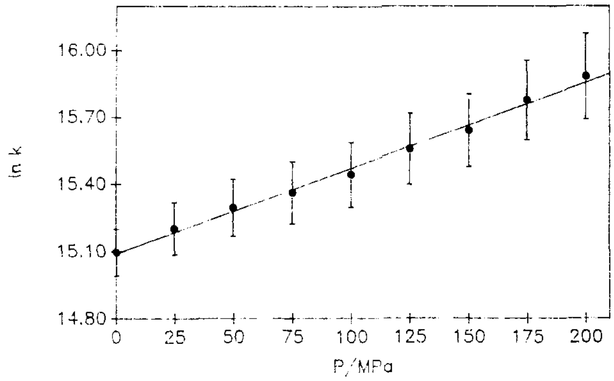

Figure 2. Activation volume data: natural logarithm of the rate constant vs pressure in MPa. $T = 0$ °C; $[\mathrm{Fe(cp)_2}] = 37.2$ mM; $[\mathrm{Fe(cp)_2^+}] = 2.7$ mM.

Samples for the atmospheric pressure studies were prepared on a vacuum line and showed no decomposition as noted by Wahl.[3]

The rate constants found in this work are larger than those of Wahl et al. by ca. 30–40%. Our k at 25 °C extrapolated to zero ionic strength is 9.3×10^6 $\mathrm{M^{-1}\ s^{-1}}$, which can be compared with that of Weaver et al.[4] of 9.1×10^6 $\mathrm{M^{-1}\ s^{-1}}$ at $\mu = 0.65$ mM. The $\Delta H^{\ddagger}$ values we found agree quite well with those of Wahl (4.7 vs 5.3 kcal $\mathrm{mol^{-1}}$), suggesting perhaps systematic errors in his rate constants. The rate constants are, in fact, very sensitive to the measured parameters. The errors are somewhat reduced at 200 MHz but are still of the order of ±5% at best.

There appears to be a small effect on k of changing the concentration of ferrocenium and/or addition of cobaltocenium. We find a decrease in k at 25 °C from $\mu = 0$ to μ 40 = mM of ca. 20%. The variation of ln k is fairly linear with $\mu^{1/2}$. One does not of course expect much effect on a 0/+1 reaction. The effect if any of μ on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is hard to assess. A similar effect, reduction of the rate constant with added salt, has been observed for the reduction of a series of cobalt(III) clathrochelates, +1 ions, by ferrocene[8] and for reactions between the neutral and +1 forms of the clathrochelates.[9] In these cases the effect has been attributed to a lower reactivity of ion-paired reactants.

A value for $\Delta V^{\ddagger}$ of -7.0 ± 2.0 $\mathrm{cm^3\ mol^{-1}}$ is not significantly different from that found for the inner-sphere ruthenocene(II)–bromoruthenocene(IV) system (-3.0 ± 0.2 $\mathrm{cm^3\ mol^{-1}}$).[7] If the outer-sphere ferrocene–ferrocenium case involves some π–π^* ring interactions as suggested by Weaver et al.[10] and the ruthenium system involves a halo bridge, the factors influencing $\Delta V^{\ddagger}$ might be similar. Formation of a "bond" would lead to a negative $\Delta V^{\ddagger}$ contribution, release of solvent between the species gives a positive $\Delta V^{\ddagger}$ contribution, and diminished electrostriction effects in the activated complex would be small and lead to a positive contribution (we estimate ca. +1 $\mathrm{cm^3\ mol^{-1}}$).

In another approach, based on Marcus theory like model, the $\Delta V^{\ddagger}$ value is predicted from the solvent reorganization term,[11] eq 5, with an additional contribution from a precursor formation

$$\Delta V_{\mathrm{SR}}{}^{\ddagger} = \frac{Ne^2}{16\epsilon_0\pi}\left[\frac{1}{r_{\mathrm{ab}}} - \frac{1}{\sigma}\right]\left[\frac{\partial}{\partial P}\left[\frac{1}{n^2} - \frac{1}{\epsilon}\right]\right] \tag{5}$$

constant. In eq 5, ϵ_0 is the permittivity of free space, r_{ab} is the assumed "radius" of the species, σ is the electron-transfer distance, n is the refractive index, and ϵ is the dielectric constant of the solvent. Assuming that r_{ab} and σ are pressure independent and using 4 Å for r_{ab} and 8 Å for σ,[12] this equation predicts a $\Delta V^{\ddagger}$ of ca. -15 $\mathrm{cm^3\ mol^{-1}}$. Larger values for r_{ab} and σ give more positive values for $\Delta V^{\ddagger}$. For example, an r_{ab} of 5 Å and a σ of 10 Å leads to a $\Delta V^{\ddagger}$ of ca. -12 $\mathrm{cm^3\ mol^{-1}}$. This is inconsistent with our result unless a large positive contribution to $\Delta V^{\ddagger}$ is made by precursor complex formation.

On the basis of a simple solvent electrostriction argument, a neutral and a +1 species should produce a transition state with a lower charge density and thus solvent should be released, leading to a positive $\Delta V^{\ddagger}$. Using a form of the Drude–Nernst equation presented previously,[1] we can roughly predict a value for $\Delta V^{\ddagger}$ of 1 $\mathrm{cm^3\ mol^{-1}}$. In the previous study[1] of electron self-exchange by manganese isocyanide complexes, both the simple Drude–Nernst equation and a method based on Marcus theory gave predictions that were not inconsistent with the results. However, in that case the reactants were +1 and +2 ions.

The lack of agreement with the above "theoretical" approaches emphasizes the need for a more detailed structural approach to $\Delta V^{\ddagger}$. Studies using a variety of solvents and substituted ferrocenes should be helpful in this regard. These studies should be done at higher magnetic fields when possible.

Acknowledgment. The authors wish to acknowledge the assistance of Don Appel with the NMR measurements. This work was supported by the National Science Foundation and by the Boeing Co. through funds for the purchase of the Nicolet instrument.

Registry No. $\mathrm{Fe(cp)_2}$, 102-54-5; $\mathrm{Fe(cp)_2PF_6}$, 11077-24-0; $\mathrm{Co(cp)_2PF_6}$, 12427-42-8.

Supplementary Material Available: Tables of reactant concentrations, temperatures, rate constants, line widths, and chemical shifts (7 pages). Ordering information is given on any current masthead page.

---

[8] Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537.

[9] Gribble, J.; Wherland, S. *Inorg. Chem.*, in press.

[10] Nielson, R. M.; Golovin, M. N.; McManis, G. E.; Weaver, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 1745.

[11] Swaddle, T. W. In *Inorganic High Pressure Chemistry*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 5.

[12] Dunitz, L. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373.

Contribution from the Department of Chemistry,
University of Wyoming, Laramie, Wyoming 82071

Synthesis and Characterization of a Bis(oxo)-Bridged $\mathrm{Mn^{III}Mn^{III}}$ Complex, Bis(μ-oxo)bis[N,N'-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) Perchlorate

Patricia A. Goodson and Derek J. Hodgson*

Received March 21, 1989

Although manganese has long served as a practical oxidant for synthetic chemists, its role in several biological redox processes has only recently been the focus of study. In particular, a polynuclear manganese unit is now known to play an essential role in the oxidation of water to oxygen in photosystem II during photosynthesis.[1,2] Several research groups have focused their attention on the mixed-valent bis(μ-oxo)dimanganese(III/IV) system, $[\mathrm{LMn(\mu\text{-}O)_2MnL}]$, a potential model for this biological redox process.[3] The first two complexes of this type, $[\mathrm{(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2}](\mathrm{ClO_4})_3$ (bpy = 2,2′-bipyridine) and $[\mathrm{(phen)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(phen)_2}](\mathrm{ClO_4})_3$ (phen = 1,10-phenanthroline), were synthesized in 1960.[4] No further examples of these compounds were generated until our report of $[\mathrm{(bispicen)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bispicen)}](\mathrm{ClO_4})_3$ (bispicen = N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine) in 1987.[5] Since then, complexes have been reported with the tetradentate ligands tris(2-pyridylmethyl)amine,[6] tris(2-aminoethyl)amine,[7] 1,4,7,10-

---

[1] Beck, W. F.; Brudvig, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 1517–1523 and references therein.

[2] Dismukes, G. C. *Photochem. Photobiol.* **1985**, *43*, 99–115.

[3] Matsushita, T.; Spencer, L.; Sawyer, D. T. *Inorg. Chem.* **1988**, *27*, 1167–1173.

[4] Nyholm, R. S.; Turco, A. *Chem. Ind. (London)* **1960**, 74–75.

[5] Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1659–1660.

0020-1669/89/1328-3606$01.50/0

tetraazacyclododecane,[8a] 1,4,8,11-tetraazacyclotetradecane,[8] and *N*,*N*-bis(2-pyridylmethyl)glycinate.[9] Electrochemical studies of these complexes reveal that they have accessible III/III and IV/IV oxidation states. However, while three bis(μ-oxo)dimanganese(IV) complexes have been reported,[6b,10] there have been no reports of the generation of a bis(μ-oxo)dimanganese(III) complex.

We are interested in systematically developing this class of compounds as potential electrocatalysts for oxidation of organic compounds. By suitable electronic and steric ligand modification, we intend to modulate the redox potential of the system. As part of our initial effort, we wish to demonstrate the profound impact of ligand modification by reporting here the synthesis and structural characterization of the first bis(μ-oxo)dimanganese(III) complex, bis(μ-oxo)bis[*N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III)perchlorate (**1**).

Experimental Section

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these should be prepared and handled behind suitable protective shields.

***N*,*N*′-Bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine.** The ligand[11] was prepared by a modification of the published procedure by condensation of 6-methylpyridine-2-carboxaldehyde (10.0 g, 0.083 mol) with ethylenediamine (2.8 mL, 0.041 mol) in 33 mL of EtOH followed by reduction with $NaBH_4$ (4.75 g, 0.126 mol) and acid workup, giving 10.1 g (90%) of a light yellow oil. ^1H NMR (270 MHz, $CDCl_3$): δ 7.53 (t, J = 7.69 Hz, 1 H), 7.12 (d, J = 7.69 Hz, 1 H), 7.00 (d, J = 7.69 Hz, 1 H), 3.87 (s, 2 H), 2.82 (s, 2 H), 2.53 (s, 3 H), 2.02 (s, 1 H).

Bis(μ-oxo)bis[*N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) Perchlorate. Syntheses of the III/IV dimers listed above were accomplished by oxidation of a solution of the ligand and an Mn(II) salt with potassium permanganate,[12] hydrogen peroxide,[5] or oxygen (air).[7] Addition of 30% aqueous hydrogen peroxide (4 drops, approximately 120 mg) to a solution of *N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine (0.252 g, 0.931 mmol) and manganese(II) perchlorate (0.337 g, 0.931 mmol) in 6 mL of H_2O affords a thick dark orange oil in contrast to the dark olive green solids characteristic of the III/IV complexes. Isolation of the complex in crystalline form was realized by slow reaction with oxygen. $Mn(ClO_4)_2{\cdot}6H_2O$ (1.87 g, 5.18 mmol) was added to a solution of *N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine (1.40 g, 5.18 mmol) in 15 mL of water. Oxygen was bubbled through the solution for 1 h. After several days, the mixture was filtered and the solids were washed with methanol to give 0.11 g (5%) of **1** as dark orange-red crystals. Anal. Calcd for $Mn_2C_{32}H_{46}Cl_2N_8O_{11}$ (includes 1 mol of H_2O): C, 42.73; H, 5.15; Cl, 7.88; N, 12.46. Found: C, 42.69; H, 5.19; Cl, 8.00; N, 12.39.

Crystallographic data were collected from an orange prismatic crystal (0.28 × 0.45 × 0.13 mm) at −100 °C on a Nicolet R3m/V diffractometer with a molybdenum tube (λ(Mo Kα) = 0.71073 Å) and a graphite monochromator. The complex crystallizes in the triclinic space group $P\bar{1}$ with two dimers in a cell of dimensions a = 8.4870 (22) Å, b = 10.8684 (21) Å, c = 20.8157 (46) Å, α = 77.336 (16)°, β = 88.281 (22)°, γ = 84.018 (21)°, and V = 1863.09 (79) Å^3. A total of 4747 data was gathered (R_{int} = 0.064), the octants collected being $+h$, $\pm k$, $\pm l$. The structure has been refined to conventional R factors of values R = 0.0759 and R_w = 0.0907 based on 2787 independent intensities in the 2θ range 4–45°. Absorption corrections have not been applied (μ = 0.86 mm^{-1}). Solutions were obtained by Patterson and difference Fourier methods and refined by least-squares techniques using the programs from the SHELXTL system.

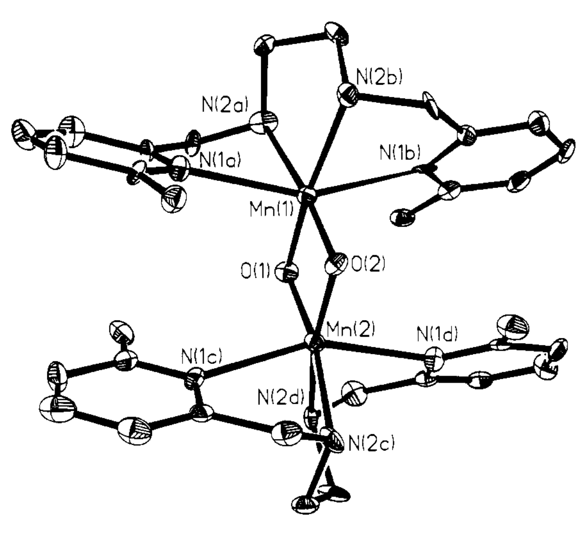

Figure 1. View of the binuclear cation in complex **1**. Selected distances (Å) and angles (deg): Mn(1)–Mn(2), 2.676 (3); Mn(1)–O(1), 1.814 (8); Mn(1)–O(2), 1.853 (9); Mn(2)–O(1), 1.830 (9); Mn(2)–O(2), 1.863 (8); Mn(1)–N(1a), 2.424 (11); Mn(1)–N(2a), 2.117 (11); Mn(1)–N(1b), 2.468 (10); Mn(1)–N(2b), 2.115 (9); Mn(2)–N(1c), 2.410 (11); Mn(2)–N(2c), 2.121 (12); Mn(2)–N(1d), 2.406 (11); Mn(2)–N(2d), 2.099 (10); Mn(1)–O(1)–Mn(2) 94.5 (4); Mn(1)–O(2)–Mn(2) 92.1 (4).

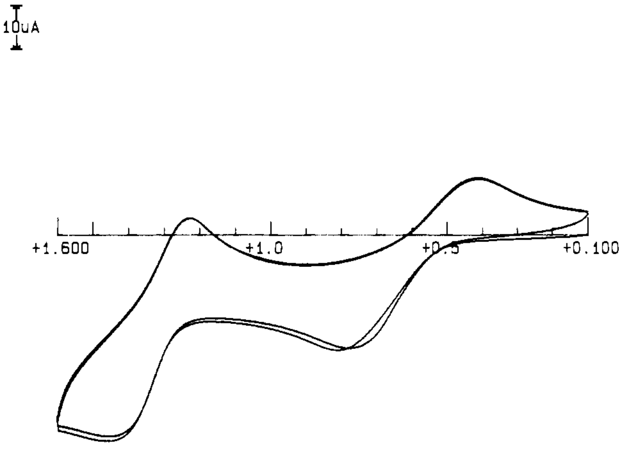

Figure 2. Cyclic voltammogram of **1** vs Ag/AgCl reference electrode with 0.1 M Et_4NClO_4 as supporting electrolyte in acetonitrile. The scan speed is 100 mV/s.

Results

Both the elemental and crystallographic analyses of the compound reveal it to be a monohydrate. The geometry of the binuclear cation is shown in Figure 1. The separation between the two independent manganese centers in each dimer is 2.676 (3) Å, which is only slightly different from the value of the "parent" (bispicen)$Mn^{III}Mn^{IV}$ complex of 2.659 (2) Å. The Mn(1)-O(1)-Mn(2) and Mn(1)-O(2)-Mn(2) bond angles are 94.5 (4) and 92.1 (4)°, respectively, and again are not substantially different from those in the (bispicen)$Mn^{III}Mn^{IV}$ complex. The Mn–O bond lengths range from 1.814 (8) Å (Mn(1)–O(1)) to 1.863 (8) Å (Mn(2)–O(2)), values consistent with the range of Mn–O bond lengths (1.833–1.856 Å) found for the Mn(III) centers in localized $Mn^{III}Mn^{IV}$ structures.[5,6,8,13] Jahn–Teller axial distortion of the octahedral geometry about each Mn center is clearly evident as expected for a high-spin d^4 ion. The manganese nitrogen bond lengths to the axial nitrogen atoms of the pyridine groups range from 2.406 (11) Å (Mn(2)–N(1D)) to 2.468 (10) Å (Mn(1)–N(1B)) while the manganese equatorial nitrogen bond lengths vary from 2.099 (10) Å (Mn(2)–N(2D)) to 2.117 (11) Å (Mn(1)–N(2A)). The Mn–N_{ax} bond length on the Mn(III) center of the (bispicen)$Mn^{III}Mn^{IV}$ complex was 2.169 Å while the Mn–N_{eq} bond length was 2.083 Å. The range of Mn–N_{ax} lengths on other localized Mn(III) centers is 2.169–2.344 Å and that of the Mn–N_{eq}

---

(6) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988**, *141*, 167–168. (b) Suzuki, M.; Tokura, S.; Suhara, M.; Uehara, A. *Chem. Lett.* **1988**, 477–480.

(7) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 967–969.

(8) (a) Brewer, K. J.; Liegeois, A.; Otvos, J. W.; Calvin, M.; Spreer, L. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1219–1220. (b) Goodson, P. A.; Hodgson, D. J.; Michelsen, K. Submitted for publication.

(9) Suzuki, M.; Senda, H.; Kobayashi, Y.; Oshio, H.; Uehara, A. *Chem. Lett.* **1988**, 1763–1766.

(10) (a) Goodwin, H. A.; Sylva, R. N. *Aust. J. Chem.* **1967**, *20*, 629–637. (b) Goodson, P. A.; Hodgson, D. J.; Michelsen, K.; Pedersen, E., Manuscript in preparation.

(11) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1960**, *82*, 5013–5023.

(12) Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623–6630.

(13) (a) Stebler, M.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1986**, *25*, 4743–4750. (b) Plaksin, P. M.; Stoufer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121–2122.

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$_4$NClO$_4$ 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$_2$O(O$_2$CCH$_3$)$_2$(HB(pz)$_3$)$_2$[14] and Mn$_2$(OH)$_2$(β-cyclodextrin),[15] which have bands at 486 nm (CH$_2$Cl$_2$; ϵ = 210) and 482 nm (DMF), respectively. Absent, however, is a weaker band at 760 nm (ϵ = 58) found in the pyrazolylborate complex.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO), through Grant No. 85/0790. We are very grateful to Dr. Jørgen Glerup for experimental assistance.

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.

---

(14) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435–1444.

(15) Nair, B. U.; Dismukes, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 124–125.

Contribution from the Department of Chemistry,
University of Southern California,
Los Angeles, California 90089-0744

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

Anton B. Burg

Received December 28, 1988

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$_2$CCl$_2$, 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$_9$C$_3$NO···H$_9$C$_3$NO··· 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$_4$·TMAO or SiF$_4$·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$_4$·4TMAO. The results were the same when TMAO in HCCl$_3$ was added slowly to SiCl$_4$ in solution. When the solvent was HCF$_2$Cl (below −52 °C), the precipitate was SiCl$_4$·4.5TMAO. Addition of TMAO to SiCl$_4$, both in H$_2$CCl$_2$ at 25 °C, led to the formula SiCl$_4$·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$_4$·2(TMAO)$_2$, implying that two H$_9$C$_3$NO···H$_9$C$_3$NO 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$_2$Cl at −62 °C, whereas it is monomeric in H$_2$CCl$_2$ 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$_2$Cl 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$_2$CCl$_2$, 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$_9$C$_3$NO···H$_9$C$_3$NO–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$_4$·2TMAO, 6-coordinate Si is reasonable. In SiF$_4$·TMAO there

---

(1) Burg, A. B.; Bickerton, J. H. *J. Am. Chem. Soc.* **1945**, *67*, 2261.

(2) Caron, A. Ph.D. Dissertation, University of Southern California Libraries, 1962. Pages 3 and 4 suggest such packing, governed by the high dipole moment (5.0), with confirmation on p 65. The related publication (*Acta Crystallogr.* **1964**, *17*, 102) is less explicit.

0020-1669/89/1328-3608$01.50/0