for a cationic 1+ chromium complex. The thermodynamic stability for nicotinic acid binding to [Cr(salen)(H_2O)$_2$]$^+$ is not particularly favorable (Q = 7.3 M^{-1}). It remains to be seen if this is general for other types of chromium–nicotinic acid complexes. Perhaps of greater concern is the recognized kinetic lability of tetragonal complexes such as [Cr(salen)(H_2O)$_2$]$^+$[8] and the rhombic structures expected for an amino acid environment.[14,15] Although results presented here do not rule out nicotinic acid ligation in a biological matrix, no evidence has been found that would grant this monodentate ligand any unusual thermodynamic or kinetic stability.

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Registry No. Cr(salen)(nicotinate)H_2O, 82665-21-2; Cr(salen)(benzoate)H_2O, 82665-22-3; [Cr(salen)(H_2O)$_2$]$^+$, 47248-16-8; pyridine, 110-86-1; nicotinic acid, 59-67-6; nicotinamide, 98-92-0; methyl nicotinate, 93-60-7; glucose, 50-99-7.

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