bonds is 2.083–2.134 Å. Thus, the Mn–N_{ax} bonds are considerably longer, and this enhanced axial distortion may be the result of steric crowding caused by the 6-methyl substituent on the pyridine ring.

The cyclic voltammogram (Figure 2) of a 2 mM acetonitrile solution of **1** containing 0.1 M Et_4NClO_4 supporting electrolyte shows two coupled anodic and cathodic waves. The first redox couple centered at 0.568 V (vs Ag/AgCl) corresponds to oxidation of the III/III ion to the III/IV ion and the second couple at 1.337 V (vs Ag/AgCl) corresponds to further oxidation of the III/IV ion to the IV/IV ion. This is quite a remarkable change from the (bispicen)$Mn^{III}Mn^{IV}$ complex, which has $E_{1/2}$ values of 0.145 and 0.855 V (vs Ag/AgCl) for these processes, over 0.4 V less than the respective potentials for **1**. In general, the potential range of the (III/III)–(III/IV) redox couple of the III/IV complexes listed above lies between 0.025 and 0.375 V while that of the (III/IV)–(IV/IV) couple is found between 0.805 and 1.305 V (vs. Ag/AgCl).[9,12]

The electronic spectrum of **1** is much less complex than those of the III/IV complexes. While the (bispicen)$Mn^{III}Mn^{IV}$ complex had bands at 661, 554, 440 (sh), and 388 nm (sh) in acetonitrile, the present complex, **1**, exhibits only a broad absorbance at 461 nm (ϵ = 141 cm^{-1} M^{-1}), which is assigned to a d–d transition centered on Mn(III). This spectrum is similar to those of the related binuclear manganese(III) complexes $Mn_2O(O_2CCH_3)_2(HB(pz)_3)_2$[14] and $Mn_2(OH)_2(\beta\text{-cyclodextrin})$,[15] which have bands at 486 nm (CH_2Cl_2; ϵ = 210) and 482 nm (DMF), respectively. Absent, however, is a weaker band at 760 nm (ϵ = 58) found in the pyrazolylborate complex.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, hydrogen atom coordinates, and thermal displacement parameters (6 pages); a table of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Lewis-Acid Behavior of Silicon Chloride and Fluoride toward Trimethylamine Oxide

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An earlier publication suggested that the bonding of dry trimethylamine oxide (TMAO) to silicon halides might be worthy of study.[1] It now is found that both $SiCl_4$ and SiF_4 bond very firmly to TMAO, with similar bond strengths, in contrast to their very different behavior toward other bases. Also unpredictably, their combining ratios with TMAO are very different. However, the anomalies can be rationalized by arguments based upon chemical physics.

Results and Discussion

Combining Ratios with Solid TMAO. Finely crystalline TMAO absorbed no more than 4.4 $SiCl_4$ per 100 TMAO during 16 h at 25 °C. At 100 °C, the limit seemed to be about 15 $SiCl_4$ per 100 TMAO. But even with only 3 $SiCl_4$ per 100 TMAO, no TMAO could be extracted by its usual solvent $HCCl_3$, nor could any TMAO be sublimed off under high vacuum at 100 °C, above which charring began.

Solid TMAO was penetrated far more easily by SiF_4. After 16 h at 0 °C, the combining ratio was near 16 SiF_4 per 100 TMAO, rising to 43 during 17 h at 80 °C. Then, with the aid of liquid H_2CCl_2, a 1:1 ratio was achieved during 19 h at 25 °C.

Relation to Crystal Structure. The X-ray crystallography of TMAO has shown closely fitting van der Waals contact of oxygen atoms nestled among H atoms in parallel $H_9C_3NO\cdots H_9C_3NO\cdots$ chains.[2] Thus, there is a weak but multiple O–H–C bonding, released when heat causes the end oxygen to vibrate against adjacent chains for incipient sublimation near 45 °C. Attachment of $SiCl_4$ to each end oxygen would block that effect. It is a reasonable hypothesis that the action of solvents such as $HCCl_3$ begins with solvation by N–O–$HCCl_3$ bonding at a chain end; $SiCl_4$ again would block the action. Penetration of the chain by $SiCl_4$ would require too much Cl–Cl compression. The smaller F atoms offer less resistance to compression, so that SiF_4 can penetrate the chains far more effectively.

Adducts Precipitated from Solution. Chloroform solutions of TMAO, treated with SiF_4 vapor under various conditions, give precipitates formulated as $SiF_4{\cdot}TMAO$ or $SiF_4{\cdot}2TMAO$, or with intermediate combining ratios. The 2:1 adduct is stable under vacuum at 80 °C. The 1:1 adduct is less stable, losing some SiF_4 under vacuum at 80 °C. This dissociation is partially reversible.

Very differently, $SiCl_4$ vapor acting on TMAO in $HCCl_3$, repeatedly in eight experiments, gave precipitates closely approaching the formula $SiCl_4{\cdot}4TMAO$. The results were the same when TMAO in $HCCl_3$ was added slowly to $SiCl_4$ in solution. When the solvent was HCF_2Cl (below −52 °C), the precipitate was $SiCl_4{\cdot}4.5TMAO$. Addition of TMAO to $SiCl_4$, both in H_2CCl_2 at 25 °C, led to the formula $SiCl_4{\cdot}3.45TMAO$.

Rationale. Such results again seem to relate to the chain polymer manner of aggregation of TMAO in its crystals. The persistence of a 4:1 ratio of TMAO to $SiCl_4$ suggests that the formula should be written as $SiCl_4{\cdot}2(TMAO)_2$, implying that two $H_9C_3NO\cdots H_9C_3NO$ fragments are bonded through oxygen to 6-coordinate Si. If Si were 5-coordinate, the observed 4:1 ratio would require an average chain length of four TMAO units, but that would be expected to vary far more with changing experimental conditions, such as a reverse order of mixing the reactants. It is even less reasonable for Si to be more than 6-coordinate or for any Cl^- ions to be displaced.

It may be significant that TMAO was found to be dimeric in $HCCl_3$ at 19 °C or in HCF_2Cl at −62 °C, whereas it is monomeric in H_2CCl_2 at 0 °C. Then it seems simple enough that two dimer fragments would attach rapidly to one $SiCl_4$. However, a slightly higher combining ratio in HCF_2Cl suggests that there may also be a mechanism whereby $SiCl_4$ captures a monomer unit from the dimer, leaving another monomer unit free to form a trimer, or there could be some monomer and trimer in the $HCCl_3$ solution.

In H_2CCl_2, we may assume that two monomer units attach directly to $SiCl_4$, but the precipitation is not quite instantaneous, allowing time for attachment of more monomer units in the $H_9C_3NO\cdots H_9C_3NO$–Si manner. The persistence of dimer units in the $SiCl_4$ adduct suggests that the O to Si dative bond strengthens the O–H_9 bonding in the TMAO dimer unit, but this inductive effect would not go far enough to capture a third TMAO unit from the solvent. The dimer effect does not occur in the TMAO adducts of SiF_4, which penetrates the chain.

When SiF_4 enters the $HCCl_3$ solution of TMAO, the dimers are cleaved (either in solution or after attachment to Si), so that the precipitate has only monomeric TMAO on Si. In $SiF_4{\cdot}2TMAO$, 6-coordinate Si is reasonable. In $SiF_4{\cdot}TMAO$ there

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might be 5-coordinate Si, but more probably there is 6-coordinate Si with Si–F–Si bridging, as has been suggested for $(CH_3)_3N\cdot SiF_4$.[3]

Mutual Displacements and Exchange Reactions. The action of SiF_4 on $SiCl_4\cdot 4TMAO$ was complicated by halogen exchanges, but the resulting mixture of volatiles included $SiCl_4$, which must have been displaced by SiF_4. Similarly, $SiCl_4$ displaced some SiF_4 from its TMAO adducts, leading to empirical formulas such as $SiCl_{1.61}F_{2.40}(TMAO)_{2.14}$ and $SiCl_{1.99}F_{2.01}(TMAO)_{2.59}$. The correlation of higher chloride content with larger TMAO:SiX_4 ratios may not be accidental. More directly, TMAO with $SiCl_2F_2$ in slight excess gave a precipitate (from $HCCl_3$) formulated as $SiCl_{1.9}F_{2.1}(TMAO)_{3.4}$; here the high ratio of TMAO to Si implies a course of reaction influenced more by Cl than by F, but again with much halogen scrambling in the remaining volatile material.

Also, HCl penetrated solid $SiCl_4\cdot 4TMAO$, liberating 80% of the $SiCl_4$ and removing some TMAO from the rest. Action by HCl on $SiF_4\cdot TMAO$ led to halogen scrambling, with volatile products including Cl_3SiF, Cl_2SiF_2, and probably $ClSiF_3$ (not easily separable from the excess HCl). Such scrambling reactions were not unexpected in view of similar effects when H_nSiCl_{4-n} combined with $(CH_3)_3N$.[4,5]

Theory of Bond Energetics. The displacement reactions indicate that TMAO bonds with about equal strength to $SiCl_4$, SiF_4, and their scramble products. Such a similarity was not expected in view of the wide differences between $SiCl_4$ and SiF_4 bonded to other bases, as judged by the following examples: $SiF_4\cdot N(CH_3)_3$, 6 mm decomposition pressure at 0 °C;[6] $SiCl_4\cdot N(CH_3)_3$, liquid $SiCl_4$ appears at −55 °C;[5] $SiF_4\cdot 2P(CH_3)_3$, liquid $P(CH_3)_3$ appears at −50 °C;[7] $SiCl_4\cdot 2P(CH_3)_3$, <2 mm observed pressure at 25 °C.[7]

The energetics of formation of all such acid–base (a·b) adducts are best discussed in terms of the cycle

$$\Delta H_f = V_a + V_b + A_a + A_b - B - C$$

For the present comparison, we may neglect the enthalpies of vaporization V_a and V_b and the small bond-angle adjustment energy A_b for each base. The energy cost A_a of Lewis-acid bond adjustments may be less for SiF_4 than for $SiCl_4$, for which Cl–Cl steric compression is serious, and the solid-state (vapor condensation) energy C also may favor SiF_4·base adducts because the dative-bond dipoles will be closer together for stronger attraction between adjacent molecules. Then the wild variable here must be B, which is the b→a dative-bond energy.

Most important for B is the quality of the bond-orbital overlap, for which the hard–soft acid–base concept may be too simple. Good overlap can occur between deep, narrow orbitals or between wide, shallow orbitals, but not between these different shapes. In $(CH_3)_3N$ the lone-pair $2sp^3$ electrons can bond fairly well to SiF_4, wherein strong electron withdrawal by F makes the acceptor orbital deeper and narrower than in $SiCl_4$. The $(CH_3)_3P$ lone-pair electrons have more s character on a larger atom, for poor overlap with SiF_4 but far better with $SiCl_4$.

What is unusual in TMAO is the single-bonded oxygen atom, with any of its three lone electron pairs able to employ almost any combination of s and p orbitals, which may be ideal for a wide variety of Lewis acids, including the very different $SiCl_4$ and SiF_4. With strong donor-bonding action due to the negative charge on oxygen, and with V_b not too high, the overlap versatility of TMAO should lead to many stable Lewis-acid adducts not yet reported in the literature.

Experimental Procedures and Details

General Methods. All volatiles were managed by modified Stock-type high-vacuum methods, with U-tubes and mercury float valves in series for separation of Cl–Si–F compounds by fractional condensation at pressures near 1 mm. At such low pressures, $ClSiF_3$ and SiF_4 were not separable, but the amount of each in a binary mixture could be calculated from the molecular weight. When HCl was a third component, a chloride analysis gave enough further information. The method was gravimetric, with HF added to prevent silicic acid from interfering with true weighing of AgCl. The same method was used for determining excess $SiCl_4$ after the reaction with TMAO in $HCCl_3$.

Formation of TMAO Adducts. TMAO in a weighed reaction bulb (with attached stopcock and ground joint leading to the vacuum line) was dehydrated first by evacuation at 40 °C and then by repeated high-vacuum sublimation until no more water came off. Now a measured gas volume of the silicon halide could be brought in, either for contact with the fine crystals or for absorption by a solution. The volatiles were assayed for proof of the formula of the precipitate. For experiments with SiX_4 always in excess, the TMAO solution was slowly dropped into the SiX_4 solution, from a side arm with a stopcock and swivel joint, all under vacuum conditions. After removal of all volatiles, the gain in weight of the reaction tube served as a recheck of the stoichiometry.

Displacement Processes. After 1.316 mmol of $SiCl_4$ had acted on a precipitate composed of 1.451 mmol of TMAO and 1.274 mmol of SiF_4 (4 h at 85 °C), the remaining volatiles (in millimoles) were as follows: SiF_4, 0.359; $ClSiF_3$, 0.236; Cl_2SiF_2, 0.402; Cl_3SiF, 0.527; $SiCl_4$, 0.389. The solid formula was $SiCl_{1.61}F_{2.40}(TMAO)_{2.14}$. With milder heating, another experiment employed $SiF_4\cdot 1.54TMAO$ with equimolar $SiCl_4$ in four nearly equal portions, each time with removal of the volatiles and return of the Cl-rich fractions. This was the experiment that gave the empirical formula of the solid as $SiCl_{1.99}F_{2.01}(TMAO)_{2.59}$. For the experiment leading to the formula $SiCl_{1.9}F_{2.1}(TMAO)_{3.4}$, pure $SiCl_2F_2$ (having the right molecular weight and volatility) was available from earlier experiments. Again there was halogen scrambling; the remaining volatiles (in millimoles) were as follows: SiF_4, 0.015; $ClSiF_3$, 0.136; Cl_2SiF_2, 0.083; Cl_3SiF, 0.158; $SiCl_4$, 0.046.

The displacement of $SiCl_4$ from $SiCl_4\cdot 4TMAO$ by SiF_4 was observed only qualitatively, with the usual halogen scrambling.

These displacement experiments indicate that all five $SiCl_nF_{4-n}$ compounds bond about equally well to TMAO.

Molecular Weights in Solution. Vapor pressure lowering by TMAO in the solvents $HCCl_3$, HCF_2Cl, and H_2CCl_2 gave the average molecular weights in those solvents. The procedure was much like that employed earlier for $(CH_3)_3NSO_2$ in liquid SO_2,[8] but with uncertainties on the order of 10%. In $HCCl_3$ at 19 °C, the mole fraction x was 0.038 (calculated for monomer, 0.075). In HCF_2Cl at −62 °C, $x = 0.014$ (calculated for monomer, 0.032). In H_2CCl_2 at 0 °C, $x = 0.032$ (calculated for monomer, 0.028). Equilibria of the monomer with some dimer, or vice versa, cannot be excluded.

Retention of TMAO Identity. The present results have validity only if TMAO retains its molecular identity when it reacts with the SiX_4 compounds—as it does not when its C–H and N–O bonds are broken in its reaction with SO_2.[9] Also, recent work in this laboratory has shown that it oxidizes PF_3 or $(CF_3)_3P$. The adduct $TMAO\cdot(CF_3)_3PO$ promptly decomposes to give some HCF_3.

When some of the $TMAO\cdot SiX_4$ adducts were treated under vacuum conditions with aqueous KOH (slightly beyond the neutral point), it was possible to pump off the water and sublime off as much as 79% of the original TMAO. Also, granular aluminum acting on one of the basic solutions gave a 68% yield of pure $(CH_3)_3N$ (proved by quantitative conversion to the pure BH_3 complex)—a result that would not have been possible for any $(CH_3)_2NCH_2X$ compound.

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Preparation and Structure of the Dimolybdenum(III) Compound $Mo_2Cl_6(PEt_3)_4$. An Anomaly in Metal–Metal-Bonded Edge-Sharing Bioctahedral Compounds

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The synthetic and structural chemistry of dinuclear transition-metal compounds containing direct metal–metal bonds has been actively investigated for over thirty years.[1] Of interest here

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