An Evaluation of the Donor Role of Octamethylcyclotetrasilazane

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Abstract: Octamethylcyclotetrasilazane $(Me_2SiNH)_4$, abbreviated OMT, reacts with halides of the early transition series to give adducts of the type $(MCl_3)_2 \cdot OMT \cdot 2L$ where M = Ti, L = THF; M = V, L = THF; and M = Cr, L = NMe_3; and $(MCl_4)_2 \cdot OMT$ where M = Ti. The stereochemistry of these neutral complexes and the coordination of the metal centers have been assessed in the light of spectral, conductivity, and chemical evidence, and possible molecular structures are proposed. Lewis base participation of the tetrameric (Si–N) ring is seen to involve only two of the four available nitrogen centers in (M–N) bonding and this bidentate behavior is reconciled with the favored metal hexacoordination of these powerful Lewis acids. Hexamethylcyclotrisilazane $[Me_2SiNH]_3$, abbreviated HMT, and titanium(IV) chloride give $(TiCl_4)_2 \cdot HMT$ as a neutral six-coordinate complex, and the donor behavior (bidentate) of the trimeric silazane ring is similarly discussed.

In an earlier investigation of the reactions between hexamethylcyclotrisilazane $(Me_2SiNH)_3$, abbreviated HMT, and titanium(III) chloride or vanadium(III) chloride we showed that six-cooordinate adducts of the type $MCl_3 \cdot HMT$ are formed in which all three of the skeletonal nitrogen atoms of the ligand are involved in metal–nitrogen σ bonding.[1] Having established HMT as a nitrogen donor (terdentate), it seemed reasonable to suppose that its tetrameric analog octamethylcyclotetrasilazane $(Me_2SiNH)_4$, abbreviated OMT, would behave in similar fashion. Indeed, with a maximum of four nitrogen atoms formally available for coordination, this tetrameric ring clearly has intriguing potential as a multidentate ligand. The present investigation is essentially concerned with an evaluation of the exact donor role of OMT following a study of its reactions with titanium(IV) chloride, titanium(III) chloride, vanadium(III) chloride, and chromium(III) chloride.

Experimental Section

Materials. HMT and OMT were prepared by ammonolysis of dimethyldichlorosilane following the method of Osthoff and Kantor.[2] Titanium(IV) chloride (Hopkin and Williams, Essex), titanium(III) chloride and vanadium(III) chloride (K and K Laboratories, Plainview, N. Y.), and chromium(III) chloride (Pfaltz and Bauer Inc., Flushing, N. Y.) were obtained as anhydrous materials and their respective adducts were prepared by standard procedures described in the literature; $MCl_3 \cdot 3THF$ where M = Ti,[3] V,[4] and Cr,[5] $MCl_3 \cdot 2NMe_3$ where M = Ti,[6] V,[7] and Cr.[7] All solvents were stored over calcium hydride and phosphoric oxide and distilled *in vacuo* when required.

Physical Measurements and Analyses. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 621 spectrometer with Nujol and fluorolube mulls held between CsI plates. Conductivity measurements were performed using a Wayne Kerr Universal B221 conductance bridge. The conductivity cell used was calibrated with standard aqueous KCl solutions and readings were taken at 298.0 ± 0.1°K on samples of approximately 10^{-4} *M* concentration in dichloromethane solution. Absorption spectra were recorded on a Cary 14 spectrophotometer with samples either as solutions in 1-cm sealed silica cells or as thin Nujol mulls between silica plates and KBr disks. Proton nmr spectra (60 MHz) were obtained on a Perkin-Elmer R12 spectrometer. Molecular weight measurements were carried out on all the reported compounds using a Mechrolab Model 301 A vapor pressure osmometer with benzil as calibrant. Except for $(TiCl_3)_2 \cdot OMT \cdot 2THF$, the results obtained were disappointing, the main problem being one of limited solubility. Even in dichloromethane, which proved to be the only real choice of solvent, the maximum concentration of the various solutions was approximately 10^{-4} *M* and whereas this sufficed for electrical conductivity measurements[8] it was outside the limit for reliable molecular weight evaluations in this instance. Furthermore, it was difficult with our instrument to simultaneously obtain good thermostating and saturated vapor pressures with this highly volatile solvent.[9]

Because of the extreme air-sensitive nature of these compounds some problems were encountered in several of the analyses undertaken to establish their stoichiometry. Carbon, hydrogen, and nitrogen analyses were performed by the A. Bernhardt Microanalytical Laboratory, Müllheim, Germany, and the F. B. Strauss Microanalytical Laboratory, Oxford, England. In several cases, *viz.*, $(TiCl_4)_2 \cdot HMT$, $(TiCl_4)_2 \cdot OMT$, and $(TiCl_3)_2 \cdot OMT \cdot 2THF$, some of the values obtained (from both sources) were poor, carbon and nitrogen being particularly obstinate, but the discrepancies are ascribed to handling techniques during analysis rather than to the presence of impurity. The agreeable results for metal and chlorine analyses and the reproducibility and reliability of the spectral data are seen to endorse this point. Chromium was determined spectrophotometrically following oxidation to chromate; likewise titanium by the method of Tribalat and Caldero.[10] Chloride was determined by the Volhard titration method.

Reactions. Manipulations were effected in a glove box under a dry oxygen-free nitrogen atmosphere and, where appropriate, in sections of a standard glass high-vacuum system.

In a typical reaction the metal halide or its adduct (~2 g) was sealed in a glass ampoule with a slight excess (for a 1:1 molar ratio) of the particular silazane ligand and benzene as solvent. The vessel was then either placed on a mechanical shaker or immersed in a water bath at 315°K until reaction was complete. After removal of solvent and unused ligand by thorough washing with *n*-pentane or *n*-hexane on the vacuum system, the solid product remaining was pumped *in vacuo* at room temperature for several hours prior to being sealed into ampoules under a nitrogen atmosphere. In a few cases the solid product was extracted with dichloromethane before being pumped dry, but the critical factor here was the limited solubility of all the complexes in this and other common organic solvents.

(a) $(TiCl_4)_2 \cdot (Me_2SiNH)_3$. Titanium(IV) chloride and HMT in benzene solution gave an immediate reaction on mixing with the formation of a yellow solution. The reaction vessel was placed on

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the shaker for 24 hr and following extraction as above, the bright yellow complex hexamethylcyclotrisilazane–di(tetrachlorotitanium (IV))[11] was isolated: mp 432°K decomposes to a brown solid; $\Lambda_M = 0.02$ ohm^{-1} cm^2 mol^{-1} for a 1×10^{-3} *M* solution in CH_2Cl_2. The infrared spectrum contained bands at 3350 (s), 3280 (s), 3240 (sh), 2970 (m), 2930 (m), 1403 (s), 1260 (vs), 1150 (w), 953 (vs), 897 (m), 863 (s), 839 (s), 804 (vs), 778 (w), 743 (m), 721 (m), 681 (w), 653 (w), 633 (w), 501 (m), 441 (m), 411 (s), 348 (vs), and 277 (m) cm^{-1}, respectively.

Anal. Calcd for $C_6H_{21}Cl_8N_3Si_3Ti_2$: C, 12.0; H, 3.5; Cl, 47.4; N, 7.0; Ti, 16.0. Found: C, 11.1; H, 3.7; Cl, 47.5; N, 7.7; Ti, 15.9.

(b) **$(TiCl_4)_2\cdot(Me_2SiNH)_4$.** Titanium(IV) chloride and OMT in benzene solution reacted immediately to give a yellow solution. Extraction as above after placing the reaction vessel on the shaker for 24 hr gave the bright yellow complex octamethylcyclotetrasilazane-di(tetrachlorotitanium(IV)):[11] mp 453°K decomposes to a brown solid; $\Lambda_M = 0.28$ ohm^{-1} cm^2 mol^{-1} for a 1×10^{-3} *M* solution in CH_2Cl_2. The infrared spectrum contained bands at 3225 (s), 3180 (s), 3125 (sh), 2960 (m), 2930 (m), 1400 (s), 1275 (vs), 1150 (m), 930 (m), 870 (m), 800 (vs), 660 (m), 600 (w), 450 (m), 350 (vs), and 300 (w) cm^{-1}, respectively.

Anal. Calcd for $C_8H_{28}Cl_8N_4Si_4Ti_2$: C, 14.3; H, 4.2; Cl, 42.2; N, 8.3; Ti, 14.3. Found: C, 13.6; H, 4.0; Cl, 42.0; N, 8.3; Ti, 14.2.

(c) **$(TiCl_3)_2\cdot(Me_2SiNH)_4\cdot 2THF$.** Tris(tetrahydrofuran)titanium(III) chloride and OMT in benzene solution gave an immediate reaction resulting in the formation of a green solution and dark green precipitate. The vessel was placed in the water bath for 24 hr and extraction in the usual manner provided the bright green complex bis(tetrahydrofuran)(octamethylcyclotetrasilazane)di(trichlorotitanium(III)):[11] darkens and decomposes to a black solid at mp 440°K; $\Lambda_M = 0.11$ ohm^{-1} cm^2 mol^{-1} at concentration 1×10^{-3} *M* in CH_2Cl_2. The infrared spectrum contained bands at 3275 (m), 3150 (m), 3090 (sh), 2930 (s), 2910 (s), 2880 (m), 2855 (m), 2830 (w), 1458 (m), 1408 (m), 1348 (m), 1260 (s), 1170 (w), 1070 (w), 1040 (m), 1011 (vs), 960 (w), 928 (m), 852 (vs), 805 (m), 722 (w), 685 (m), 630 (vw), 352 (vs), and 297 (m) cm^{-1}, respectively.

Anal. Calcd for $C_{16}H_{44}Cl_6N_4Si_4Ti_2O_2$: C, 25.8; H, 5.9; Cl, 28.6; N, 7.5; Ti, 12.8; mol wt, 745. Found: C, 26.4; H, 5.4; Cl, 28.8; N, 6.6; Ti, 12.8; mol wt (osmometric), 809.

(d) **$(VCl_3)_2\cdot(Me_2SiNH)_4\cdot 2THF$.** Tris(tetrahydrofuran)vanadium(III) chloride and OMT in benzene solution gave no immediate reaction. The vessel was placed in the water bath for 1 week when the characteristic brick-red solution slowly decolorized leaving a dark brown mass. Extraction in the usual manner gave bis(tetrahydrofuran)(octamethylcyclotetrasilazane)di(trichlorovanadium(III))[11] as a black solid: decomposes with charring at mp 435°K; $\Lambda_M = 0.29$ ohm^{-1} cm^2 mol^{-1} for a 1×10^{-3} *M* solution in CH_2Cl_2. The infrared spectrum contained bands at 3289 (m), 3220 (m), 3140 (sh), 2955 (s), 2920 (w), 2895 (w), 2860 (w), 1440 (m), 1410 (m), 1345 (w), 1260 (vs), 1168 (w), 1085 (m), 1035 (m), 1025 (s), 960 (m), 928 (m), 852 (m), 800 (s), 712 (w), 682 (w), 630 (vw), 465 (w), 345 (vs), and 305 (w) cm^{-1}, respectively.

Anal. Calcd for $C_{16}H_{44}Cl_6N_4Si_4V_2O_2$: C, 25.5; H, 5.8; Cl, 28.3; N, 7.5. Found: C, 25.4; H, 5.7; Cl, 28.1; N, 7.8.

(e) **$(CrCl_3)_2\cdot(Me_2SiNH)_4\cdot 2NMe_3$.** Treatment of a benzene solution of bis(trimethylamine)chromium(III) chloride and OMT gave an immediate reaction with bubbling, resulting in the formation of a purple precipitate. The vessel was placed on the shaker for 48 hr and extraction as above gave bis(trimethylamino)(octamethylcyclotetrasilazane)di(trichlorochromium(III))[11] as a purple solid and a small volume of gaseous material identified through its infrared spectrum as trimethylamine:[12] decomposes with charring to a dark blue-black solid at mp 425°K; $\Lambda_M = 1.26$ ohm^{-1} cm^2 mol^{-1} at concentration 1×10^{-3} *M* in CH_2Cl_2. The infrared spectrum contained bands at 3200 (m), 3110 (m), 3080 (sh), 3023 (m), 2990 (w), 2955 (m), 2930 (m), 2910 (m), 2870 (w), 2855 (w), 2790 (w), 2720 (w), 1508 (w), 1480 (vs), 1460 (s), 1405 (m), 1258 (vs), 1235 (m), 1170 (s), 1070 (m), 1035 (w), 975 (vs), 930 (m), 890 (m), 855 (m), 815 (s), 790 (m), 675 (m), 632 (m), 525 (m), 478 (m), 370 (vs), 340 (s), 287 (w), and 250 (w) cm^{-1}, respectively.

Anal. Calcd for $C_{14}H_{46}Cl_6N_6Si_4Cr_2$: C, 23.1; H, 6.3; Cl, 29.2; N, 11.5; Cr, 14.3. Found: C, 22.6; H, 5.8; Cl, 28.9; N, 10.1; Cr, 14.4.

(f) A similar reaction to (e) above but now using HMT resulted in the release of trimethylamine and the formation of a purple-blue solid which was not, however, the expected simple adduct $CrCl_3\cdot$HMT.

Anal. Calcd for $C_6H_{21}Cl_3N_3Si_3Cr$: C, 19.1; H, 5.5; Cl, 28.1; N, 11.1; Cr, 13.7. Found: C, 29.5; H, 9.5; Cl, 38.9; N, 5.6; Cr, 20.2. The infrared spectrum showed bands at 1240 ν_{as}(CN), 1012 $\rho(CH_3)$, and 810 cm^{-1} ν_s(CN) indicative of coordinated trimethylamine[7] but the characteristic HMT bands at 925 ν_{as}(SiNSi) and at 620 cm^{-1} ν_s(SiNSi)[13] were not detected. The presence of bands at 850 $\nu_{as}(SiC_3)$, 720 $\nu_s(SiC_3)$, 812 $\delta(SiCH_3)$, and 370 cm^{-1} δ(SiN), however, is strongly suggestive of silazane fragments, *e.g.*, degradation of the ring has occurred.

The experiment was repeated with tris(tetrahydrofuran)chromium(III) chloride as the reactant metal species when a green-brown intractible oil was obtained which was not investigated further.

Discussion

OMT reacts with halides of the early transition series to give isolable adducts of the type $(MX_4)_2\cdot$OMT and $(MX_3)_2\cdot$OMT$\cdot$2L where L = THF and NMe_3. Treatment with titanium(IV) chloride gives bright yellow $(TiCl_4)\cdot$OMT almost immediately on mixing, whereas with the lower halides MCl_3, where M = Ti, V, and Cr, no reaction is apparent. In similar stiuations when complex formation involving these tervalent metal halides is lamentably slow or otherwise elusive, their respective tetrahydrofuran, trimethylamine, or acetonitrile adducts have been used to good effect,[14] and adopting this ploy the green $(TiCl_3)_2\cdot$OMT$\cdot$2THF, the black $(VCl_3)_2\cdot$OMT$\cdot$2THF, and the purple $(CrCl_3)_2\cdot$OMT$\cdot 2NMe_3$ complexes were successfully obtained. The reaction of titanium(IV) chloride with HMT was quite straightforward giving bright yellow $(TiCl_4)_2\cdot$HMT on direct addition. All the complexes are agonizingly air-sensitive with immediate decomposition to metal and silicon oxide residues and release of ammonia. Another common feature is their limited solubility in most organic solvents; they all dissolve sufficiently in dichloromethane, however, to give solutions of very low conductance and are clearly nonelectrolytes. Although $(TiCl_3)_2\cdot$OMT$\cdot$2THF was the only member established directly as being monomeric, we have supposed a similar identity for the remainder by inference and comparison with the $MCl_3\cdot$HMT analogs.[1]

Several important points concerning the stereochemistry of the complexes and the coordination of the metal centers were established from the infrared study (4000–200 cm^{-1}). In the first place the trimethylamine and tetrahydrofuran ligands present in the $(MCl_3)_2\cdot$OMT$\cdot$2L series are coordinated to the metal in the normal fashion, *e.g.*, *via* the nitrogen atom (ν_{as}(CN) and ν_s(CN) of free species decreased by ~25 cm^{-1})[7] and the oxygen atom (decreases of ~50 cm^{-1} with splitting of ν_{as}(COC) and ν_s(COC) of free species),[3] respectively. Secondly, both HMT and OMT are not behaving to their fullest capacity as nitrogen donor systems. On coordination

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(11) Alternative nomenclature: $(TiCl_4)_2\cdot$OMT, di-μ-chloro-(octamethylcyclotetrasilazane)hexachlorodititanium(IV) and similarly for $(TiCl_4)_2\cdot$HMT; $(TiCl_3)_2\cdot$OMT$\cdot$2THF, di-μ-chloro-(octamethylcyclotetrasilazane)tetrachlorodi(tetrahydrofuran)dititanium(III) and similarly for $(VCl_3)_2\cdot$OMT$\cdot$2THF and $(CrCl_3)_2\cdot$OMT$\cdot 2NMe_3$. See IUPAC Nomenclature of Inorganic Chemistry: *J. Amer. Chem. Soc.*, **82**, 5523 (1960).

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Table I. Spectral Data for the HMT- and OMT–Metal Halide Complexes

Complex	Medium	Electronic absorption maxima, cm^{-1}						Nmr absorption maxima, τ^{a-c}
HMT	*c*						44,100	9.90
OMT	*c*						44,200	9.70
$(TiCl_4)_2$, HMT	*c*				35,100 (sh)	38,400	43,800	9.03 (1), 9.25 (2),
	d				34,500	39,100	45,000	9.40 (2), 9.85 (1)
$(TiCl_4)_2$, OMT	*c*				35,700 (sh)	39,700 (sh)	43,820	9.15 (1), 9.40 (1)
	d				34,200	39,400	45,500	
$(CrCl_3)_2$, OMT, $2NMe_3$	*e*	15,580	19,340	30,860				
	d	15,510	19,510	30,560			43,810	
$(TiCl_3)_2$, OMT, 2THF	*d*	12,390 (sh)	13,250	25,700 (sh)		38,450 (sh)	44,200	
$(VCl_3)_2$, OMT, 2THF	*c*				34,700 (sh)	41,400 (sh)	43,800	
	d	13,150	20,610 (sh)		34,450 (sh)	40,800 (sh)	43,700	

[a] TMS as internal reference standard. [b] Relative intensity in parentheses. [c] CH_2Cl_2 solution. [d] Nujol mull. [e] KBr disk.

the single N–H stretching band of these secondary amines assumes a new profile made up of two peaks with the higher wavelength band showing a distinct shoulder. Based on the premise that electron drainage from a nitrogen atom involved in (M–N) bonding not only weakens the immediate N–H bond but, following p_π–d_π interaction across intervening silicon groups, can also influence the N–H bonds of adjacent uncommitted nitrogen atoms, we have assigned bands in the 3500–3200-cm^{-1} region, *viz.*, $(TiCl_4)_2 \cdot$HMT, 3350 ν(NH) uncoordinated and 3280 cm^{-1} ν(NH) coordinated with a shoulder at 3240 cm^{-1}; $(TiCl_4)_2 \cdot$OMT, 3225 ν(NH) uncoordinated and 3180 cm^{-1} ν(NH) coordinated with a shoulder at 3125 cm^{-1}; and the $(MCl_3)_2 \cdot$OMT·2L series, ~3255 ν(NH) uncoordinated and ~3160 cm^{-1} ν(NH) coordinated with a shoulder ~3110 cm^{-1}. It is possible that solid-state effects, *e.g.*, intermolecular hydrogen bonding, also contribute to these variations in ν(NH) and the lowering by ~160 cm^{-1} on coordination and by ~70 cm^{-1} following internal ligand transfer is as expected[15] and is consistent with nonequivalent N–H bonds in the complexes. Other ring absorption bands, *e.g.*, $\nu_{as}(CH_3)$ 2960, $\nu_s(CH_3)$ 2890, ν_{as}(SiNSi) 925, and ν_s(SiNSi) 610 cm^{-1}, are also modified on coordination but these are of little consequence in terms of diagnostic value. The ν(MCl) modes, on the other hand, are of great importance in this respect, and from the data obtained in the (500–200)-cm^{-1} region it is evident that all the complexes are six coordinate. Thus $(TiCl_4)_2 \cdot$HMT, ν(TiCl) 348 cm^{-1} and $(TiCl_4)_2 \cdot$OMT ν(TiCl) 350 cm^{-1} show the strong broad band in the 350–400-cm^{-1} region characteristic of octahedral complexes of titanium(IV) chloride[16] and a medium broad band at 277 cm^{-1} for the former is tentatively assigned also to a ν(TiCl) mode, possibly bridging, in the absence of ligand and ν(Ti-N)[17] absorptions in that vicinity. For the $(MCl_3)_2 \cdot$OMT·2L series the evidence for bridging ν(MCl) modes is more compelling, *viz.*, the broad strong bands at 352 and 297 cm^{-1} in the spectrum of $(TiCl_3)_2 \cdot$OMT·2THF can be assigned to ν(TiCl) modes with the latter involved with bringing halogen.[16] Complications arising from possible coupling of metal–halogen with ligand (OMT and L) and ν(TiL) modes in this region cannot be excluded, and it seems likely that the 352-cm^{-1} band contains a contribution from the OMT out-of-plane ring deformation at 393 cm^{-1};[18] similarly the 297-cm^{-1} band, present in α-$TiCl_3$ at 289 cm^{-1}, could be augmented by components of the ν(TiO)[4] (255 cm^{-1}) and internal OMT (299 cm^{-1})[18] absorptions. Under the same strictures, the broad and intense bands at 345 and 305 cm^{-1} for $(VCl_3)_2 \cdot$OMT·2THF and those at 370 and 287 cm^{-1} for $(CrCl_3)_2 \cdot$OMT·$2NMe_3$ are similarly assigned to ν(MCl) modes, respectively.[16,17,19]

The electronic spectra are summarized in Table I and can be discussed in terms of the metal ions being in an essentially octahedral (O_h) ligand field,[20] *viz.*, six coordinate as presaged by the infrared and chemical evidence. Both $(TiCl_4)_2 \cdot$OMT and $(TiCl_4)_2 \cdot$HMT (d^0 systems) show charge-transfer bands at ~35,000, ~39,000, and ~44,000 cm^{-1}, the first two being assigned to titanium(d) ← chlorine(π) transitions[21] and the latter to an internal ligand transition.[22] The ligand field peak ($^2E_g \leftarrow {}^2T_{2g}$) observed for $(TiCl_3)_2 \cdot$OMT·2THF shows distinct double structure with a band at 13,250 cm^{-1} (10*Dq*) and a shoulder at 12,390 cm^{-1} indicating that the field must contain a component of lower symmetry than O_h. Using the 10*Dq* values for $TiCl_3$,[23] $TiCl_3 \cdot$3THF,[3] and $TiCl_3 \cdot$HMT[1] (here three chlorine atoms and three nitrogen atoms of the *trimeric* silazane ring comprise the octahedral titanium(III) environment) and Jørgensen's rule of average environment, the predicted peak position is at 14,010 cm^{-1} which implies a weaker donor ability ~760 cm^{-1} of the nitrogen atoms of OMT as compared to HMT. The charge-transfer bands at 25,700 and 38,450 cm^{-1} are assigned to titanium(d) ← chlorine(π) transitions[21] in the absence of suitable metal–ligand interaction.

The spectrum of $(VCl_3)_2 \cdot$OMT·2THF contains two bands in the visible region, these being assigned as $^3T_{2g} \leftarrow {}^3T_{1g}(F)$ at 13,150 cm^{-1} and $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ at 20,610 cm^{-1}. Two intense bands at ~34,500 and at ~41,000 cm^{-1} are assigned to vanadium(d) ← chlorine(π) transitions,[21] and these almost certainly obscure the third expected "d–d" band ($^3A_{2g} \leftarrow {}^3T_{1g}(F)$) which is by necessity of very weak intensity. Accepting prior

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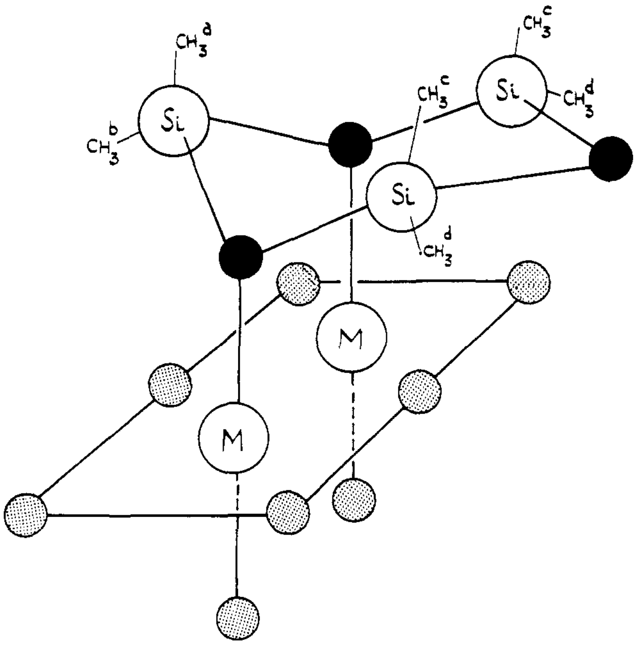

Figure 1. Schematic representation of $(TiCl_4)_2 \cdot HMT$ where M = Ti, (●) NH, and (dotted circle) Cl.

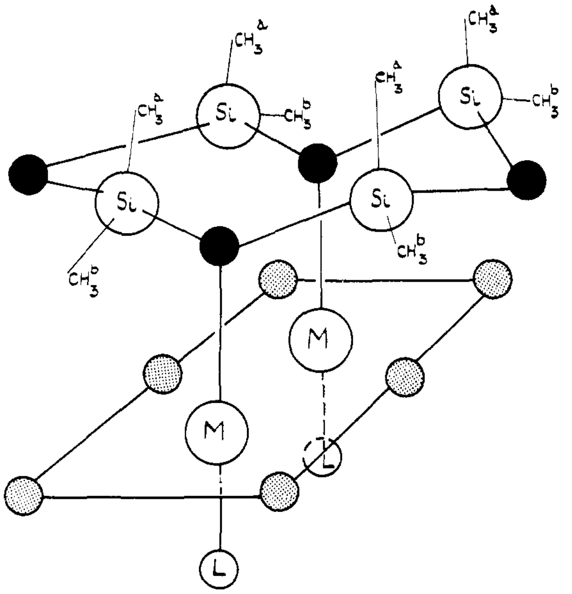

Figure 2. Schematic representation of $(TiCl_4)_2 \cdot OMT$ [L = Cl, M = Ti] and of $(MCl_3)_2 \cdot OMT \cdot 2L$ [M = Ti, L = THF; M = V, L = THF; M = Cr, L = NMe_3]; (dotted circle) Cl and (●) NH.

assignments, the position of this latter transition can be calculated by a first-order perturbation treatment[24] and the value obtained, *viz.*, 27,900 cm^{-1}, is well into the uv region as supposed [B = 566 cm^{-1}; $10Dq$ = 14,460 cm^{-1}]. With $(CrCl_3)_2 \cdot OMT \cdot 2NMe_3$ all three of the expected bands were observed and can be assigned, *viz.*, $^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ ($10Dq$), 15,510 cm^{-1}; $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$, 19,510 cm^{-1}; $^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$, 30,560 cm^{-1}.

Summary

A major factor emerging from our study of the Lewis base behavior of HMT and OMT with halides of the early transition series is the seemingly dogged insistence of hexacoordination on the part of the metal species involved. This immediately refutes the possibility of a seven-coordinate $TiCl_4 \cdot HMT$ complex, and rather suggests that it is the prerequisites of the metal ion rather than the number and availability of nitrogen atoms which exert the greater influence over the choice of molecular configuration adopted by a particular metal–silazane complex. Turning first to $(TiCl_4)_2 \cdot HMT$ and $(TiCl_4)_2 \cdot OMT$, it is clear that maximum ligand donation cannot be involved if the coordination preference of titanium(IV) is to be maintained, and the most likely bonding situation involves the silazane ligand acting as a link between the two titanium centers, *i.e.*, monodentate to each, with halogen bridging completing the sixth (d^2sp^3) coordination site (see Figures 1 and 2). This type of octahedral dinuclear chlorine-bridged structure, established by X-ray analysis for the 1:1 phosphorus oxychloride[25] and ethyl acetate[26] adducts of titanium(IV) chloride, has been previously proposed where similar dilemmas over the extent of ligand participation were present, *e.g.*, with Δ^2-tetraazaborolines,[27] tetrasulfur tetranitride,[28] bis(dimethylamino)haloboranes,[29] and thiourea.[30] Indeed, for $(TiCl_4)_2 \cdot HMT$ in particular, terdentate behavior for the trimeric ring, already ruled out by spectral evidence, can be similarly revoked from simple bond energy and steric considerations since any involvement of the third nitrogen center would necessitate a mixed penta- and hexacoordinate titanium(IV) species[31] at the expense of halogen bridging. The proton nmr results (see Table I) for these two quadrivalent complexes substantiate the proposed molecular structures and confirm bidentate behavior for the two silazane ligands. The spectrum of $(TiCl_4)_2 \cdot OMT$ exhibits two signals of equal intensity at Γ 9.15 and 9.40 assigned to the nonequivalent methyl groups at positions b and a, respectively (see Figure 2), the less hindered proton environment of the latter being correlated with the smaller downfield shift relative to free ligand (Γ 9.70). Similar considerations in the case of $(TiCl_4)_2 \cdot HMT$ would suggest four nonequivalent methyl environments (see Figure 1) and peaks were observed at Γ 9.85 a, 9.03 b, 9.40 c, and 9.25 d with relative intensities 1:1:2:2.

The proposed molecular structure for the $(MCl_3)_2 \cdot OMT \cdot 2L$ series (see Figure 2) evokes little comment. An octahedral environment for the tervalent metal species is realized through halogen bridging (as found in the metal halides themselves) in conjunction with a trimethylamine or tetrahydrofuran molecule filling the sixth coordination site, and the resulting molecular framework is an exact replica of that assumed by the quadrivalent complexes. In metal complexes where

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other tetrameric ring systems, *i.e.*, S_4N_4[32] and $P_4N_4(NMe_2)$,[33] have been used as ligands, the preferred (M–N) bonding always involves apposite nitrogen centers and clearly the presence of L is vital for OMT to be similarly bidentate.[33a]

Having established the overall donor role of HMT and OMT only one anomaly remains, namely, the inability of the former to give adduct formation with chromium(III) chloride. The possibility of exchange reactions occurring, as found in the analogous borazole–metal halides system,[34] seems remote since products obtained from the interaction of several chromium(III) chloride species and HMT were invariably nonstoichiometric with a conspicuous lack of ν(SiNSi) modes in their infrared spectra. Ring degradation of cyclosilazanes by metal halides *via* cleavage of (Si–N) bonds has been demonstrated for $FeCl_3$, $CoCl_2$, and $CuCl_2$[35] with HMT > OMT in terms of susceptibility, and it is now evident that chromium(III) chloride can bring about similar skeletal breakdown in HMT.

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Possible Transition-State Analogs for Ribonuclease. The Complexes of Uridine with Oxovanadium(IV) Ion and Vanadium(V) Ion[1]

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Abstract: The hydrolysis of uridine 2′,3′-phosphate that is catalyzed by ribonuclease is competitively inhibited by uridine, 2′-deoxyuridine, and oxovanadium(IV) ion and is probably competitively inhibited by the 1:1 complexes of uridine with oxovanadium(IV) ion and vanadium(V) ion. The kinetically determined values of the dissociation constants for the binding of these inhibitors to ribonuclease at pH 7.0 and 25° are 9×10^{-3}, 45×10^{-3}, 6×10^{-5}, 1.0×10^{-5}, and 1.2×10^{-5} M, respectively. Under the same conditions the value of the association constant for formation of the 1:1 complex of uridine and metal ion is 160 M^{-1} in the case of oxovanadium(IV) ion and about 80 M^{-1} in the case of vanadium(V) ion. These association constants were obtained from measurements of the effect of uridine upon the solubility of oxovanadium(IV) ion and of the effect of uridine upon the ultraviolet spectrum of vanadium(V) ion. The complexes probably have structures in which the *cis*-glycol function of uridine coordinates with the vanadium atom, since methyl β-D-ribofuranoside forms similar complexes and 2′-deoxyuridine does not. The strong binding of the complexes to ribonuclease may be explained by either the coordination of groups of the enzyme to vanadium or by the resemblance of structures of the complexes to the structure of the substrate portion of the transition state for ribonuclease-catalyzed hydrolysis of uridine 2′,3′-phosphate.

This paper describes the potent inhibition of the enzyme ribonuclease (RNase) by complexes that the nucleoside uridine (U) forms with oxovanadium(IV) ion (V(IV)) and with vanadium(V) ion (V(V)). The rationale for this investigation has been the hypothesis that these complexes may resemble the substrate portion of the transition state for RNase-catalyzed hydrolysis of uridine 2′,3′-phosphates and so act as transition-state analogs.[3] This hypothesis is discussed in more detail in the Discussion.

Experimental Section

Materials. RNase A, lyophilized and phosphate-free, was purchased from Worthington Biochemical Corp. Stock solutions of enzyme were prepared in distilled water and were used for 3–4 weeks. The sodium salt of uridine 2′,3′-cyclic phosphate (U-2′,3′-P) was prepared from a mixture of uridine 2′- and 3′-phosphates (U-2′- and -3′-P), purchased from Sigma Chemical Corp., by the procedure of Szer and Shugar[4] with the modification that the reaction time was

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