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RESEARCH AND DEVELOPMENT OF HIGH

TEMPERATURE RESISTANT POLYMERIC FILM

FORMING MATERIAL

FINAL SUMMARY REPORT

March 1st 1961 to April 17th 1962

by

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Prepared for:

GEORGE C. MARSHALL SPACE FLIGHT CENTER

HUNTSVILLE, ALABAMA

May 15th 1962

Weston, Michigan

FOREWARD

This report was prepared at the Anderson Chemical Division, Stauffer Chemical Company, Weston, Michigan on the National Aeronautics and Space Administration Contract Number NAS8-1532, Control Number TP 85-063, CPB-02-1034-61, "Research and Development of High Temperature Resistant Polymeric Film Forming Material", and was administered by the Contracts Branch (M-P&C-CA) of the George C. Marshall Space Flight Center, Huntsville, Alabama with Gene A. Zerlaut as Administrator.

The report covers the period of work from March 1st 1961 to April 17th 1962.

The personnel assigned to the project were Dr. I. M. Thomas, Principle Investigator, and Mr. F. C. Davis, Research Chemist, on a full-time basis, and Mr. R. S. Towers, Research Chemist, on a part time basis.

ABSTRACT

A new method of preparation of poly-organometallosiloxane polymers
has been discovered. This involved the reaction between bis-dialkylamino-
metal derivatives and silanediols from which linear polymers containing
an alternating -M-O-Si-O- backbone structure should theoretically be
obtained. The metals used were titanium, zirconium, aluminum, vanadium
and tantalum; diphenylsilanediol was used almost exclusively.

The work was divided into three main sections: the preparation of
reactive intermediates, the preparation of model compounds and the
preparation of polymers.

Polymers of titanium and aluminum containing trialkylsiloxy
ligands on the metal atoms were found to rearrange at low temperatures
to give the monomeric $M(OSiR_3)_4$ derivatives and a cross-linked residue.
Those polymers containing triphenylsiloxy ligands were also found to
degrade at comparatively low temperatures. A mechanism for this
rearrangement has been proposed and involved covalency expansion of the
metal atom by co-ordination from an external agency.

By using quinolin-8-oxy ligands, covalency expansion in the case
of titanium, vanadium and tantalum should be satisfied by intramolecular
co-ordination. Polymers of titanium containing this ligand were found
not to rearrange; steric difficulties arose with the other two elements.
With zirconium and aluminum the covalency expansion is not satisfied by
this ligand and rearrangement at low temperature was found to take place.

The infrared spectra, physical properties and thermal stabilities of
model compounds and polymers were measured and are tabulated.

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A) OBJECTIVE OF THE INVESTIGATION AND FIELD OF STUDY

The objective of this investigation was the synthesis and characterization of new thermally stable polymers capable of film formation. After a literature survey on polymeric systems which might be suitable for this task, the field of poly-organometallosiloxanes and poly-organometalloxanes was selected for investigation and reasons for this choice are given in the next section.

It was hoped that initially linear polymers containing an ordered $-M-O-M'-O-$ backbone structure could be prepared where M was titanium, zirconium, vanadium, aluminum or tantalum and M' was either silicon (giving metallosiloxanes) or equal to M (giving metalloxanes). Properties would be modified by attachment of suitable organic ligands on the metal.

An entirely new synthetic procedure for these polymers was to be used.

B) GENERAL INTRODUCTION

Among the most stable polymeric materials known at the present time are the linear polysiloxanes. Despite their stability however, these polymers do have their limitations and undergo extensive rearrangement to form cyclic siloxanes of much lower molecular weight at high temperatures. It may be assumed that the resistance of the silicone polymers to thermal degradation is largely determined by the stability of the -O-Si-O-Si-O- bonding system, and consequently improved thermal stability might be obtained by modifying the electronic character of these bonds. As bonds become more ionic, or as covalent bonds become more polar, greater thermal stability usually results. In modifying the siloxane structure by replacing silicon atoms with more electropositive metals, a more polar bond will be formed leading to a more nearly ionic polymer which should be more resistant to thermal degradation. The nature of the ligands attached to the polymer chain provide a means of varying the final properties of the polymer. A compromise must be reached between hard and brittle heat resistant resins of a highly polar nature and low organic content, and soft fluid polymers of low thermal stability containing a high percentage of non-polar covalently bonded organic ligands.

In general, two lines of approach have been used for the modification of the silicone polymers. One school considers it essential that ordered positioning of the elements in the polymer chain is necessary for the accurate understanding of the predicted temperature improvement, and consequently initially linear polymeric chains were built up from essentially monomeric units. Subsequent cross-linkage was then carried out if necessary to give

the product the desired properties. This process involved a preliminary study of simple compounds containing the proposed bonding system, with a view to obtaining information as to the ease of formation, thermal stability and other properties of the system. Monomeric building units were then selected as to their individual properties in the belief that the resulting polymer would retain these properties.

The second school of thought believes in modifying existing silicone polymers by reaction with metallic reagents which will further cross-link and/or exchange ligands or linkages to produce products with properties more in line with those required. This essentially trial-and-error method has had limited success in a number of cases, but in the long run should not be as good as the more logical preceding method.

It appears necessary to incorporate multivalent elements into the siloxane chain in order that suitable modifying ligands may be attached. The uni- and bivalent strongly electropositive elements, i.e. alkali and alkaline earth metals, will in any case give rigid crystalline and highly polar oxide-type compounds, which would probably be unsuited for this purpose i.e. surface coating. This limits the choice to the elements of groups III and IVb and the transition metals.

The literature survey carried out during the first two months of the contract indicated that aluminum and titanium showed most promise. Little work has been carried out on other transition elements and proposals for research on systems containing zirconium, vanadium, niobium and tantalum in addition to titanium and aluminum were accepted by the Contract Supervisor. The next section reviews the relevant literature in this field and in general

is divided up for each metal as follows:

a) The preparation and properties of monomeric species containing M-O-Si linkages.

b) A description of the various monomeric "building blocks" available for polymer formation with particular regard to thermal stability and reactivity.

c) The methods available for polymer formation and description of polymers that have been prepared.

An introductory section on the formation and properties of silicone polymers precedes the section on polyorganometallosiloxanes.

C) HISTORICAL REVIEW

1. Silicone polymers

The general methods of preparation of the silicone polymers in principle apply equally well to the preparation of other polymeric systems. Two types of polymer may be prepared, linear and cross-linked; we may consider these individually.

Linear polymers may be prepared by direct hydrolysis of bifunctional silicon derivatives such as R_2SiCl_2 or $R_2Si(OR')_2$. Equal quantities of cyclic compounds $(R_2SiO)_n$ and linear polymers of the type $HOR_2Si(OSiR_2)_nOSi-R_2OH$ of low molecular weight are intially obtained. Further condensation of the silanol end groups may be brought about by heating in the presence of catalysts; opening of the cyclic siloxane rings and redistribution of the siloxane linkages also occurs. The average molecular weight increases with the extent of the heating but however large the polymers they must, if linear, have hydroxy end groups. In order to stabilize these groups, trialkylsilyl groups may be introduced in the form of R_3SiCl to act as end stoppers. Linear polymers of the type $R_3Si(OSiR_2)_nOSiR_3$ are then formed and these are fluids even with $n > 2000$.

Cross-linked polymers result when trifunctional units, e.g. $RSiCl_3$, are added to the dichloride prior to hydrolysis. This increases the viscosity of the polymer, and in excess of a certain proportion, a resin results. More monofunctional chain-stoppering groups may be incorporated to keep down the molecular weight, and in an equilibrated system the final average molecular weight will depend only on the R/Si ratio, although the actual structure of the

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polysiloxanes will be governed by the relative proportions of mono-, di- and tri-functional units. The greater the proportion of trifunctional groups, the greater is the degree of branching of the siloxane. Tetrafunctional units e.g. $SiCl_4$ may be introduced, and this results in an even greater degree of cross-linking of the chains.

The higher the alkyl groups attached to silicon the less readily the condensation of silanols to siloxanes and the redistribution of siloxane linkages takes place.

Rather brittle resins can be prepared by condensation of the silanols and low molecular weight siloxanes which are obtained on hydrolysis of Ph_2SiCl_2 and $PhSiCl_3$. These condensations require higher temperatures and longer times than those with methyl silicones. Mixed chlorides of the type $PhMeSiCl_2$ etc. may be hydrolyzed to give methyl-phenyl siloxanes, or alternatively a mixture of chlorides Me_2SiCl_2 and Ph_2SiCl_2 will give similar products.

The nature of the various siloxane polymers varies considerably. Resins of Me/Si ratios of 1.0 - 1.7 have been prepared; below 1.2 these resins are sticky syrups which cure at room temperature or with moderate heating to hard, brittle glassy masses. Between 1.2 and 1.5 the polymers are colorless solids which harden after several hours at $100^{\circ}C$. Above 1.5, and particularly 1.7, the products are oily and volatile but set to a gel after several days at $200^{\circ}C$.

Substitution of ethyl and higher groups for methyl yield compositions which are softer, more soluble and slower to cure. The preferred range is 0.5 - 1.5 ethyl groups per silicon atom; at about 1:1 the products are suitable as coatings, have good adhesiveness and fair flexibility. Above 1.5

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ethyl groups, the compounds are difficult to condense, and above 2.0 the silicones are non-resinous oils.

The aryl derivatives have properties distinctly different from those of the alkyl silicones. The resins soften at elevated temperatures, are weak and brittle when cold and burn with a sooty flame. By chlorinating the nucleus, brittle fusible resins are produced which are less flammable but still weak.

With regard to thermal stability, the Si-Me bond breaks at about 450°-500° in the absence of air and about 200° in the presence of air. Oxidation causes cleavage of the Si-C bond with liberation of organic groups; thermal degradation results in rearrangement of the siloxane linkages to give cyclic structures of low molecular weight and increased volatility. Increase in the size of alkyl groups decreases thermal and oxidative stability; for example, ethyl silicones oxidize at 140° and n-butyl at 120° as fast as methyl silicones at $200^\circ C$.

The Si-Ph group is very stable towards heat and oxidation, and phenyl silicone resins will stand temperatures of 400°-$500^\circ C$. in air at least for a few hours. Phenyl silicone resins are also very stable to high energy radiation, and it has been suggested that this is due to the damping out of absorbed energy through the resonance structure of the molecule.

The exceptional heat stability of tetra-triphenylsiloxysilane $Si(OSiPh_3)_4$ should be mentioned; this compound has a melting point of 235° and a boiling point of about 320°, however, little change was observed on heating to 605°(1).

Co-polymers such as methyl-phenyl silicone resins have properties better in some cases than either methyl or phenyl silicone polymers alone. They

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are harder and more heat stable than methyl silicone resins and much less
brittle than phenyl silicone resins.

2. Polyorganoaluminosiloxanes

Methods of preparation of tris-trialkyl (aryl) siloxyaluminum are as follows:

1. $3R_3SiOH + Al \longrightarrow (R_3SiO)_3Al + 3/2\ H_2$ (2)

2. $3R_3SiOH + Al(OR')_3 \longrightarrow (R_3SiO)_3Al + 3R'OH$ (3) (5)

3. $3R_3SiONa + AlCl_3 \longrightarrow (R_3SiO)_3Al + 3NaCl$ (4) (5)

4. $3R_3SiOAc + Al(OR')_3 \longrightarrow (R_3SiO)_3Al + 3R'OAc$ (6) (7)
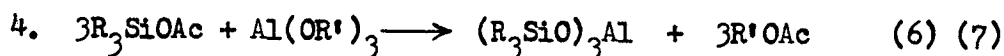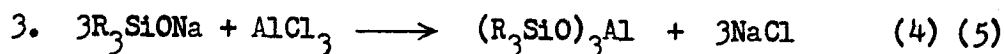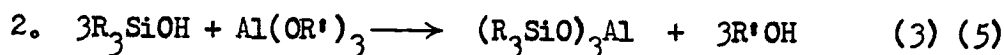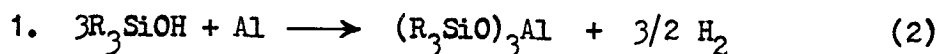
Tris-trimethylsiloxy-aluminum is a white solid m.p. 195°, subl. 160°/0.1mm (6) (7) which is easily hydrolyzed in water and decomposes when heated to 260°-280° to give hexamethyldisiloxane and a resinous benzene soluble residue with a molecular weight of 1200 (7), presumably containing an Al-O-Al-O- chain with trimethylsiloxy ligands. Tris-triphenylsiloxy-aluminum however, also a solid, is much more hydrolytically stable and thermal decomposition studies in air (5) indicated that at 300° the Si-C bond only ruptured after several hours; this compound was reported to melt without decomposition in the absence of air at about 485°C, but when it was prepared in this laboratory, by a different method, a sharp melting point of 193°-5° and boiling point of 300°/0.2 mm was observed.

We should note here that $Al(OSiMe_3)_3$ and $Al(OSiEt_3)_3$ have been found to be dimeric in refluxing benzene (3). The metal expands its covalency to four in these compounds giving structures of the following type:
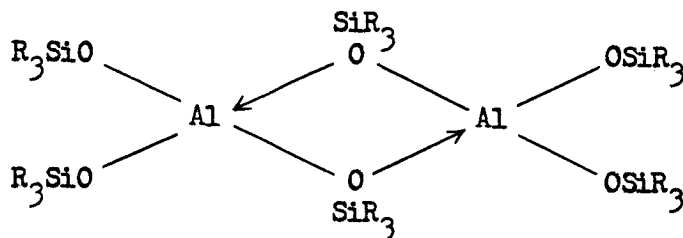
Although no molecular weight determinations have been carried out on $Al(OSiPh_3)_3$ it can be assumed that this too will be dimeric. The increased hydrolytic stability of $Al(OSiPh_3)_3$ over the alkyl derivatives is probably due in part to increased steric shielding of the central aluminum atoms.

As a four covalent aluminum compound, will in general be more stable than a three covalent one, a chelating group attached to the metal should increase stability. Thus, in addition to the normal trivalent alkyls, alkoxides or chlorides which might be used as reactive species for polymer formation, Gibbs et.al. (8) have prepared a series of compounds of the following type:

$Y = -R, -OR, -Cl$

$R = -CH_3, -C_6H_5$
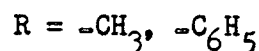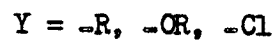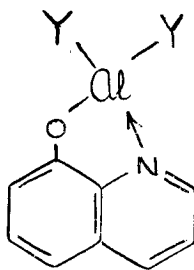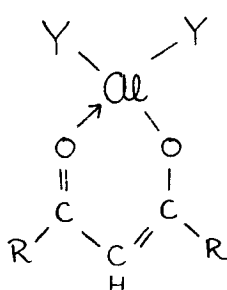
This work indicated that 1:3 diphenyl - 1:3 propane dione chelates had the greatest hydrolytic stability with melting points $315^O - 325^O$ without decomposition, whereas the 8-hydroxyquinoline complexes were more thermally stable (m.p.'s $380^O - 400^O$ without decomp.) but less resistant to hydrolysis.

Woods and Iverson (7) also studied the stabilities of a number of aluminum chelates and other compounds and concluded that the phenoxy-, quinolin-8-oxy-, triphenylsiloxy- and trimethylsiloxy- groups were thermally stable when attached to aluminum, and should bear further investigation as substituents in poly-organoaluminosiloxane polymers.

A method of satisfying the electron deficient nature of aluminum in a polymer chain was proposed by Crain and Koenig (9). They suggested the use of anions as electron donors in a structure of the following type:

$$\left[\begin{array}{c} \mathrm{Na}^{+}_{\ominus} \quad \underset{|}{\mathrm{OSiPh_3}} \quad \underset{|}{\mathrm{Ph}} \\ -\!\!-\; \mathrm{Al} - \mathrm{O} - \mathrm{Si} - \mathrm{O} - \\ \underset{}{\mathrm{OSiPh_3}} \quad \mathrm{Ph} \end{array} \right]_n$$
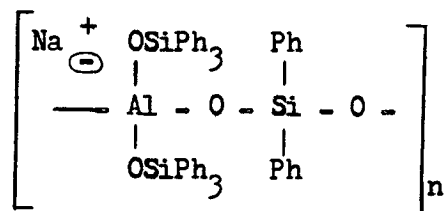
While this particular structure might be subject to facile hydrolysis, the analogous polymers using different cations in place of sodium (e.g. Hg^+ or aluminum) might be quite inert both to hydrolytic and thermal decomposition. The synthesis of the above compound was attempted by reaction of sodium aluminum hydride with triphenylsilanol and reaction of the product with diphenylsilanediol:

$$NaAlH_4 + 2Ph_3SiOH \longrightarrow NaAl(OSiPh_3)_2H_2 + ?\ H_2$$

$$mNaAl(OSiPh_3)_2H_2 + nPh_2Si(OH)_2 \longrightarrow \left[\begin{array}{c} \mathrm{Na}^{+}\ \underset{}{\mathrm{OSiPh_3}} \\ \underset{}{\ominus|} \\ -\!\!-\mathrm{Al}\text{-}\mathrm{O}-\!\!- \\ \underset{}{|} \\ \mathrm{OSiPh_3} \end{array} \right]_m \left[\begin{array}{c} \mathrm{Ph} \\ | \\ \mathrm{Si}\text{-}\mathrm{O}-\!\!- \\ | \\ \mathrm{Ph} \end{array} \right]_n$$
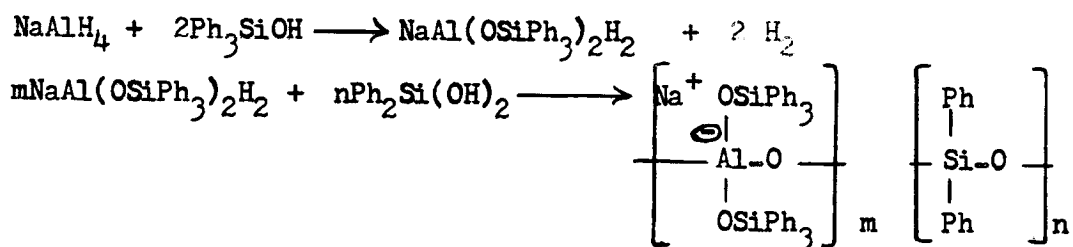
This compound had good heat stability but was easily hydrolyzed as expected. No further work on this system has been reported.

Several methods of polymer formation from build up of monomeric units have been used. The intermolecular heterofunctional condensation reaction between bifunctional silicon and bifunctional aluminum theoretically should give long chain polymers. It was found (5) that with alkoxy- and chlorine groups attached to aluminum and silicon respectively exchange of these groups between the two elements was all that occurred during reaction, and Al-O-Si bonds could not be formed by this method.

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Proposed: $n\ R_2SiCl_2\ +\ n\ R'Al(OR'')_2 \rightarrow$ $\left[\begin{array}{c} Al - O - Si(R)_2 - O \\ | \\ R \end{array}\right]_n$ $+\ 2\ nR''Cl$

Observed: $R_2SiCl_2\ +\ R'Al(OR'')_2 \longrightarrow R_2Si(OR'')_2\ +\ R'AlCl_2$
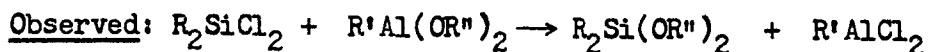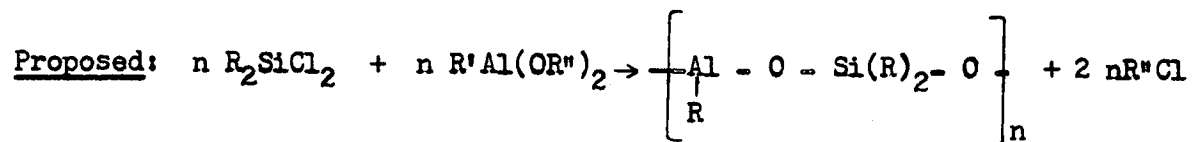
Variation of alkoxide groups on the aluminum did not circumvent this difficulty nor did altering the substituent groups on the dichlorosilane. Aluminum compounds having substituent groups such as piperidyl or quinolin-8-oxy should lower reactivity towards silicon compounds, resulting in slower or no exchange.

These exchange reactions are avoided in the reaction between an alkali metal salt of a silanol and an aluminum halide with the elimination of the alkali halide;

$$n\ R_2Si(ONa)_2\ +\ n\ R'AlCl_2 \longrightarrow \left[\begin{array}{cc} & R \\ & | \\ Al - O - & Si - O \\ | & | \\ R' & R \end{array}\right]_n + 2\ n\ NaCl$$
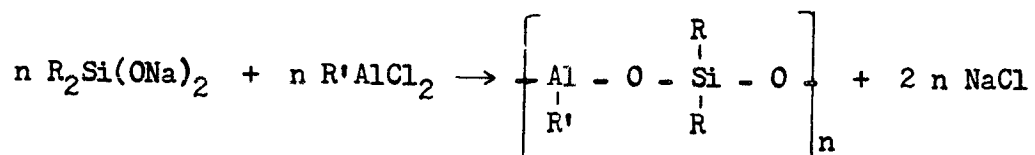
Gibbs (5) has stated that although this method is useful for the preparation of model compounds it does not appear conductive to the formation of polymers of high or useful molecular weight. However, Andrianov (10) obtained a hard polymer corresponding to $(PhSiO_2)_3\ Al$ from the reaction between $AlCl_3$ and $PhSi(OH)_2ONa$, and a similar compound was obtained from the ethyl derivative. The interaction of the sodium salts of $PhSi(OH)_3$ and $EtSi(OH)_3$ with $AlCl_3$ also led to polymer formation (11). These products were hard, brittle and glass-like but soluble in organic solvents; from the nature of the reactants it can be assumed that they were highly cross-linked.

It was found that the replacement of two of the chloride or alkoxide groups of $AlCl_3$ or $Al(OP_r^i)_3$ by $-OSiR_3$ stabilized the remaining group, and

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consequently reaction between $AlCl_3$ or $Al(OR)_3$ with a bifunctional silicon monomer was attempted in an endeavor to obtain a linear polymer. Reaction of $AlCl_3$, $Al(OR)_3$ or AlR_3 with $R_2Si(OH)_2$ or R_2SiCl_2 in no case gave a product with a degree of polymerization greater than two (5). The difficulty in obtaining high molecular weights seems to be the reactivity of the silicon compounds. Reactions involving silanediols require the other substituents on the silicon to be phenyl, otherwise the diol will react with itself to form polyorganosiloxanes. Conversely the diol may be too unreactive to form high molecular weight polymers. Limited success, however, was obtained by a transesterification reaction between aluminum alkoxides and acetoxysilanes. (5) (6) (12):

$$nR_2Si(OAc)_2 + nR'Al(OR'')_2 \longrightarrow \left[\begin{array}{c} R \\ | \\ Si-O-Al-O \\ | \quad\quad | \\ R \quad\quad R \end{array}\right]_n + 2nR''OAc$$
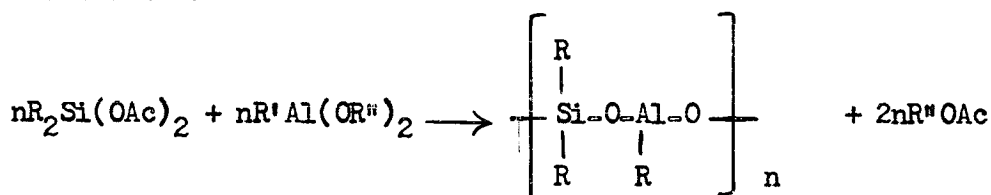
The ester produced could be removed by distillation leaving the polymer as a residue. By this means, polymers have been obtained with molecular weights up to 40,000 ranging in properties from soft resins and waxes to powdery solids (5).

Straight hydrolysis of simple siloxy-aluminum compounds also gives rise to polymer formation. Thus, Andrianov (13) percolated moist air through $Al(OSiEt_3)_3$ at its melting point ($170^\circ C$) and ultimately obtained a polymer with (AlO_2SiEt_3) units in the chain. The proposed mechanism was:

$$Al(OSiEt_3)_3 + H_2O \longrightarrow Al(OSiEt_3)_2OH + Et_3SiOH$$

$$2Al(OSiEt_3)_2OH \longrightarrow Et_3SiO - \underset{\underset{OSiEt_3}{|}}{Al} - O - \underset{\underset{OSiEt_3}{|}}{Al} - OSiEt_3 + H_2O \quad\quad \text{etc.}$$

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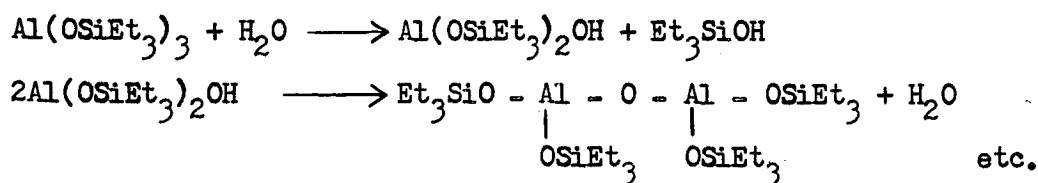
Partial oxidation of some ethyl groups involving cleavage of the Si-C bond had also apparently taken place. Straight hydrolysis of the compound with varying quantities of water gave polymers initially soluble in organic solvents becoming insoluble as the quantity of water, and therefore the molecular weight, increased. The former when applied to metal surface gave hard heat - resistant films on evaporation of the solvent. Later work by Andrianov (4) in which $Al(OSiEt_3)_3$ was heated in a stream of moist air at 170° gave a glassy polymer, with molecular weight 4100, and hexaethyldisiloxane.

$$(n+1)Al(OSiEt_3)_3 \rightarrow (Et_3SiO)_2Al \left[OAl(OSiEt_3) \right]_n OSiEt_3 + 2n(Et_3Si)_2 O$$
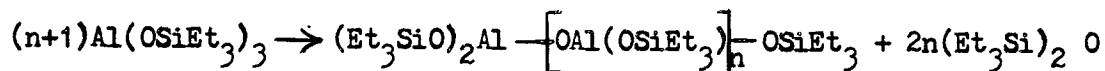
Aluminum trichloride is capable of cleaving -Si-O-Si- linkages (5) (14) (15) and attempts were made to prepare polymers by the action of $AlCl_3$ on poly-organo siloxanes (16) (17). However, only low molecular weight cyclic compounds of the type $(R_2SiO_2AlCl)_2$ could be obtained. It was suggested that these compounds could perhaps be used as starting materials for further polymerization (5), although it has previously been stated that replacement of two of the chlorines of $AlCl_3$ causes stabilization of the third, and consequently we should expect these compounds to be comparatively unreactive.

In this content it should be mentioned that there are numerous examples, mainly in the patent literature, of small quantities of aluminum compounds, e.g. $Al(OR)_3$, used as curing agents for polyorganosiloxanes (17) (18). The quantities used were of the order of 0.1% - 5% and consequently the final polymers could not truly be classified as polyaluminosiloxanes; no doubt these compounds acted as cross-linking agents between siloxane chains:

$$
\begin{array}{ccc}
\mathrm{-Si-O-Si-O-Si-O-} & & \mathrm{-Si-O-Si-O-Si-O-} \\
\ \ |\ \ \ \ \ \ \ \ \ |\ \ \ \ \ \ \ \ \ | & & \ \ |\ \ \ \ \ \ \ \ \ |\ \ \ \ \ \ \ \ \ | \\
\mathrm{OH}\ \ \ \ \ \ \ \ \ \mathrm{OH} & & \mathrm{O}\ \ \ \ \ \ \ \ \ \mathrm{O} \\
& & \ \ |\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ | \\
\ \ \ \ \ \ \ \ \ \ \mathrm{+\ 2Al(OR)_3} \longrightarrow & & \mathrm{AlOR}\ \ \ \ \ \mathrm{AlOR}\ \ \ \mathrm{+\ 2ROH} \\
\mathrm{OH}\ \ \ \ \ \ \ \ \ \mathrm{OH} & & \mathrm{O}\ \ \ \ \ \ \ \ \ \mathrm{O} \\
\ \ |\ \ \ \ \ \ \ \ \ |\ \ \ \ \ \ \ \ | & & \ \ |\ \ \ \ \ \ \ \ \ |\ \ \ \ \ \ \ \ | \\
\mathrm{-Si-O-Si-O-Si-O-} & & \mathrm{-Si-O-Si-O-Si-O-}
\end{array}
$$
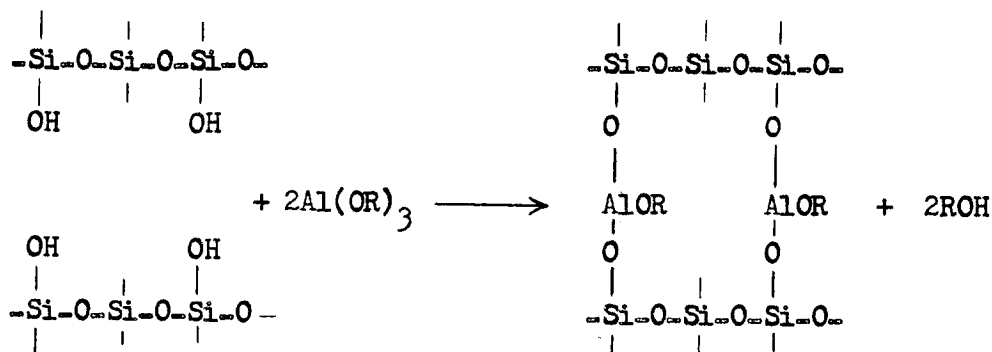
A polyaluminophenylsiloxane was obtained by Andrianov (19) by heating together a polyphenylsiloxane and $Al_2(SO_4)_3$ with aqu. NaOH in an organic solvent at 70°. The average degree of complexity of this polymer after evaporation of the solvent was 10. A similar ethyl derivative was obtained. The solubility of these two polymers declined when heat treated at 150°- $500^{\circ}C$, the latter temperature giving insoluble and non-fusible products. The ethyl derivative lost its solubility under these circumstances quicker than the phenyl one, from which one can assume that cross-linking was more rapid. The thermochemical properties of these polymers have been studied by Andrianov (20) and they were found to be non-fusible up to $600^{\circ}C$ and it was postulated that this was due to the rigidity of their molecules. It is unfortunate that the original paper is not available as few details are available in the abstract.

The co-hydrolysis of Me_2SiCl_2, $PhSiCl_3$ and $AlCl_3$ in aqueous NaOH gave a liquid product which on heat treatment at 200° for 33 hours turned to an infusible poly-alumino-tetra-dimethylphenyldisiloxane (21).

Finally the reaction of tetraethyldisiloxane 1:3 diol with aluminum metal gave a poly-ethylaluminosiloxane which was reported to possess high thermal and chemical stability with respect to mineral acids (11) (22). A similar reaction however with diethylsilanediol did not take place, a poly-diethylsiloxane being the only product (23).

3. Polyorganotitanosiloxanes

Numerous methods are available for the preparation of tetrakistrialkyl (aryl) siloxy – titanium derivatives.

1. $Ti(OR)_4 + 4R_3SiOH \longrightarrow Ti(OSiR'_3)_4 + 4ROH$ (1) (24) (25)

2. $Ti(OR)_4 + 4R_3SiOAc \longrightarrow Ti(OSiR'_3)_4 + 4ROAc$ (24) (26)

3. $TiCl_4 + 4R_3SiOH \longrightarrow Ti(OSiR_3)_4 + 4HCl$ (27) (28) (29) (1)

4. $TiCl_4 + 4R_3SiONa \longrightarrow Ti(OSiR_3)_4 + 4NaCl$ (4) (30)

5. $Ti(NR_2)_4 + 4R_3SiOH \longrightarrow Ti(OSiR_3)_4 + 4R_2NH$ (31)

These compounds, with the exception of the trimethylsiloxy– derivatives show good hydrolytic stability, and $Ti(OSiPh_3)_4$ for example was unaffected by hot dilute acid or alkali (1). The thermal stability in all cases was also good and $Ti(OSiMe_3)_4$ could be refluxed ($230^\circ C$) for several hours under nitrogen without decomposition (3), and $Ti(OSiPh_3)_4$ decomposed in an open tube at 460°–70° [m.p. in sealed tube 501°–$05^\circ C$ (1)].

Compounds containing tetravalent titanium are susceptible to nucleophilic attack involving covalency expansion of the metal to six. Efficient shielding of the metal atoms by bulky ligands will however reduce this susceptibility, and the greater hydrolytic stability of $Ti(OSiPh_3)_4$ compared to $Ti(OSiMe_3)_4$ is no doubt due in part to steric effects. Ebullioscopic molecular weight measurements on $Ti(OSiMe_3)_4$ in benzene have indicated that about 10% trimer units are present in this compound (24) in which titanium exhibits a covalency of six. The structure of this trimer is as follows:
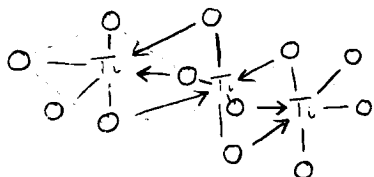
The SiMe$_3$ groups have been omitted for clarity.

We should expect chelate compounds of titanium in which the metal exerts its maximum covalency of six, by intramolecular co-ordination, to be more stable than purely tetravalent compounds. The former will have the added advantage that better steric shielding will also be present.

Various chelated model compounds of titanium have been prepared and their properties studied. Frank et.al. (32) found that bis-quinolin-8-oxy-titanium di-isopropoxide could be heated to 260° without decomposition and Breed and Haggerty (6) (33) studied the properties and thermal decomposition of a series of compounds of the general formula:

$$ Y - Ti - Y $$

$Y = OPr^i,\ Cl,\ OSiPh_3\ or\ OSiPh_2Me$

= Acetylacetonate, 8-quinolinate or 2-oxy-2-(3-methyl)-pentane-4-one

The 8-quinolinate compounds showed the greatest stability and were recommended for use in polymer formation. Compounds of this type have also been prepared and studied by Rust (34).

Condensation reactions between titanium oxide alkoxides $(RO)_2TiO$ and silicon alkoxides $Si(OR')_4$ were carried out by Nesmeyanov et.al. (35) and model compounds of the type $(RO)_3 TiOSi(OR')_3$ and $(R'O)_2Si[OTi(OR)_3]_2$ were obtained. These, however, were found to be thermally unstable and disproportionation occurred on distillation to give titanium tetra-alkoxides $Ti(OR)_4$ and presumably an alkoxy-siloxane residue.

A series of trialkylsiloxy-titanium chlorides $(R_3SiO)_n TiCl_{4-n}$ was obtained by Andrianov (36) from titanium tetrachloride and various mole proportions of sodium trialkylsilanolate. The same compounds were obtained by Orlov (37) from titanium tetrachloride and hexaalkyldisiloxanes at reflux in the presence of a small amount of aluminum chloride. These compound

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have possibilities as reactive intermediates in polymer formation.

Comparative thermal decomposition studies have been carried out on titanium alkoxides and titanium trialkylsilyloxides (38) and it was found that two different mechanisms were involved. With alkoxides at the decomposition point, a chain reaction was set up by water formed by thermal degradation of free alcohol, that may be present from traces of hydrolysis:

$$H_2O + 2Ti(OR)_4 \longrightarrow \left[(RO)_3Ti\right]_2O + 2 ROH$$

$$2 ROH \longrightarrow olefin + 2 H_2O \text{ etc.}$$
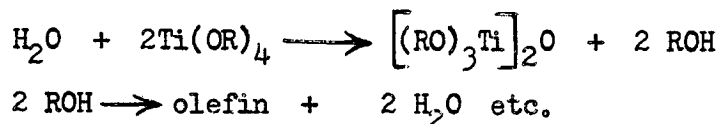
Theoretically it is then possible for one single water molecule to initiate a chain reaction resulting in the decomposition of a large quantity of alkoxide.

With trialkylsilyloxides however, the following mechanism takes place:

$$H_2O + 2 Ti(OSiR_3)_4 \longrightarrow \left[(R_3SiO)_3Ti\right]_2O + 2 R_3SiOH$$

$$2R_3SiOH \longrightarrow (R_3Si)_2O + H_2O$$
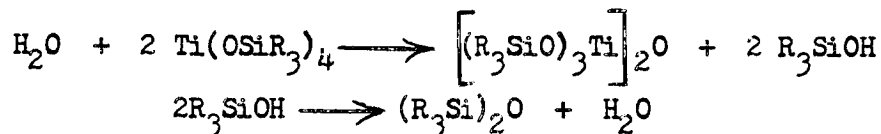
Thus, one molecule of water gives one molecule of water after decomposition i.e. no chain reaction.

We may thus conclude that whereas titanium alkoxides may be useful as intermediates, they will not give thermally stable polymers; on the other hand, trialkylsiloxy groups may make good ligands. It is unfortunate that the Ti-C bond is not stable, as this limits the range of ligands that could be attached to titanium in a polymer chain.

Most of the methods of polyorganoaluminosiloxane polymer formation may be applied in the case of titanium. The alkoxy-acyloxy condensation reaction appears to be the best to date, but has one disadvantage in that undesirable side-reactions are liable to occur. Rust (39) prepared a yellow waxy solid

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polymer of molecular weight about 11,000 from the reaction between bis(tri-
methylsiloxy)-titanium di-isopropoxide and dimethyldiacetoxysilane:

$$n(Pr^iO)_2 Ti(OSiMe_3)_2 + nMe_2Si(OAc)_2 \longrightarrow Pr^iO \left[\begin{array}{c} OSiMe_3 \\ Ti - O - Si \\ OSiMe_3 \end{array} \begin{array}{c} Me \\ \\ Me \end{array} \right]_n O - Ac + 2nPr^iOAc$$
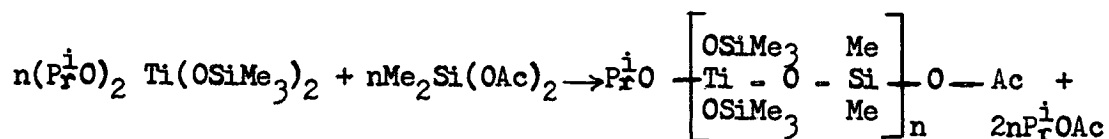
The linearty of this polymer was established by its solubility, fus-
ibility and reasonably high molecular weight (i.e. not cyclic). A similar
compound was prepared from $(PrO)_2Ti(OSiPh_3)_2$ and $Ph_2Si(OAc)_2$ which was fus-
ible and soluble and from whose melt a fibre could be drawn. The same auth-
ors prepared compounds with a -O-Ti-O-Ti- backbone structure and trialkyl-
siloxy ligands:

$$n(Pr^iO)_2Ti(OSiMe_3)_2 + nAc_2O \longrightarrow Pr^iO \left[\begin{array}{c} OSiMe_3 \\ Ti - O \\ OSiMe_3 \end{array} \right]_n Ac + 2nMe_3SiOAc$$
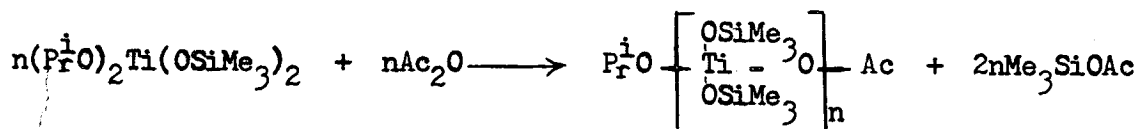
This produce was soluble in polar and non-polar solvents, had a molec-
ular weight of 26,000 and a melting point of greater than $300^{\circ}C$ without
signs of discolouration. Films were prepared by the evaporation of solvent
or fusion of the solid resin.

In all these reactions, undesirable by-products were produced by side-
reactions caused probably by cleavage of the trialkylsiloxy ligands, and
the Si/Ti ratios in all cases were lower than the theoretical for the poly-
mers as proposed. Low reaction temperatures and controlled purification
conditions were considered essential for maximum yields.

Breed and Haggerty (6) (33) reacted diphenyldiacetoxysilane with bis-
8-quinolino-titanium di-isopropoxide and obtained a sparingly soluble orange
solid of molecular weight 1750, thought to contain the repeating units:

$$\left[\begin{array}{c} \text{Ph} \\ | \\ \text{Si} \text{---} \text{O} \text{---} \text{Ti} \text{---} \text{O} \\ | \\ \text{Ph} \end{array} \right]$$
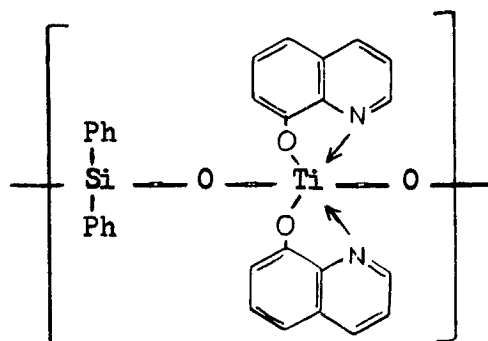
The low molecular weight however casts doubt as to its linearity, and it probably consists of cyclic units.

The same authors reacted chelated titanium alkoxides with diphenyl-silanediol (33) and obtained polymers which were stable up to 315° in a sealed tube and only partially soluble in hot chloroform. It is noteworthy that the chelating ligand was not displaced by the silanediol during the reaction. A similar reaction between diphenylsilanediol and condensed butyl-titanate resulted in the formation of an extraordinary double ring compound (40):

$$\begin{array}{cccccc}
\text{Ph}_2 & & \text{Ph}_2 & & \text{Ph}_2 & \text{Ph}_2 \\
\text{Si} - \text{O} - \text{Si} - \text{O} & & \text{O} - \text{Si} - \text{O} - \text{Si} \\
\text{O} & & & \text{Ti} & & & \text{O} \\
\text{Si} - \text{O} - \text{Si} - \text{O} & & \text{O} - \text{Si} - \text{O} - \text{Si} \\
\text{Ph}_2 & & \text{Ph}_2 & & \text{Ph}_2 & \text{Ph}_2
\end{array}$$
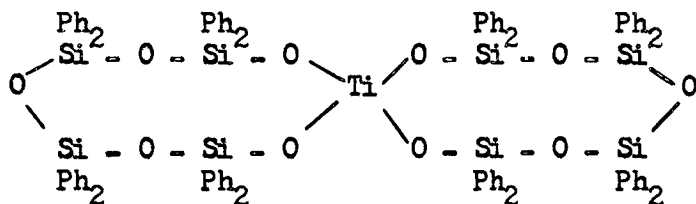
Boyd (41) refluxed titanium tetraalkoxides and dialkylsilicon dialkoxides in benzene and hydrolyzed the mixture by the slow addition of water over 4 hours. A clear viscous polymer was obtained after solvent evaporation.

Similar reactions were carried out by Andrianov et.al. (42) who obtained vitreous soluble polymers by the hydrolysis of a mixture of alkyl(aryl)chloro-silanes and butyl orthotitanate followed by condensation at $200^{\circ}C$. With di-

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methyldichlorosilane, phenyltrichlorosilane and butyl orthotitanate, poly-
mers were obtained with Si/Ti ratios of 25 to 40. With diethyldichlorosilane
instead of dimethyldichlorosilane, ratios of 18 to 24 were obtained.

Post (44) has attempted to prepare titanosiloxane polymers containing
cyclopentadienyl ligands on the titanium atom. No reaction was observed
between bis-cyclopentadienyl-titanium dichloride and either dimethyldiethoxy-
silane or dimethylsilanediol. However in the latter case the presence of an
organic base caused reaction to ensue and a dark brown sticky product was
obtained. The co-hydrolysis of dimethyldichlorosilane and bis-cyclopenta-
dienyltitanium dichloride gave an orange plastic solid of the bouncing
putty type. In neither of these cases was analytical or structural data on
the products given.

The unreactivity of the cyclopentadienyltitanium derivative was con-
firmed by Hammer et.al. (45) who were unable to prepare monomeric siloxy-
titanium compounds from this derivative by reaction with silanols or their
sodium salts. A series of hydrolysis experiments on tetrakis-trimethyl-
siloxy-titanium was carried out by Andrianov and co-workers (13) (4). They
claimed that when 1 mole $Ti(OSiMe_3)_4$ was heated at 50° for 3 hours in acetone
solution with 0.5 mole water, no dimer of the type $(Me_3SiO)_3Ti-O-Ti(OSiMe_3)_3$
was formed and the monomer was almost quantitatively recovered on distill-
ation of the reaction mixture. Subsequent experiments by Bradley (43) have
shown that this claim is probably false and that the dimer is in fact formed
but disproportionates back to the monomer and TiO_2 on subsequent distillation:

$$2 \ (Me_3SiO)_3Ti - O - Ti \ (OSiMe_3)_3 \longrightarrow 3 \ Ti \ (OSiMe_3)_4 + TiO_2$$
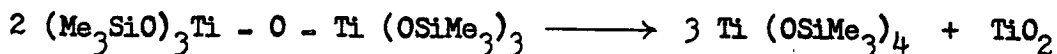
The introduction of acid catalysts when the water content exceeded one mole
per mole of $Ti(OSiMe_3)_4$ led, however, to polymer formation with hexamethyl-

disiloxane and trimethylsilanol as by-products (13) (4). These polymers were soluble in organic solvents in the early stages of hydrolysis but became insoluble in heating with an excess of water.

The reaction mechanism proposed was:

$$Ti(OSiMe_3)_4 + H_2O \longrightarrow (Me_3SiO)_3 TiOH + Me_3SiOH$$

$$2(Me_3SiO)_3 TiOH \longrightarrow (Me_3SiO)_3 Ti-O-Ti-(OSiMe_3)_3 + H_2O \text{ etc.}$$
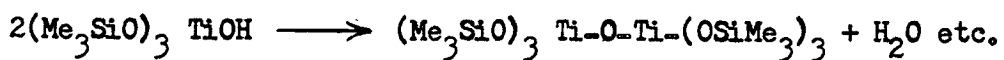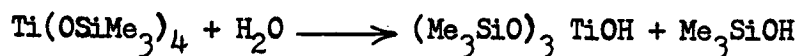
The soluble polymers when applied as a solution to metal surfaces were reported to form hard films on evaporation of the solvent.

It is evident that so far the only satisfactory method available for obtaining high molecular weight polymer of titanium, rather than cyclic compounds, is the alkoxy-acyloxy condensation reaction, in spite of its inherent disadvantages.

4. Polyorganometallosiloxanes containing other transition elements.

Monomeric trialkylsiloxy- derivatives of zirconium, hafnium, niobium and tantalum have been prepared by methods 1. and 2. and 5. used for titanium (24) (31). Compounds of tetravalent vanadium V^{IV} have been prepared by methods 4. and 5. (31) (46). There are a number of other methods used for the preparation of trialkylsiloxy - vanadates:

1. $3Me_3SiCl + Ag_3VO_4 \longrightarrow (Me_3SiO)_3VO + 3AgCl$ (47)

2. $3(Me_3Si)_2O + V_2O_5 \longrightarrow 2(Me_3SiO)_3VO$ (47)

3. $6R_3SiOH + V_2O_5 \longrightarrow 2(R_3SiO)_3VO + 3H_2O$ (48) (49)

4. $3R_3SiOH + VOCl_3 \longrightarrow (R_3SiO)_3VO + 3HCl$ (49)

5. $3R_3SiOH + (R'O)_3VO \longrightarrow (R_3SiO)_3VO + 3R'OH$ (49)

6. $3R_3SiONa + VOCl_3 \longrightarrow (R_3SiO)_3VO + 3NaCl$ (50)
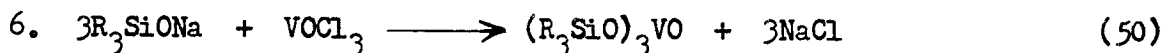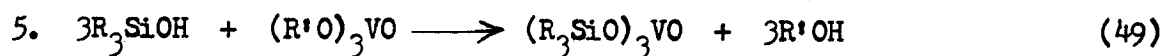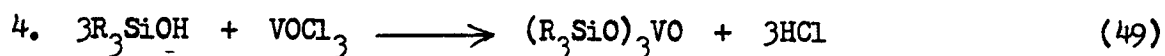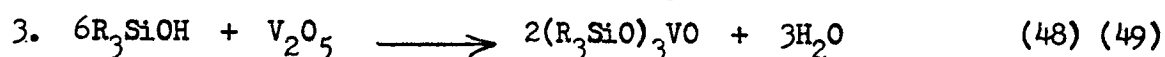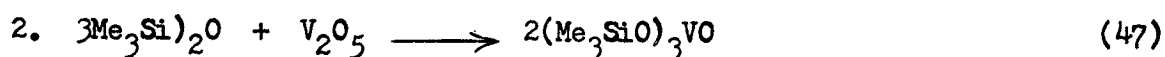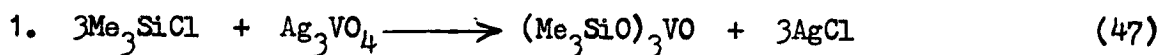
In general, the trialkylsiloxy- derivatives of these transition metals exhibit properties similar to those of the titanium derivatives. Thermal stability in the case of vanadium^{IV} and niobium was reduced however and partial decomposition on distillation was observed; niobium tended to form compounds of the type $[(R_3SiO)_4Nb]_2O$ or $(R_3SiO)_3NbO$ (23), vanadium^{IV} tended to disproportionate to volatile vanadium^{V} compounds on distillation with corresponding formation of vanadium^{III} compounds as residues, and the vanadates were noted to be thermally unstable, no doubt forming compounds containing -V-O-V- or -VO$_2$ groups.

However, the triarlysiloxy-derivatives of vanadium, $V(OSiPh_3)_4$ and $(Ph_3SiO)_3VO$, were both high melting solids stable in cold water (46).

Chamberlain et.al. (46) prepared polyphenylvanadosiloxane polymers from vanadium tetrachloride and diphenylsilanediol, and report a product consisting of a benzene soluble sticky viscous yellow material of about the

same color and consistency of "caramel candy on a warm day". This compound was highly water repellent, stable in hot or cold, weak or strong acids but hydrolysable in strong aqueous alkali. The presence of tetravalent vanadium was indicated by air oxidation in benzene solution to a green insoluble inorganic vanadium^V compound.

Work is in progress on the thermal stability of this and other vanadium polymers but no details are yet available.

Several patents describe the use of zirconium alkoxides (51), zirconium salts (52) (53) and zirconium chelates (54) in the curing of siloxane resins and there is no doubt that -Zr-O-Si-O-Zr- linkages are present in the products, as fairly large percentages of the zirconium compounds were used. The products were in the main used for their water repellent characteristics from which one can assume that the hydrolytic stability was good.

A polymer prepared from a methyl-phenyl silicone gum and a metallic zirconate in benzene spread onto a panel and air dried for 2 hours at room temperature survived 1 hour heating at 455° in air before peeling and cracking and 6 hours at 400° (55).

5. Conclusions

1. The silicone polymers are of moderate thermal stability. The -Si-O-Si-O- chain has a tendency to rearrange at high temperature to low molecular weight products; the Si-alkyl bond is sensitive to nucleophilic attack and breaks down at about 200° in air. The Si-aryl bond is somewhat more stable and breaks down at about 400° in air.

2. The replacement of alternate silicon atoms in a silicone chain by certain metal atoms increases the thermal stability of the resultant polymer chain because of the increased polar nature.

3. Increase in polar nature results in a more inorganic oxide type structure with resultant tendency to hardness and brittleness.

4. The organometalloxane polymers also show this tendency.

5. The two metals that have shown most promise in both the organo-metalloxane and organometallosiloxane polymers are titanium and aluminum. Insufficient work has been carried out on other metals to come to any definite conclusions, although we can discount the alkali and alkaline earth elements as being too electropositive and probably tin as being too large and heavy. In both cases, rigid crystalline structures are obtained.

6. Organic ligands must be attached to the polymer chain to reduce the tendency to brittleness and give a more plastic polymer.

7. Chelating groups make good ligands for two reasons: The chelate ring structure has additional stability because of the ring formation, and covalency expansion of the metal is satisfied by intramolecular co-ordination rather than co-ordination from an external agency leading to degradation.

8. Among the most consistently good chelating groups attached to the metal as regards thermal stability is quinolin-8-oxy. Non-chelating ligands

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which are of good stability are phenoxy and trialkyl(aryl) siloxy groups.
In general, alkoxy , alkyl and aryl groups are unsuitable.

9. Methyl, aromatic and trialkyl(aryl) siloxy groups attached to
silicon show the most promise.

10. There are two general methods of polymer formation.

For polyorganometallosiloxane systems, the modification of existing
silicone polymers by the addition of metal compounds, and for all systems
the build up of polymer chains from monomeric units have been used. Of
these the latter is the most promising as the structure of the resulting
polymer should then be known. Hydrolysis, co-hydrolysis and pyrolysis of
monomers are in general of too random a nature to give satisfactory results.
Of the various condensation-type reactions, the alkoxy-acyloxy reaction has
had the widest application and the greatest success, but has the disadvant-
age that by-products are produced and the reaction conditions must be care-
fully controlled. These by-products are obviously detrimental to the thermal
stability of the resultant polymer.

D) DISCUSSION OF RESULTS

1. Introduction and summary

In view of the somewhat unsatisfactory nature of the known reactions for the synthesis of poly-organometallosiloxanes, initial efforts on this contract were directed towards the development of an entirely new synthetic procedure.

Monomeric trialkylsiloxy-derivatives of transition metals have recently been prepared by Thomas (31) by reaction between dialkylamino- metal compounds and trialkylsilanols.

$$M(NR_2)_x + xR_3'SiOH \longrightarrow M(OSiR_3')_x + xR_2NH$$
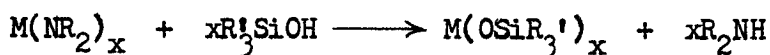
The reaction is carried out by the addition of the trialkylsilanol to the metal derivative in an inert solvent. There are a number of advantages in this method over other methods of preparation for these compounds. The reaction is quantitative, no by-products are formed; this is because reaction conditions are mild (room temperature or lower) and the stability of silanols in the presence of dialkylamines is good, the tendency to condense to a disiloxane which is usually catalysed by acidic or "Lewis acidic" reagents (24) or heat is therefore eliminated, this condensation liberates water which hydrolyzes the starting material or product.

The method is of wide applicability and metals that have been used are titanium, zirconium, vanadium^{IV}, niobium, tantalum and tin.

This reaction has now been modified for the preparation of polyorganometallosiloxanes. Theoretically the reaction between silanediols and bisdialkylamino-metal derivatives should give linear polymers containing an alternating -M-O-Si-O- backbone structure:

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$$n \underset{/}{\overset{\diagdown}{}} M(NR_2)_2 \ + \ n(HO)_2Si \underset{\diagdown}{\overset{/}{}} \longrightarrow \left[\begin{matrix} | \\ M \\ | \end{matrix} - O - \begin{matrix} | \\ Si \\ | \end{matrix} - O \right]_n + \ 2nR_2NH$$
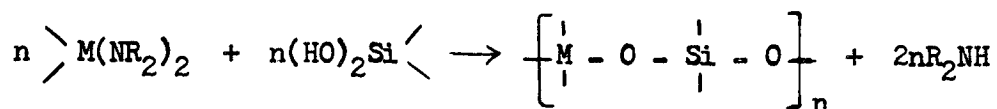
Cross-linked and end-stoppered polymers may be prepared by the intro-
duction of tetra- tri- or monofunctural metal derivatives $M(NR_2)_x$, $ZM(NR_2)_{x-1}$,
$Z_{x-1} M(NR_2)$ (Z = stable ligand), the first two should give cross-linked
polymers and the last act as an end-stopper. Alternatively silanetriols
may be used for cross-linking and silanols for end-stoppering.

However, the work initially was directed towards the preparation of
linear polymers and was in general divided into three main sections. These
were: the preparation of the intermediate bis-dialkylamino-metal derivatives,
the preparation of monomeric model compounds of known structure and finally
the preparation of polymers.

The fully substituted dialkylamino-derivatives of aluminum, titanium,
zirconium, vanadium^{IV} and tantalum are all known and were used as starting
materials for the preparation of intermediates containing these elements;
this involved the substitution of ligands of known thermal stability for all
but two of the dialkylamino- groups. Quinolin-8-oxy intermediates were
prepared in every case, triphenyl- and trimethylsiloxy- intermediates for
titanium and aluminum, and the triethylsiloxy -intermediate for titanium.
Unsuccessful attempts were made to prepare cyclopentadienyl- intermediates
of titanium.

Model compounds were generally prepared by reaction between intermediates
and trialkyl(aryl)silanols; these compounds therefore contained all the
linkages present in the proposed polymer and were of known structure. The
physical properties, thermal stability and infrared spectra of these com-
pounds were measured and provided useful data for subsequent elucidation of

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polymer structure.

Polyorganometallosiloxane polymers were then prepared by reaction of the intermediates with a silanediol. Most of the work involved diphenylsilanediol, and reactions with all the metal intermediates and this reagent were carried out with varying results to be discussed later. Several reactions were also carried out with diethylsilanediol.

In addition some polyorganometalloxanes (-M-O-M-O- type) were prepared by the straight hydrolysis and subsequent heat treatment of intermediates.

Solubilities, hydrolytic and thermal stabilities and the infrared spectrum were measured for all polymeric products prepared.

2. Preparation of intermediates

a) Dialkylamino-metal derivatives

Dialkylamino- derivatives of titanium (56), zirconium (56), vanadium (57) and tantalum (58) have recently been prepared by reaction between the metal chloride and lithium dialkylamide in ether:

$$MCl_x + xLi(NR_2) \longrightarrow M(NR_2)_x + xLiCl$$
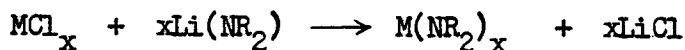
All these derivatives are covalent compounds, which may be distilled without decomposition under high vacuum; they are extremely sensitive to moisture and must be handled under anhydrous conditions.

At the start of the contract no methods for the preparation of dialkyl-amino- aluminum compounds could be found in the literature, and consequently two attempts were made to prepare these compounds, both unsuccessful, before a method was fortunately published.

The reaction between aluminum chloride and lithium diethylamide in ether, analogous to those described above, did not give the desired $Al(NEt_2)_3$; a volatile product was obtained, the analysis of which suggested a structure of the following type $(Et_2N)_2Al(NEt)Al(NEt_2)_2$.

The reaction between diethylamine and triethylaluminum,which is readily obtainable in this Company, gave a volatile liquid product corresponding to ethylaluminum sesquidiethylamide with the liberation of ethane:

$$2\ AlEt_3 + 3\ Et_2NH \longrightarrow Et_3Al_2(NEt_2)_3 + 3\ EtH$$
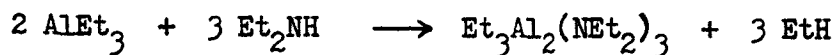
Prolonged reflux of this product with diethylamine failed to effect further substitution.

A very recent publication (59) has described the preparation of tris-dimethylamino- aluminum, $Al(NMe_2)_3$. This involves reaction between lithium aluminum hydride and dimethylamine followed by reaction with aluminum chloride:

$$\text{Li AlH}_4 + 4 \text{ Me}_2\text{NH} \longrightarrow \text{Li Al(NMe}_2)_4 + 4 \text{ H}_2$$

$$3 \text{ LiAl(NMe}_2)_4 + \text{AlCl}_3 \longrightarrow 4 \text{ Al(NMe}_2)_3 + 3 \text{ LiCl}$$
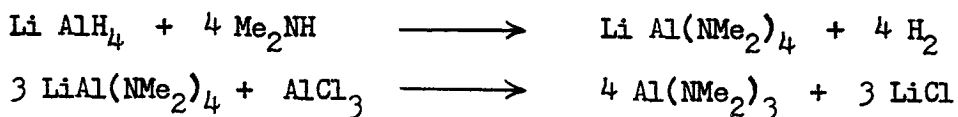
These reactions were carried out, and the desired product was obtained as a white crystalline solid m.p. ca. $85°$ and b.p. $90°/0.1$ mm. It exhibited all the usual properties of dialkylamino- metal derivatives.

However when this reaction was repeated with diethylamine, a volatile liquid, similar to that produced in the reaction between AlCl_3 and LiNEt_2, was obtained.

There seems no reason to doubt that $\text{Al(NEt}_2)_3$ is intially formed in both the reactions mentioned in the preceeding paragraph, but we must deduce that it is unstable and decomposes either during the reaction or on attempted distillation to compounds containing Al-N-Al bonds. We may note that $\text{Al(NMe}_2)_3$ has a molecular complexity of 2.22 in freezing benzene, and therefore contains Al-N$\rightarrow$Al bridges between molecules; this co-ordination is no doubt the first step in the decomposition of $\text{Al(NEt}_2)_3$.

It is interesting to note also that whereas $\text{Nb(NMe}_2)_5$ and $\text{Ta(NMe}_2)_5$ can be obtained and may be sublimed without decomposition (60) (58), on the attempted distillation of the corresponding penta- diethylamino- derivatives, in the case of niobium reduction takes place and $\text{Nb(NEt}_2)_4$ is obtained (60), and in the case of tantalum the metal remains pentavalent but $(\text{Et}_2\text{N})_3\text{Ta} = \text{NEt}$ distils (58). These results are attributed to steric factors which may also be the cause of the results obtained for aluminum.

In the light of these results it seems highly likely that $\text{Al(NMe}_2)_3$ could be obtained from AlCl_3 and lithium dimethylamide.

Attempts were also made to prepare tris-dialkylamino -vanadates, $(\text{R}_2\text{N})_3\text{V=O}$, from vanadium oxytrichloride and lithium dialkylamides, but in every case a

low yield of the tetravalent derivative, $V(NR_2)_4$, was all that could be distilled from the reaction mixture. The reducing power of lithium dialkylamides has already been mentioned in the case of niobium, and one must assume that $VO(NR_2)_3$ is initially formed in this reaction but is immediately reduced by the reagent:

$$VOCl_3 + 3 LiNR_2 \longrightarrow VO(NR_2)_3 + 3LiCl$$
$$2VO(NR_2)_3 + 4 LiNR_2 \longrightarrow 2V(NR_2)_4 + 2 Li_2O + Et_2NNEt_2$$
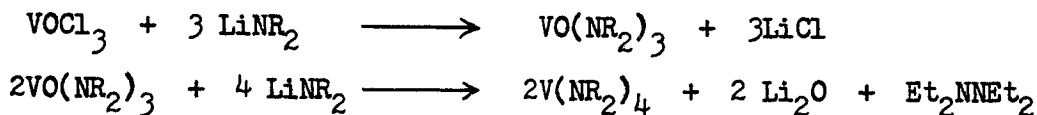
This is consistent with the low yield of $V(NR_2)_4$, as a considerable quantity of the reagent, $LiNR_2$, is required for the reduction.

Another method of preparation of $VO(NEt_2)_3$ was attempted, and this involved the passage of gaseous oxygen though a solution of $V(NEt_2)_4$ in heptane. The proposed reaction was as follows:

$$2 V(NEt_2)_4 + O_2 \longrightarrow 2 VO(NEt_2)_3 + Et_2NNEt_2$$
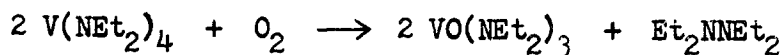
Initially in this reaction the solution became very warm and turned deep red. However on subsequent distillation of the reaction mixture a small quantity of $V(NEt_2)_4$ was all that distilled and a black apparently decomposed residue remained. It would appear that some kind of reaction had taken place and obviously this bears further investigation; it may be that the desired product, $VO(NEt_2)_3$, is thermally unstable and cannot be distilled without decomposition.

b) Intermediates containing trialkyl(aryl)siloxy ligands

Initial research on the preparation of intermediates of this type was undertaken using compounds of titanium. Three possible reactions for the preparation of bis-dialkylamino-bis-trialkyl(aryl)siloxy- titanium intermediates were considered.

1. $Ti(NR_2)_4 + Ti(OSiR'_3)_4 \longrightarrow 2 Ti(NR_2)_2(OSiR'_3)_2$

2. $Ti(NR_2)_4 + 2 R'_3SiOH \longrightarrow Ti(NR_2)_2(OSiR'_3)_2 + 2 R_2NH$

3. $TiCl_2(NR_2)_2 + 2 NaOSiR'_3 \longrightarrow Ti(NR_2)_2(OSiR'_3)_2 + 2 NaCl$
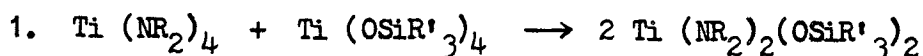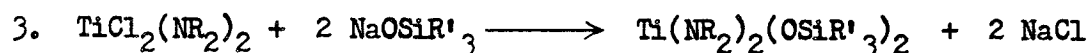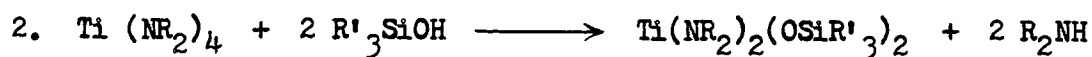
When $Ti(NEt_2)_4$ and $Ti(OSiPh_3)_4$ were refluxed together in benzene no reaction was observed during 10 hours reflux and the starting materials were recovered unchanged. A similar reaction was carried out with $Ti(NEt_2)_4$ and $Ti(OSiEt_3)_4$ and a product was obtained which was separated into two fractions by distillation under high vacuum; one fraction had an analysis correspond- ing to approximately $Ti(NEt_2)_3 (OSiEt_3)$ and the other to $Ti(NEt_2) (OSiEt_3)_3$. This could correspond to a number of possibilities; each fraction could be substantially pure product as indicated by the analysis, or they could be azeotropic mixtures of unchanged starting materials; or they could be dis- proportionation products of $Ti(NEt_2)_2(OSiEt_3)_2$ formed by the action of heat on this latter compound.

At this stage work on reaction 1. was suspended in the hope that one of the other methods would be more convenient.

The slow addition of a solution of triphenylsilanol in benzene to a stirred solution of $Ti(NEt_2)_4$ in benzene in a 2:1 molar ratio gave a benzene soluble product which was shown to be a mixture of $Ti(NEt_2) (OSiPh_3)_3$, $Ti(NEt_2)_2(OSiPh_3)_2$ and $Ti(NEt_2)_3 (OSiPh_3)$ by fractional crystallization. A similar reaction with triethylsilanol gave an impure sample of the re- quired product, $Ti(NEt_2)_2(OSiEt_3)_2$.

We may note here that reaction between triphenylsilanol and $Ti(OBu)_4$ in a 2:1 molar ratio gave 50% $Ti(OSiPh_3)_4$ and 50% unreacted $Ti(OBu)_4$(1). How- ever trimethylsilanol has been reported to give all three intermediates when reacted with $Ti(OPr^i)_4$ in the correct molar ratios (61).

It would seem that there would be difficulty in isolating the required

products from the crude reaction mixtures obtained from these reactions, and consequently work too was suspended on reaction 2.

Fortunately reaction 3. has proved to be entirely satisfactory for the preparation of the required intermediates in the pure state. Bis-dialkyl-aminotitanium dichlorides may be prepared by a simple equilibration reaction between equimolar quantities of $Ti(NR_2)_4$ and $TiCl_4$ in an inert solvent (62)(57).

$$TiCl_4 + Ti(NR_2)_4 \longrightarrow 2\ TiCl_2(NR_2)_2$$
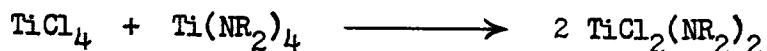
The products may be obtained in near quantitative yield, and can be purified by volatalization under high vacuum. Subsequent reaction with the sodium salts of trialkyl(aryl)silanols, prepared by reaction between metallic sodium and the silanol in ether, then enables the required intermediates to be prepared:

$$TiCl_2(NR_2)_2 + 2\ NaOSiR'_3 \longrightarrow Ti(NR_2)_2(OSiR'_3)_2 + 2\ NaCl$$
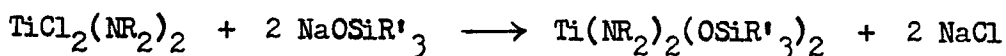
$Ti(NMe_2)_2(OSiMe_3)_2$ and $Ti(NEt_2)_2(OSiEt_3)_2$ were both prepared by this method, and were separated from sodium chloride by distillation of the reaction mixture under high vacuum, both being volatile liquids; this also served as a purification procedure. Unfortunately the triphenylsiloxy derivative, $Ti(NEt_2)_2(OSiPh_3)_2$, was found to decompose on attempted distillation and could only be separated from sodium chloride by filtration. This filtration was tedious as the precipitate is very fine and the operation must be carried out under nitrogen to avoid hydrolysis. However analytical data on the product indicated it to be quite satisfactory for subsequent use although it was not purified.

In an attempt to discover a simpler method of preparation of $Ti(NMe_3)_2$ $(OSiMe_3)_2$ which does not involve the use of $TiCl_2(NMe_2)_2$, $Ti(NMe_2)_4$ was refluxed in hexamethyldisiloxane under a fractionating column. The proposed

reaction was as follows:

$$Ti(NMe_2)_4 + Me_3SiOSiMe_3 \longrightarrow Ti(NMe_2)_3(OSiMe_3) + Me_3SiNMe_2$$

$$Ti(NMe_2)_3(OSiMe_3) + Me_3SiOSiMe_3 \longrightarrow Ti(NMe_2)_2(OSiMe_3)_2 + Me_3SiNMe_2$$
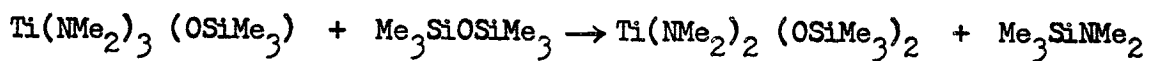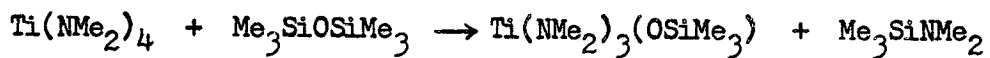
Unfortunately no drop in temperature at the column head below the boiling point of the disiloxane, indicating the formation of Me_3SiNMe_2, was observed during 9 hours reflux, and after this period the $Ti(NMe_2)_4$ was recovered unchanged.

Having established the dialkylamino-titanium chloride method as quite suitable for the synthesis of titanium intermediates, exactly similar reactions were carried out for aluminum and $Al(NMe_2)_2(OSiMe_3)$ was prepared as a volatile liquid and $Al(NMe_2)_2(OSiPh_3)$ as a non-volatile solid.

c) Intermediates containing quinolin-8-oxy ligands

In view of the chelating property of the quinolin-8-oxy group the synthesis of intermediates containing this ligand is facilitated. The straight reaction between dialkylamino- metal derivatives and 8-hydroxyquinoline in the stoichiometric proportions gave the required intermediate in all cases except that of tantalum which is discussed later:

$$M (NR_2)_x \ + \ (x-2) \quad \text{[quinoline structure with OH, N]} \ \longrightarrow \ \left[\text{[chelate structure N}\rightarrow\text{, O}\rangle \right]_{x-2} M(NR_2)_2 \ + \ (x-2) \ R_2NH$$
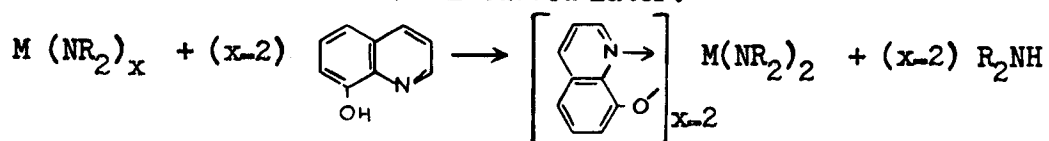
All products were orange or red solids, sensitive to moisture, which could be crystallized from benzene. No mixed products containing mono- di- and tri- substituted derivatives were obtained and this can quite simply be explained. In the case of titanium and vanadium[IV] the covalency maximum of six for these elements makes it extremely unlikely that substitution of more than two dialkylamino groups will take place, as no further co-ordination of nitrogen to the metal atom can occur. The small size of these elements also means that steric factors probably play a prominent part.

However with zirconium and aluminum, with covalency maximum of eight and six respectively, further substitutions beyond that required can take place, and in fact the fully substituted derivatives, $Al(OC_9H_6N)_3$ and $Zr(OC_9H_6N)_4$, may be obtained with the stoichiometric quantities of 8-hydroxyquiroline. But the covalencies of six and four respectively, which are exhibited by these elements in the intermediates, are also exhibited in numerous other compounds of these metals and as such represent an "energy plateau" or stable state. The energy barrier to further substitution appears to be sufficient to ensure that a mixture of products is not obtained.

The extreme stability of the tetrachelated derivative $Zr(OC_9H_6N)_4$ was illustrated by its lack of reactivity when refluxed with a stoichiometric

quantity of $Zr(NEt_2)_4$ in an attempt to prepare $Zr(NEt_2)_2(OC_9H_6N)_2$.

We may note that these quinolin-8-oxy intermediates of titanium, zirconium and vanadium^{IV} can exist in two geometrical isomeric forms:
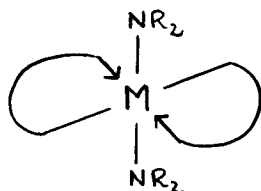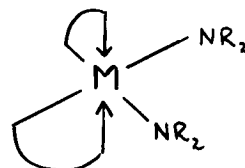
Trans-form   Cis-form

The trans-form would obviously be the more suitable for the preparation of linear polymers as the cis-form may encourage the formation of low molecular weight cyclic products. However one must assume that equal quantities of both forms occur during synthesis and this might be expected to show in the melting point which would not be sharp; it was not possible to show this as all derivatives decomposed without melting at about $120°-150°/0.1$ mm.

When $Ta(NMe_2)_5$ and 8-hydroxyquinoline were reacted in a 1:3 molar ratio, $Ta(OC_9H_6N)_3(NMe_2)_2$ should theoretically have been obtained:

$Ta(NMe_2)_5 + 3$ $\longrightarrow$ $Ta(NMe_2)_2 + 3 Me_2NH$
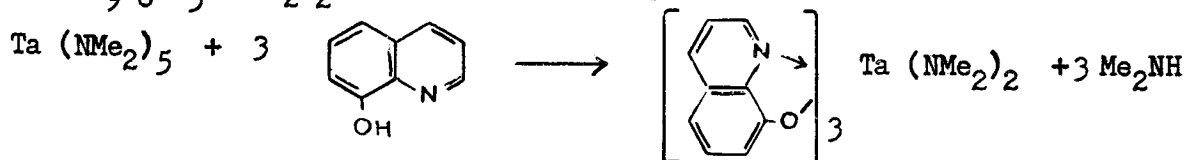
In fact the product obtained had a Ta/basic N ratio of 1:0/1.50 and, as it is obvious that not more than three dimethylamino groups could have been substituted, a structure involving a Ta-N-Ta linkage is probably present. This would involve an elimination reaction of the following type, perhaps caused by steric factors:

$2 Ta(OC_9H_6N)_3 (NMe_2)_2 \rightarrow (NH_6C_9O)_3(Me_2N) Ta-\underset{Me}{N}-Ta(NMe_2)(OC_9H_6N) + Me_3N$
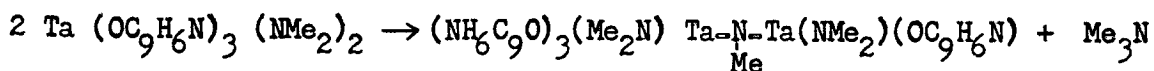
It is noteworthy that the covalency maximum of eight for tantalum is satisfied in this compound. It is also of note that it will react with hydroxylic reagents in exactly the same way as the desired intermediate

and will be entirely suitable as a replacement for this intermediate. This was found experimentally to be the case.

d) Intermediates containing other ligands

Several attempts were made to prepare bis-dialkylamino-bis-cyclopentadienyl- derivatives of titanium. When $Ti(NMe_2)_4$ was heated with cyclopentadiene a monosubstituted derivitive only could be isolated:

$$Ti\ (NMe_2)_4\ +\ C_5H_6 \longrightarrow Me_2N \ - \underset{NMe_2}{\overset{\text{⬠}}{Ti}} - NMe_2\ +\ Me_2NH$$
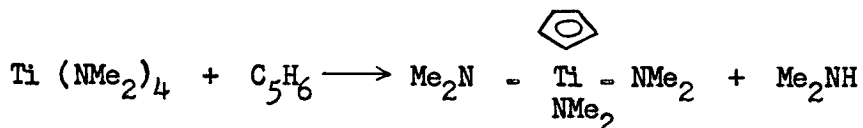
This unusual compound was a volatile red solid, very susceptible to hydrolysis.

A very small quantity of the desired product was obtained from the reaction between $TiCl_2(NEt_2)_2$ and cyclopentadienyl sodium:

$$TiCl_2(NEt_2)_2\ +\ 2\ NaC_5H_5 \longrightarrow \ Et_2N - \overset{\text{⬠}}{\underset{\text{⬠}}{Ti}} - NEt_2\ +\ 2\ NaCl$$
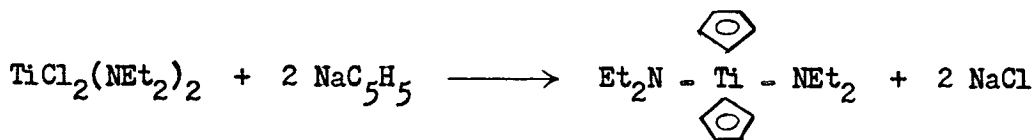
The derivative was distilled from the reaction mixture with much decomposition, and the non-volatile residue was found to contain a large quantity of lower valent titanium.

In the reaction between lithium diethylamide and bis-cyclopentadienyl-titanium dichloride in ether, heat was liberated but,on distillation of the reaction mixture,unchanged titanium starting material was all that was isolated.

$$2\ Li\ NEt_2\ +\ Cl - \overset{\text{⬠}}{\underset{\text{⬠}}{Ti}} - Cl \longrightarrow Et_2N - \overset{\text{⬠}}{\underset{\text{⬠}}{Ti}} - NEt_2\ +\ 2\ LiCl$$
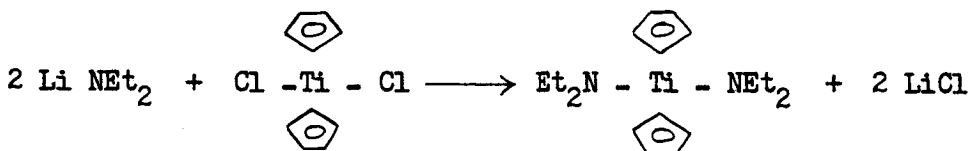
These results would seem to confirm those of Post (44) and Hammer (45)

in showing that the reactions of these cyclopentadienyl derivatives are not simple and side reactions appear to take place. Although this line of research probably bears further investigation it was decided to suspend it at this stage.

Two preliminary reactions have been carried out in an attempt to prepare intermediates of titanium containing chelating ligands other than quinolin-8-oxy. When acetylacetone was added dropwise to $Ti(NMe_2)_4$ in benzene in a 2:1 molar ratio considerable heat was evolved and the solution turned deep red. The proposed reaction was as follows:

$$Ti\ (NMe_2)_4\ +\ 2\ Me - \underset{O}{\overset{\ }{C}} - CH_2 - \underset{O}{\overset{\ }{C}} - Me \longrightarrow$$

$$+\ 2\ Me_2NH$$
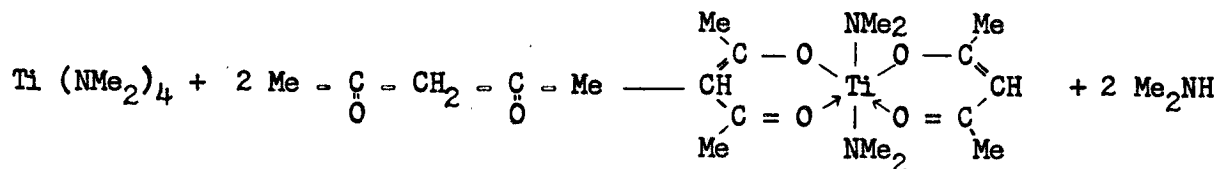
Evaporation of the solvent gave a thick red liquid product; on attempted distillation under high vacuum a low melting pale yellow solid distilled in low yield, this was not completely identified but was shown to contain no titanium.

In view of the volatility of dialkoxytitanium bis-acetylacetonates, $(RO)_2\ Ti\ \left[(CH_3CO)_2\ CH\right]_2$, one might expect that the required product in this case would be volatile. It is then likely that side reactions are taking place; Ketones are known to condense with amines with the liberation of water which of course would hydrolyze the titanium derivative leading to non-volatile products.

This reaction will be re-examined and modifications will include attempted removal of the dimethylamine as it is formed with dropwise addition of the acetylacetone solution.

A reaction was also carried out using acetylsalicylic acid and $Ti(NMe_2)_4$;

this should also form a chelated derivative:

$$\text{Ti (NMe}_2)_4 \quad + \quad 2 \quad [\text{C}_6\text{H}_4 \text{ with COOH and OCOCH}_3] \quad \longrightarrow \quad [\text{chelated Ti complex structure}]$$

$$+ \quad 2 \text{ Me}_2\text{NH}$$
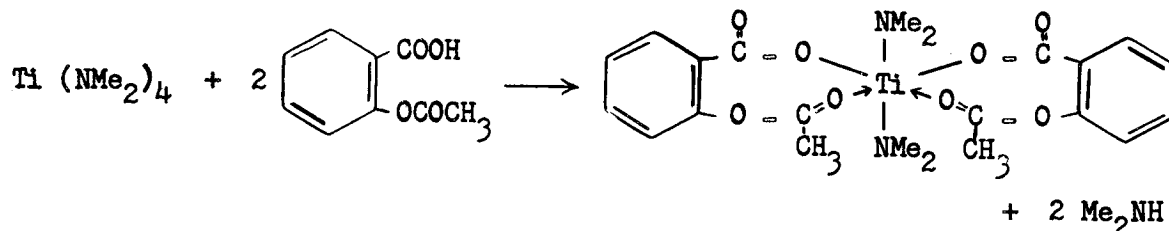
Considerable heat was evolved in this reaction and an insoluble yellow powder was isolated. This product had a Ti/N atomic ratio of 1.0/1.06 and we are unable at this time to fit a precise structure to it. It is obvious that this reaction is not simple and no doubt by-products are formed; the possibility of salt formation between the acid and dimethylamine, which is strongly basic, should not be discounted. Here again re-examination with modifications in the reaction procedure is required.

Table I lists the physical properties of all the pure polymer inter-mediates which were prepared.

TABLE I

Physical properties of polymer intermediates

Compound	Nature	Volatility	Solubility
$Ti(NMe_2)_2(OSiMe_3)_2$	orange liquid	b.p. 60°/0.1 mm	sol. organic
$Ti(NEt_2)_2(OSiEt_3)_2$	yellow liquid	b.p. 140°/0.1 mm	sol. organic
$Ti(NEt_2)_2(OSiPh_3)_2$	orange-yellow viscous liquid	decomp. 300°/0.1 mm	sol. benzene
$Al(NMe_2)_2(CSiMe_3)$	colorless liquid	b.p. 105°/0.1 mm	sol. organic
$Al(NMe_2)_2(OSiPh_3)$	pale yellow solid	m.p. 50° decomp. 250°/0.1 mm to $Al(NMe_2)_3$	sol. benzene
$Ti(NMe_2)_2(OC_9H_6N)_2$	light orange solid	decomp. 150°/0.1 mm without melting	sol. benzene
$Ti(NEt_2)_2(OC_9H_6N)_2$	orange red solid	decomp. 120°/0.1 mm to give $Ti(NEt_2)_4$	crystalizes from benzene
$Zr(NMe_2)_2(OC_9H_6N)_2$	bright yellow solid		crystalizes from benzene
$Al(NMe_2)_2(OC_9H_6N)$	bright yellow solid	decomp. from 120°/0.1 mm	insol. benzene
$V(NEt_2)_2(OC_9H_6N)_2$	dark brown solid	———	sol. benzene
$[Ta(OC_9H_6N)_3(NMe_2)]_2$ NMe?	dark maroon solid	decomp. 140°/0.1 mm without melting	sol. benzene
$TiCl_2(NMe_2)_2$	brown solid	subl. 70°/0.1 mm	sol. ether, benzene insol. pet. ether
$TiCl_2(NEt_2)_2$	deep red liquid	b.p. 100°/0.1 mm	sol. organic
$AlCl(NMe_2)_2$	white solid	m.p. ca 50° b.p. 90°/0.2 mm	sol. organic
$Ti(cp)(NMe_2)_3$	deep red solid	m.p. ca 60° b.p. 110°/0.1 mm	sol. ether

3. Preparation of model compounds

Model compounds were prepared for a number of reasons.

The reaction between trialkylsilanols and dialkylamino-metal derivatives has already been shown to proceed smoothly and in near quantitative yield (31), but this had to be confirmed for reactions with triphenylsilanol and suitable reaction conditions discovered. It was then assumed that reactions with dialkyl- and diphenylsilanediols would be similar.

The synthesis of model compounds provides products of known structure and containing all the groups present in the analagous polymer. Thermal stability measurements should then give an indication as to what might be expected from the polymer, and the infrared spectrum should be useful in the subsequent elucidation of polymer structure.

a) Triphenylsiloxy derivatives

No difficulty was encountered in the preparation of triphenylsiloxy derivatives of titanium, zirconium, vanadium^{IV}, aluminum and tantalum from the corresponding dialkylamino- metal compounds and triphenylsilanol in benzene:

$$M(NR_2)_x + xPh_3SiOH \longrightarrow M(OSiPh_3)_x + xR_2NH$$
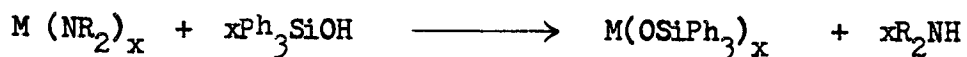
Tris-triphenylsilyl -vanadate, $VO(OSiPh_3)_3$, could not be prepared by this method because of the failure to obtain the dialkylamino derivative. Consequently this compound was prepared by an interchange reaction between isopropylvanadate and triphenylsilanol in refluxing benzene; this is an equilibrium reaction and the isopropanol was removed during the reaction as the minimum boiling binary azeotrope with benzene using a fractionating column.

$$VO(OPr^i)_3 + 3 Ph_3SiOH \rightleftharpoons VO(OSiPh_3)_3 + 3 Pr^iOH$$
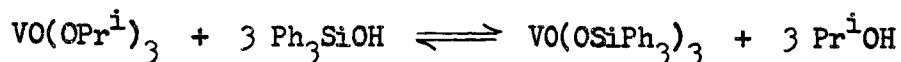
The physical properties of the triphenylsiloxy- metal compounds are listed in table II and several points are of note.

TABLE II

Physical properties of triphenylsiloxy-metal derivatives

Compound	Nature	m.p.	b.p.	decomp.	reference
$Ti(OSiPh_3)_4$	white solid	ca. 490° (in air)	subl. 390° 0.05 mm	ca. 490° in air	(1)
$Zr(OSiPh_3)_4$	white solid	ca. 450° (in air)	subl. 400°/ 0.05 mm	ca. 450° in air	-
$V^{IV}(OSiPh_3)_4$	pale blue solid	360°	-	sudden at 360°/0.1mm	(46) (63)
$VO(OSiPh_3)_3$	white solid	213°-15°	330°/0.1mm	sudden at 400°in air	(46) (49)
$Al(OSiPh_3)_3$	white solid	193°-5°	300°/0.1mm	350°in air	(5)
$Ta(OSiPh_3)_5$	white solid	410°	410°/0.1mm	410°/0.1mm	-

Note

Temperatures above 300° are approximate.

Decomposition points are visual.

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All compounds except $Zr(OSiPh_3)_4$ and $Ta(OSiPh_3)_5$ have been previously reported and references are given, in two cases however the results obtained in this laboratory do not agree with those in the literature.

$V(OSiPh_3)_4$ has been prepared by the reaction between sodium triphenyl-silanolate and vanadium tetrachloride in benzene. Chamberlain (46) reports it as a pale blue-green solid, insoluble in benzene, with m.p. $264^{o}-8^{o}$; Cohen (63) reports this compound as being soluble in benzene and with m.p. 260°. The method used in this laboratory gives a pale blue solid, insoluble in benzene, with m.p. 360° (decomp.); several repeat preparations gave the same result. The alkoxides and triethylsilanolates of tetravalent vanadium have physical properties very similar to the corresponding titanium deriv-atives (31) (57) and consequently one might expect $V(OSiPh_3)_4$ to have a melting point of about $480^{o}-500^{o}$. A likely impurity in this compound would be $VO(OSiPh_3)_3$ and it may be that small traces drastically lower the observ-ed melting point.

Gibbs et. al. (5) prepared a compound from aluminum chloride and sodium triphenylsilanolate which they claimed was $Al(OSiPh_3)_3$ although their analy-tical data would suggest otherwise; this had a m.p. 485° (sealed tube) and a decomposition temperature in air of about 300°. The analytical data on the compound prepared in this laboratory was correct for $Al(OSiPh_3)_3$ and a fairly sharp melting point of $193-5^{o}$ and a decomposition temperature in air of 350° was obtained.

All compounds except $V(OSiPh_3)_4$ and $Ta(OSiPh_3)_5$ may be volatalized with-out decomposition under high vacuum. The excellant thermal stabilities of $Ti(OSiPh_3)_4$ and $Zr(OSiPh_3)_4$ and the comparatively low ones of $Al(OSiPh_3)_3$ and $V(OSiPh_3)_4$ are of note. $Ta(OSiPh_3)_5$ is probably exceptional, this

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compound distilled at $410°/0.1$ mm with decomposition giving volatile siloxane compounds; an elimination of the following type probably takes place:

$$\geqslant Ta \longrightarrow OSiPh_3 + Ph_3Si \longrightarrow OTa \leqslant \longrightarrow \geqslant Ta - O - Ta \leqslant + Ph_3SiOSiPh_3$$
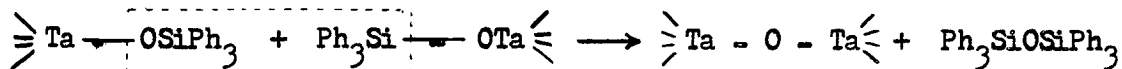
Steric factors must play a prominent part; the presence of five bulky triphenylsiloxy groups around the small tantalum atom (atomic radius 1.34 $\overset{O}{A}$, c.f. Ti, 1.36 $\overset{O}{A}$ and Zr, 1.48 $\overset{O}{A}$) will set up considerable steric strain.

b) (Quinolin-8-oxy)(triphenylsiloxy) derivatives

As with the triphenylsiloxy derivatives no difficulty was encountered in the preparation of these compounds of titanium, zirconium, aluminum and tantalum from the corresponding dialkylamino intermediates and triphenyl-silanol in benzene.
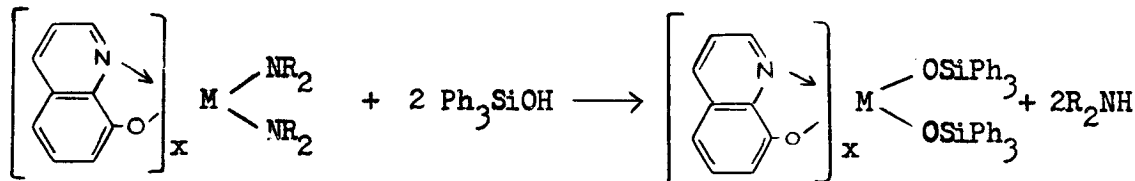
Reaction between V $(NEt_2)_2(OC_9H_6N)_2$ and triphenylsilanol did not how-ever give the expected bis-triphenylsiloxy- derivative; a compound was obtained in moderate yield which had a V/Si ratio of 1.0/0.92 and this perhaps indicates that there is difficulty in substituting both diethylamino groups with the bulky triphenylsiloxy ligands. Here again this is probably due to steric factors, the vanadium atom is considerably smaller than, for example, the titanium atom (atomic radii Ti, 1.36 $\overset{O}{A}$; V, 1.23 $\overset{O}{A}$) and it may be sterically impossible to fit two quinolin-8-oxy and two triphenylsiloxy groups around a vanadium atom. Added evidence for this is presented later in the attempted polymer formation with diphenylsilanediol.

In the absence of a suitable dialkylamino- derivative for the prepara-tion of vanadyl compounds, $VO(OSiPh_3)_2$ (OC_9H_6N) was prepared by a similar

method to that used by Rust (34) for the preparation of $Ti(OSiMe_3)_2(OC_9H_6N)_2$. This involved reaction between 8-hydroxy-quinoline and tris-triphenylsiloxy-vanadate:
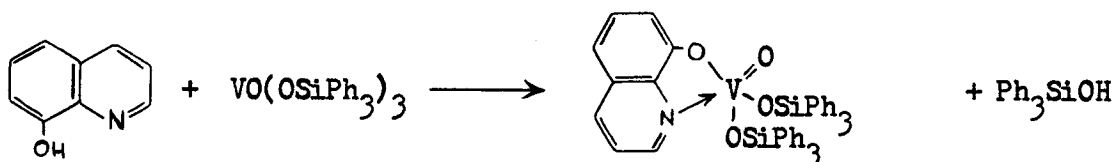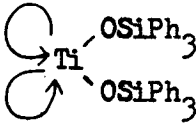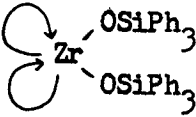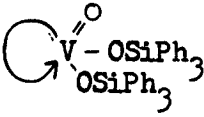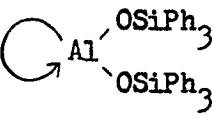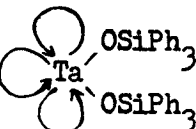
This reaction is irreversible and the triphenylsilanol was removed by crystallization of the product from an ether-benzene mixture.

Al $(OSiPh_3)_2$ (OC_9H_6N) was also prepared from Al $(OSiPh_3)_3$ and 8-hydroxy-quinoline in like manner.

The physical properties of all the derivatives which were prepared are listed in table III.

TABLE III

Physical properties of (quinolin-8-oxy)(triphenylsiloxy) metal derivaties

Compound	Nature	m.p.	b.p.	decomp.
Ti(OSiPh$_3$)$_2$ structure	bright yellow solid	187°-90°	330°/0.05 mm	460° in air
Zr(OSiPh$_3$)$_2$ structure	bright yellow solid	202°-05°	340°/0.05 mm	490° in air
V=O (OSiPh$_3$)$_2$ structure	dark green solid	180°-81°	320°/0.05 mm	330° in air
Al(OSiPh$_3$)$_2$ structure	yellow solid	210°	380°/0.1 mm	380°/0.1 mm
Ta(OSiPh$_3$)$_2$ structure	bright yellow solid	--	-	135°/0.1 mm

Note

Q represents quinolin-8-oxy

Temperature above 300° are approximate

Decomposition points are visual.

Only $Ti(OSiPh_3)_2(OC_9H_6N)_2$ has been reported previously, Breed and Haggerty(33) give m.p. $189°-91°$ for this compound but no volatility or decomposition measurements were carried out.

Once again the excellent thermal stabilities of the titanium and zirconium derivatives should be noted. The low thermal stability of the tantalum compound is no doubt due to steric considerations and the comments made for Ta $(OSiPh_3)_5$ previously will apply equally well in this case, the quinolin-8-oxy ligand appear to exert greater steric strain than the triphenylsiloxy group. Steric factors may also contribute to the comparatively low thermal stability of the vanadyl compound. One might expect the thermal stability of the aluminum compound to be no higher than that of $Al(OSiPh_3)_3$ and this is approximately the case.

c) Other model compounds

Bis-quinolin-8-oxy- bis-triethylsiloxy- metal derivatives of titanium and zirconium were prepared in like manner to the bis-triphenylsiloxy compounds from triethylsilanol and the corresponding bis-dialkylamino metal intermediate:
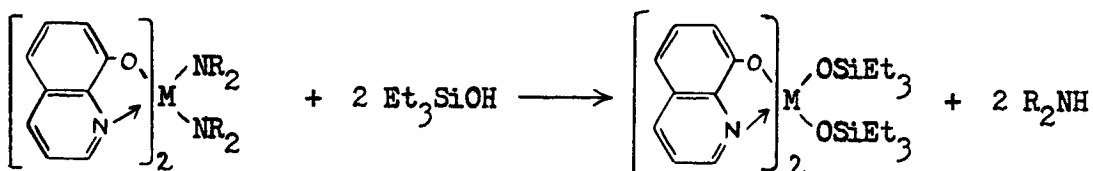
Both products were stable yellow solids which could be distilled under high vacuum without decomposition.

The fully substituted quinolin-8-oxy derivatives of aluminum and zirconium were prepared from the dialkylamino- metal compounds and 8-hydroxy-quinoline.

49
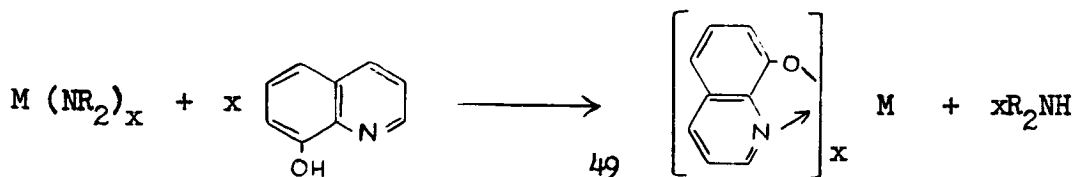
These are of carse examples of compounds in which the covalency maximum of the metal is satisfied by intramolecular co-ordination, and because of this one would expect the stability to be high.

Tetrakis-triethylsiloxy-titanium was prepared from $Ti(NEt_2)_4$ and triethyl-silanol in the usual manner:

$$Ti\ (NEt_2)_4 \ + \ 4\ Et_3SiOH \ \longrightarrow \ Ti\ (OSiEt_3)_4 \ + \ 4\ Et_2NH$$

The trimethylsiloxy analogue could have been prepared in like manner from trimethylsilanol, however an alternative synthetic method was used to test the feasibility of a possible new reaction for the preparation of poly-organometallosiloxanes. In the preparation of these polymers, containing alkyl groups attached to silicon, the standard preparation used in this work will involve the use of dialkylsilanediols; the instability of these reagents may possibly preclude their use, and consequently a possible alternative route to these polymers was sought. This involved the reaction between diacetoxysilanes and bis-dialkylamino-metal intermediates and since it was not known whether these reagents would react together, a model reaction was carried out. It was found that trimethylacetoxysilane reacted with $Ti(NMe_2)_4$ to give $Ti\ (OSiMe_3)_4$ and N:N dimethylacetamide:

$$Ti\ (NMe_2)_4 \ + \ 4\ Me_3SiOAc \ \longrightarrow \ Ti\ (OSiMe_3)_4 \ + \ 4\ Me_2NAc$$
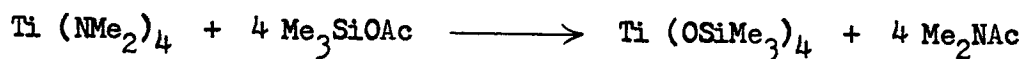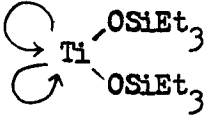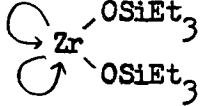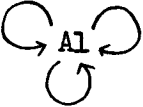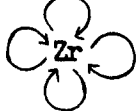
The yield however was only 44% and some solid non-volatile residue remained after distillation of the product from the reaction mixture. In view of the known tendency for trimethylacetoxysilane to cause acetylation as a side reaction to the main one (24), it can be assumed that this residue contained Ti-OAc groups.

This acetylation tendency appears to decrease when diacetates are used, and polymer formation using this method is reported later.

Table IV lists the physical properties of the model compounds described in this section.

TABLE IV

Physical properties of other model compounds

Compound	Nature	m.p.	b.p.	decomp.
$Ti(OSiMe_3)_4$	colourless liquid	-	60°/0.1 mm	230° under N_2
$Ti(OSiEt_3)_4$	colourless liquid	110°	150°/0.1 mm	
(quin)$_2$Ti(OSiEt$_3$)$_2$	yellow solid	133°-5°	240°/0.1 mm	300° in air
(quin)$_2$Zr(OSiEt$_3$)$_2$	yellow solid	139°-41°	240°/0.1 mm	310° in air
(quin)$_3$Al	bright yellow solid	350°	-	350°/0.1 mm
(quin)$_4$Zr	bright yellow solid	420°	subl. 350°/0.05 mm	460° in air

Note
$\frown$ represents quinolin-8-oxy

Temperatures above 300° are approximate.

Decomposition points are visual.

d) Conclusions

Several conclusions can be reached from the results obtained in the preparation of model compounds.

The reaction between triphenylsilanol and bis-dialkylamino- metal inter- mediates was found to proceed smoothly and almost quantitatively in all but one case, and we can therefore conclude that basically these intermediates should be quite suitable for polymer formation. The one exceptional case was that involving the preparation of $V(OSiPh_3)_2$ $(OC_9H_6N)_2$ from $V(NEt_2)_2$ $(OC_9H_6N)_2$ and the lack of complete substitution was attributed to steric factors.

The thermal stability observations on the products, although carried out on a purely qualitative basis, showed trends that might be expected to occur in polymers containing similar groups. The most stable compounds were those of titanium and zirconium; aluminum compounds in all cases were of considerably lower stability. Conclusions regarding tantalum compounds are hampered by steric factors which caused complications, and the same can be said for those of tetravalent vanadium. At the time that vanadyl model compounds were prepared we still lived in hope that a suitable intermediate for polymer formation would be prepared, but due to the failure in this line comments on these compounds are not relevant.

4. Preparation of polymers

a) Poly-trialkyl(aryl)siloxy-metallo-phenylsiloxanes

1. Titanium

The reaction between $Ti(OSiMe_3)_2$ and diphenylsilanediol proceeded at room temperature in ether, and resulted in an apparently hetrogeneous product consisting of a white opaque gel dispersed in a pale yellow liquid. The reaction theoretically should proceed as follows:

$$n Ti(OSiMe_3)_2(NMe_2)_2 + n\ Ph_2Si(OH)_2 \rightarrow \left[\begin{matrix} OSiMe_3 & Ph \\ Ti-O-Si-O- \\ OSiMe_3 & Ph \end{matrix} \right]_n + 2\ n Me_2NH$$
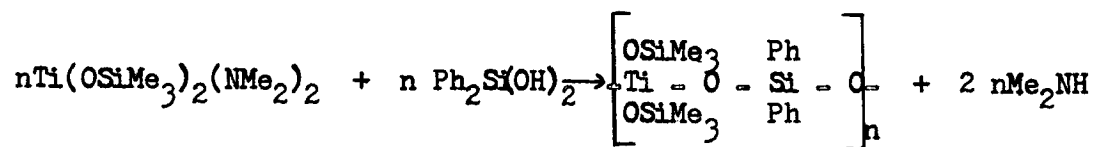
The product was obtained in quantitative yield (no free dimethylamino groups present), was highly water repellant but was soluble in all common organic solvents. Hydrolysis with the liberation of trimethylsilanol occurred in aqueous acetone. On heating under high vacuum a colourless liquid distillate was obtained at 60°-200° and this was shown to be substantially pure $Ti(OSiMe_3)_4$ (b.p. $60^\circ/0.1$ mm). The yield corresponded approximately to 50% based on the total trimethylsiloxy ligands present. The low distillation temperature and properties of the original product would suggest that $Ti(OSiMe_3)_4$ had been formed during the reaction and not during the subsequent heat treatment.

The gummy residue from this first distillation was heated further and an additional quantity of liquid distillate was obtained from 200°-$500^\circ/0.1$ mm and a black apparently decomposed residue remained. This liquid had a Ti/Si atomic ratio of 1.0/7.7 and the infrared spectrum indicated that Si-O-Si, Ti-O-Si, Si-Me and Si-Ph groups were all present; this then probably consisted of a further quantity of $Ti(OSiMe_3)_4$ admixed with a phenylsilicone oil.

The analagous reaction with $Ti(NEt_2)_2(OSiEt_3)_2$ and diphenylsilanediol in benzene produced a viscous liquid in quantitative yield with solubility and hydrolysobility similar to that of the trimethylsiloxy product; the infrared spectrum indicated the presence of Si-O-Si linkages in addition to those expected. On heating to $200°/0.1$ mm, $Ti(OSiEt_3)_4$ (b.p. $150°/0.1$ mm) was distilled off, the yield corresponding to 45% based on total triethylsiloxy ligands present. Here again it is highly likely that this monomer was present in the original product before heating although an additional quantity may have been formed on heating.

The reaction between $Ti(NEt_2)_2(OSiPh_3)_2$ and diphenylsilanediol in benzene produced an insoluble and a soluble product:

$$nTi(OSiPh_3)_2(NEt_2)_2 + nPh_2Si(OH)_2 \longrightarrow \begin{bmatrix} OSiPh_3 & Ph \\ Ti - O - Si - O \\ OSiPh_3 & Ph \end{bmatrix}_n + 2\ nEt_2NH$$
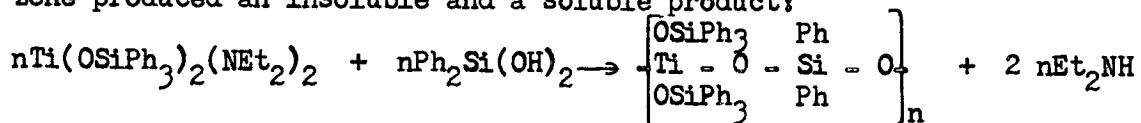
The soluble portion, a pale yellow solid, constituted about 20% of the total product and the infrared spectrum showed bands at 1070 cm^{-1} and 738 cm^{-1} corresponding to Si-O-Si and Ti-O-Ti linkages respectively, and a strong broad band at 915 cm^{-1} corresponding to the Ti-O-Si linkage. The insoluble portion, a white solid, constituted 80% of the product and had an infrared spectrum almost identical to that of the model compound $Ti(OSiPh_3)_4$, no bands were present attributable to either Si-O-Si or Ti-O-Ti linkages. The analytical data on this compound gave a Ti/Si atomic ratio of 1.0/3.2 (theoretical for infinite polymer 1.0/3.0). However on heating under high vacuum to $400°$ for 75 minutes, a small quantity of white sublimate was obtained, which was shown to be $Ti(OSiPh_3)_4$, and analysis of the non-volatile residue indicated it to be the substantially pure infinite chain polymer written above containing only Ti-O-Si linkages. Unfortunately this product was non-fusible and

insoluble in all common organic solvents; it was also very stable chemically and required warm concentrated sulphuric acid for breakdown.

2. Aluminum

Reaction between $Al(OSiMe_3)(NMe_2)_2$ and diphenylsilanediol in benzene gave a light brown solid product in quantitative yield:

$$nAl(OSiMe_3)(NMe_2)_2 \ + \ nPh_2Si(OH)_2 \longrightarrow \left[\begin{array}{c} OSiMe_3 \quad Ph \\ Al - O - Si - O \\ \qquad\quad Ph \end{array} \right]_n \ + \ 2\ nMe_2NH$$
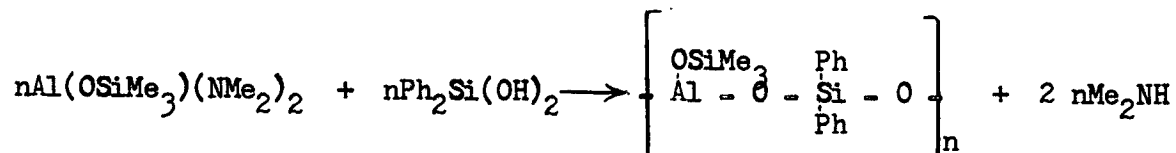
The analytical values for aluminum and silicon were in agreement with the polymer as written above and the infrared spectrum contained all bands corresponding to the groups present. It was not possible to tell whether Si-O-Si linkages were present because the band due to this group is completely hidden by the very strong and broad band due to Al-O-Si at $1053\ cm^{-1}$; however there were no bands present which could be attributed to the Al-O-Al linkage.

The product was highly water-repellent but could be hydrolyzed in dilute HCl to give a clear aqueous solution and an immiscible upper layer (probably hexamethyldisiloxane). It was soluble in acetone, ether and benzene and insoluble in ethanol and hexane.

On heating under high vacuum fusion occurred at 120° and a white sublimate appeared at 180°; this was shown to be substantially $Al(OSiMe_3)_3$, the yield corresponding to approximately 50% based on the available trimethylsiloxy ligands. Further heating gave a few drops of liquid distillate at $320^{\circ}-360^{\circ}$ and left a light brown non-fusible and insoluble residue with a Al/Si ratio of 1.0/1.35 and exhibiting all the properties of a cross-linked oxide-type polymer.

The analagous reaction with $Al(OSiPh_3)(NMe_2)_2$ and diphenylsilanediol gave a hard and brittle light brown solid in quantitative yield and analytically correct for the required linear polymer. The infrared spectrum was almost identical to that of the model compound $Al(OSiPh_3)_3$ but here again any bands due to Si-O-Si linkages would be masked.

The product was again highly water repellent, but could be hydrolyzed in dilute acid or alkali; the solubility data was identical to that of the preceeding polymer.

On heating under high vacuum fusion occurred at 200° and slight gaseous evolution started at 240°. A viscous yellow liquid distilled at $300^{\circ}-400^{\circ}$, which contained no aluminum but infrared and silicon analysis suggested that it was probably hexaphenyldisiloxane. A light brown powdery residue, unfused at 400°, insoluble in organic solvents and with increased aluminum content, remained. This had all the characteristics of a cross-linked oxide-type polymer.

3. Conclusions

The physical properties and thermal stabilities of the compounds described in the preceeding two sections are summarized in tables V and VI.

TABLE V

Nature and thermal stabilities of poly-trialkyl(aryl)siloxy-metallo-

phenylsiloxanes

Compound	Nature	m.p.	Thermal stability
$\begin{bmatrix} OSiMe_3 & Ph \\ Ti-O-Si-O \\ OSiMe_3 & Ph \end{bmatrix}_n$?	white opaque gel in pale yellow liquid	–	$Ti(OSiMe_3)_4$ distills off at $60-200°/0.1$ mm-gummy brown residue decomposes further at $200-500°/0.1$ mm to give liquid with Ti/Si ratio $1.0/7.8$
$\begin{bmatrix} OSiEt_3 & Ph \\ Ti-O-Si-O \\ OSiEt_3 & Ph \end{bmatrix}_n$?	viscous colourless liquid	–	decomp. to $Ti(OSiEt_3)_4$ and viscous liquid residue at $200°/0.1$ mm
$\begin{bmatrix} OSiPh_3 & Ph \\ Ti-O-Si-O \\ OSiPh_3 & Ph \end{bmatrix}_n$ –	white solid	$450°$	Stable at $450°/0.1$ mm
$\begin{bmatrix} OSiMe_3 & Ph \\ Al-O-Si-O \\ & Ph \end{bmatrix}_n$ –	brittle light brown solid	ca $120°$	Solidifies at $180°$ and $Al(OSiMe_3)_3$ sublimes at $180°/0.1$ mm. Fusion again at $320°$ and decomp. to light brown non-fusible solid at $360°$
$\begin{bmatrix} OSiPh_3 & Ph \\ Al-O-Si-O \\ & Ph \end{bmatrix}_n$ –	brittle light brown solid	ca $200°$	phenylsilicone distills off at $300°/0.1$ mm. light brown insoluble & non-fusible residue unchanged to $400°/0.1$ mm

TABLE VI

Solubilities of poly-trialkyl(aryl)siloxy-metallo-phenylsiloxanes

Compound	Water	Dil. HCl	Dil. NaOH	other solvents
$\left[\begin{array}{l}\text{OSiMe}_3\quad\text{Ph}\\ \text{Ti-O}^3\text{-Si-O}\\ \text{OSiMe}_3\quad\text{Ph}\end{array}\right]_n$	hydrol in aqueous acetone	hydrol at room temp.	hydrol on warming	soluble common organic solvents
$\left[\begin{array}{l}\text{OSiEt}_3\quad\text{Ph}\\ \text{Ti-O}^3\text{-Si-O}\\ \text{OSiEt}_3\quad\text{Ph}\end{array}\right]_n$?	hydrol in aqueous acetone	hydrol on warming	hydrol on warming	soluble acetone, benzene and ether slightly sol. hot ethanol insol. hexane
$\left[\begin{array}{l}\text{OSiPh}_3\quad\text{Ph}\\ \text{Ti-O}^3\text{-Si-O}\\ \text{OSiPh}_3\quad\text{Ph}\end{array}\right]_n$	unchanged on boiling	unchanged on boiling	unchanged on boiling	insoluble all common solvents
$\left[\begin{array}{l}\text{OSiMe}_3\quad\text{Ph}\\ \text{Al-O}^3\text{-Si-O}\\ \qquad\qquad\text{Ph}\end{array}\right]_n$	slow hydrol. on boiling	complete hydrol. giving clear sol.	slow hydrol. on heating	soluble acetone, benzene & ether. insoluble ethanol, hexane
$\left[\begin{array}{l}\text{OSiPh}_3\quad\text{Ph}\\ \text{Al-O}^3\text{-Si-O}\\ \qquad\qquad\text{Ph}\end{array}\right]_n$	slow hydrol. on boiling	slow hydrol. on boiling	slow hydrol. on boiling	soluble acetone, benzene & ether slightly sol. hot ethanol- insol. hexane

Note   All compounds were highly water repellent.

One satisfying feature of the reactions described has been the quant-itative yields obtained and the absence of dialkylamino groups (and conse-quently hydroxyl groups) in the products. This means that polymers must have initially been formed as the reaction can take no other course; the stabil-ities of these polymers, except in one case, have however been disappointing.

The rearrangements to low molecular weight compounds that appears to take place are not unique in polymer chemistry. For example the partial hydrolysis products of metal alkoxides and trialkylsilyloxides, which are metalloxane polymers containing -M-O-M-O- linkages with alkoxy or trialkyl-silyloxy ligands attached to the metal atom, also rearrange on heating to give the metal alkoxide or trialkylsilyloxide monomer, which may be distilled off, and a more highly polymerized metalloxane residue (43). The silicone polymers also rearrange under the influence of heat to give volatile cyclic products of low molecular weight.

The silicon and metal atoms in a polyorganometallosiloxane are capable of expanding their covalency to a maximum of six and it is highly likely that the rearrangement mechanism will initially involve such a covalency expansion. This would require co-ordination from oxygen (donor) atoms in one polymer chain to the metal (acceptor) atoms in a neighboring chain, followed by cleav-age of the chain. A suggested mechanism, with aluminum as an example, is as follows:

etc.

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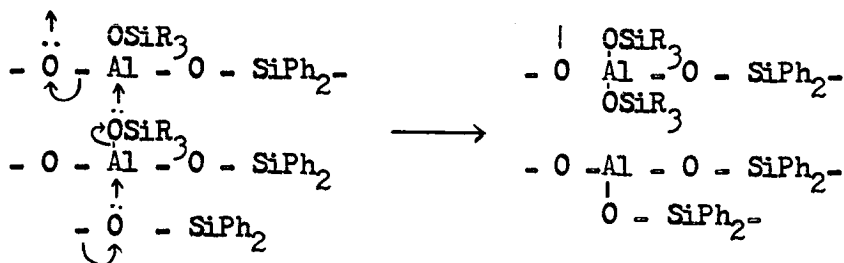
It is immediately apparent from this that steric factors will play an important part and bulky $-OSiR_3$ ligands attached to the metal atom will shield it from covalency expansion and stop rearrangement. This is probably the case with the triphenylsiloxy derivatives; that of titanium is thermally stable to $450°/0.1$ mm whereas that of aluminum decomposes at about $300°/0.1$ mm without giving $Al(OSiPh_3)_3$.

Another point of note is that this mechanism postulates a cross-linked residue and obviously cross-linking provides excellent steric shielding compared to linearity. A stage should then be reached when formation of the monomer $M(OSiR_3)_x$ will stop due to the extent of cross-linking even though $OSiR_3$ ligands are still available for co-ordination. This then explains the experimental fact that only about 50% of the $OSiR_3$ ligands present end up on $M(OSiR_3)_x$.

We need not perhaps discount trialkyl(aryl)siloxy ligands entirely in high temperature resistant polymers, as there seems to be no reason why cross-linked polymers of sufficient cross-linking to prevent rearrangement should not be synthesized from trifunctional derivatives such as $Ti(OSiR_3)(NMe_2)_3$. The high thermal stability of the $M-OSiR_3$ linkage could then be utilized.

If the rearrangement does involve covalency expansion of the metal atom in the chain, as seems highly likely, it is obvious that the use of chelating ligands on the metal atom, which will satisfy covalency expansion by intramolecular co-ordination, should repress rearrangement. Experiments along these lines are described in the next section.

b) Poly-quinolin-8-oxy-metallo-phenylsiloxanes

1. Titanium

The general reaction for the formation of this polymer was as follows:

$$n \ R_2N - Ti - NR_2 + nPh_2Si(OH)_2 \longrightarrow \left[Ti - O - Si - O \right]_n + 2 \ nR_2NH$$

(with quinolin-8-oxy ligands on Ti and Ph groups on Si)
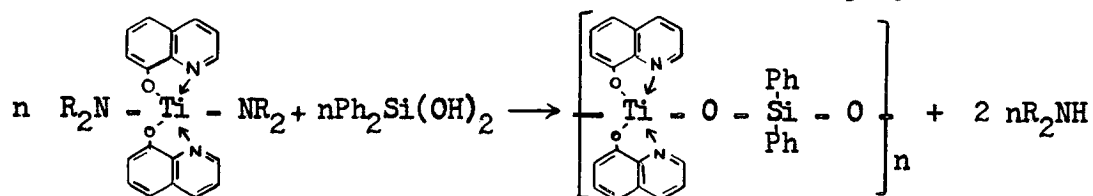
Several sets of reaction conditions were used. Initially the diol was added dry over five minutes to a stirred solution of the intermediate, prepared in situ from 8-hydroxyquinoline and $Ti(NEt_2)_4$, in benzene at room temperature. A clear orange solution resulted but this soon turned yellow and a yellow solid was precipitated. One can assume that a soluble polymer of comparatively low molecular weight was initially formed but this then became insoluble as it polymerized further. Filtration of the solid after one hours reflux gave a fine bright yellow powder in about 90% yield which on analysis had titanium and silicon values lower than theoretical for the infinite chain polymer shown above but with a Ti/Si atomic ratio of 1.0/0.93, also no residual diethylamino groups could be identified. The infrared spectrum was almost identical with that of the model compound $Ti(OC_9H_6N)_2$ $(OSiPh_3)_2$ except that the Ti-O-Si stretching frequency had shifted from 910 cm^{-1} in the model compound to 940 cm^{-1} in the polymer, there was also increased intensity of one of the quinolin bands at 745 cm^{-1} which corresponds to the presence of some Ti-O-Ti linkage, this is confirmed by the low Ti/Si atomic ratio (theoretical 1.0/1.0).

Evaporation of the filtrate from the reaction gave the balance of the product as a yellow solid with Ti/Si ratio of 1.0/1.37 and the infrared spectrum indicated a fairly strong band at 1060 cm^{-1}, corresponding to Si-O-Si

linkage, no enhanced bands at 819 cm^{-1} and 740 cm^{-1}, indicating lack of Ti-O-Ti linkage, and merging of Si-Ph and Ti-O-Si bands to one broad band at 980 cm^{-1}.

The product was highly water repellent, stable in boiling water, boiling dilute HCl and boiling dilute NaOH; it was also insoluble in all common organic solvents except dimethylformamide (D.M.F.) in which it had a high solubility. A hard glossy film could be formed on a spatula by the evaporation of a D.M.F. solution, and this could be flexed several times without cracking; a water repellent film on filter paper could be formed likewise.

On heating under high vacuum no change was observed to $320^{\circ}C$; at this temperature fusion to a deep red liquid occurred and gaseous products were liberated, subsequently only the solvent could be identified in the cold-trap condensate. On cooling a brittle solid breaking up to a yellow powder was obtained; about 10% weight loss was observed and elemental analysis gave individual values for titanium and silicon slightly higher than theoretical with a Ti/Si ratio of 1.0/0.99.

Two major changes had taken place in the infrared spectrum. Moderate absorption in the form of a broad plateau had appeared at 1050-1090 cm^{-1} and the Ti-O-Si stretching frequency at 940 cm^{-1} had merged with the Si-Ph band at 990 cm^{-1} to give one broad band at 980 cm^{-1}; the significance of the latter is not clear but the former indicates the presence of Si-O-Si linkages. This would suggest that some rearrangement or degradation had taken place.

A thermal stability test in air was carried out and on slow heating from 320° upwards decomposition, in the form of gaseous products given off, started slowly at 370°, the product was still liquid however after 30 minutes at 430° and long brittle fibres could be drawn from the melt; this is perhaps

evidence for the linearity of the polymer chain. Complete decomposition to a black solid occurred after 20 minutes at 470°.

Another reaction was carried out in which the total reaction product (soluble and insoluble) was heated to its fusion point(310°) under high vacuum until gaseous evolution ceased; on cooling a brittle solid breaking up to a yellow powder was obtained in quantitative yield which had titanium, silicon, nitrogen, carbon and hydrogen analytical values correct for the linear chain polymer. The infrared spectrum however was identical to that of the fused product from the preceeding reaction ie. Si=O=Si and Ti=O=Ti absorption bands were present.

A sample was reheated under high vacuum. A red distillate solidifying to a dark red solid was collected at 350-380°/0.1 mm over a period of one hour. The yield was about 25% and the analytical data gave a Ti/Si atomic ratio of 1.0/2.97. The infrared spectrum contained strong Si=Ph and quinolin-8-oxy bands, strong Si=O=Si, medium Ti=O=Ti and a weak Ti=O=Si band.

A black decomposed non-volatile residue remained.

The results so far have indicated that a small amount of rearrangement appears to take place during the reaction and also in the subsequent heat treatment of the insoluble portion of the product. One possible, but unlikely, alternative explanation for the results obtained on the unheated product is that the free amine liberated during the reaction, being basic, causes self-condensation of the silanediol forming Si=O=Si linkages; this condensation liberates water which then causes hydrolysis of the titanium intermediate forming Ti=O=Ti linkages.

Reaction conditions were then modified to test this hypothesis. $Ti(NMe_2)_2$ $(OC_9H_6N)_2$ was used as the titanium intermediate in order that the liberated

dimethylamine, which is a gas, could easily be removed from the system; this intermediate was prepared in the usual way from $Ti(NMe_2)_4$ and 8-hydroxyquinoline in benzene and the solution was then refluxed to remove the liberated amine; after cooling to room temperature, the diol in T.H.F. solution was then added dropwise over a period of about one hour to the vigorously stirred solution of the intermediate. By this means the concentrations of free amine and diol were kept to a minimum. The results obtained by this method were however very similar to those obtained previously. An insoluble portion constituting 80% of the total yield was filtered off and had properties, analysis and infrared spectrum almost identical to those of the insoluble portion examined earlier; the soluble portion was also similar to its predecessor, ie. had a Ti/Si ratio of 1.0/1.39 and the presence of Si-O-Si linkages was confirmed by the infrared spectrum.

On heating the insoluble portion under high vacuum, fusion did not occur until 350° and gaseous evalution ceased after 20 minutes at this temperature. On cooling, the physical properties, analytical data and infrared spectrum remained identical with the corresponding product obtained by the other method. However this product was found to be almost completely soluble in T.H.F. and consequently an extraction with this solvent was carried out. About 6% was found to be insoluble, and its infrared spectrum showed the presence of strong Ti-O-Ti bands at 730 cm^{-1} and 820 cm^{-1} but very weak Ti-O-Si absorption at 940 cm^{-1}. On reheating the soluble portion under high vacuum the fusion temperature had dropped to 200°, but the analytical values for titanium and silicon were correct for the infinite chain polymer. A schematic summary of these reactions is presented in table VII.

TABLE VII

Poly-bis-(quinolin-8-oxy)-titanophenylsiloxane reaction summary

$$Ti(OC_9H_6N)_2 (NR_2)_2 + Ph_2Si(OH)_2$$

soluble (20%)   insoluble (80%)

orange-yellow solid   bright yellow solid

Ti/Si :: 1.0/1.39   Ti/Si :: 1.0/0.95

Ti-O-Si and Si-O-Si   Ti-O-Si and Ti-O-Ti

         hydrolytically stable, soluble

————   D.M.F. insoluble other solvents

         | heat under vacuum

total reaction product   to 350°

heated to 310°/0.1 mm

         orange-yellow solid m.p. 350°.

         Ti/Si :: 1.0/0.95. Ti-O-Si,

         Ti-O-Ti and Si-O-Si present.

orange-brown solid m.p. 310°   Soluble T.H.F.

Ti/Si :: 1.0/0.99

Ti-O-Si, Si-O-Si and Ti-O-Ti.

hydrolytically stable. soluble   heat in air

D.M.F. insoluble other organic

solvents   m.p. 310°, decomp. starts at 370°,

         | heat under vacuum   brittle fibres drawn from melt,

red distillate from 350°-380°/0.1 mm   complete decomp. to black residue

solidifying to red solid (25% of total)   after 20 minutes at 470°.

Ti/Si :: 1.0/2.97

Si-O-Si, Ti-O-Si and Ti-O-Ti present.

black decomposed residue

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A logical explanation can be put forward for these results. There seems no reason to doubt that the insoluble portion is polymeric and of fairly high molecular weight; the possibility of its being cyclic and of low molecular weight can probably be discounted because of steric considerations. At a temperature of about $350°$ however (fusion point) rearrangement to volatile and soluble low molecular weight compounds takes place; there also seems to be a tendency to rearrange in solution, hence during synthesis some soluble product is formed. It is noteworthy that in the reaction in which the diol was added quickly and the polymer precipitated quickly, only 10% of the product remained soluble, however when the diol was added slowly and the polymer only precipitated after some time, about 20% of the product remained soluble.

The rearrangement products were not identified, but it was evident that Si-O-Si and Ti-O-Ti linkages were being formed.

2. Zirconium

The analagous reaction between bis-dialkylamino-bis-quinolin-8-oxy-zirconium intermediates and diphenylsilanediol was studied:

$$n\ R_2N - Zr - NR_2 + n\ Ph_2Si(OH)_2 \longrightarrow \left[Zr - O - Si - O \right]_n + 2\ nR_2NH$$
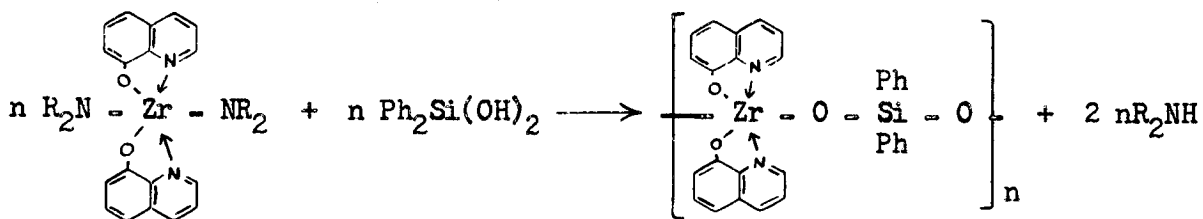
Two reaction procedures were used. In the first the intermediate, $Zr\ (OC_9H_6N)_2\ (NEt_2)_2$, was prepared in situ from $Zr\ (NEt_2)_4$ and 8-hydroxy-quinoline in benzene and the diphenylsilanediol then added as a solid over 10 minutes. A bright yellow precipitate formed, and after refluxing the mixture for several hours, the solvent was evaporated and the residue heated to its fusion point $(320°)$ under high vacuum until gaseous evolution ceased. On cooling a yellow-brown solid was obtained in about 90% yield, which had a

Zr/Si atomic ratio of 1.0/0.98 with the individual values slightly higher than the theoretical for the chain polymer. The infrared spectrum contained all the bands that were present in the model compound $Zr(OC_9H_6N)_2(OSiPh_3)_2$, but had in addition medium absorption at 1065-1090 cm^{-1}, which can be attributed to the presence of Si-O-Si linkages, and enhanced absorption at 735 cm^{-1}, which can be attributed to the presence of Zr-O-Zr linkage. In contrast to the heated titanium analogue however the strong Zr-O-Si and Si-Ph bands at 940 cm^{-1} and 980 cm^{-1} respectively were resolved.

The product was highly water repellent and unaffected during 5 minutes boiling in water, dilute HCl and dilute NaOH solutions. It was slightly soluble in benzene, acetone, ether and ethanol but insoluble in hexane. Complete solubility in D.M.F. was observed, and a glossy hard film could be formed on a spatula by evaporation of a D.M.F. solution; a similar film could be formed on a spatula by fusion.

On heating a sample in air, fusion occurred at 330° and the first signs of decomposition (gaseous evolution) at 370°. Over a period of one hour at 390°-400° the deep red liquid became more viscous and samples removed at intervals solidified to a brittle solid, brittle fibres could be drawn from the melt. Complete decomposition to a black solid residue occurred after a further 1½ hours at 390°-400°.

On heating another sample under high vacuum, fusion occurred at 330° and a trace of yellow distillate appeared at 370°. Heating was continued over a period of two hours while the temperature was slowly raised to 500°. At this stage a few drops of liquid distillate had been collected and a black non-volatile residue remained; the sample weight loss was 30%. The infrared spectrum of the distillate showed strong Si-Ph and Si-O-Si bands and moderate

quinolin-8-oxy bands; there was complete absence of any bands attributable to Zr-O-Si. The spectrum of the residue showed a corresponding reduction in Si-Ph absorption but strong Zr-O-Si and Zr-O-Zr absorption.

The second procedure involved the slow addition of the diol in T.H.F. solution to the vigorously stirred intermediate $Zr(NMe_2)_2 (OC_9H_6N)_2$ in T.H.F. solution at room temperature. The dimethylamine liberated during the formation of the intermediate had been removed by refluxing prior to the addition. A bright yellow precipitate formed just before the end of this addition, and after several hours reflux this was removed by filtration. The latter constituted about 20% of the product and elemental analysis and the infrared spectrum indicated it to be substantially pure $Zr (OC_9H_6N)_4$; this contained about 44% of the total quinolin-8-oxy-ligand present.

Evaporation of the filtrate gave the balance of the product as a yellow solid; this had a Zr/Si atomic ratio of 1.0/1.24 and the infrared spectrum showed the presence of Si-O-Si linkage (1040 cm^{-1}), strong and resolved Zr-O-Si linkage (940 cm^{-1}) and no enhancement of absorption at 735 cm^{-1} indicating the absence of Zr-O-Zr linkage.

This product was heated to its fusion point ($340°$) at 0.1 mm pressure for one hour; a slight weight loss was observed with corresponding change in the individual analytical values for zirconium and silicon (ratio 1.0/1.30), the infrared spectrum was unchanged. The compound was hydrolytically stable, soluble in benzene, acetone, T.H.F. and D.M.F. but insoluble in pet. ether, ether, hexane and ethanol. Hard glossy films could be formed by evaporation of a solution.

A sample of this product was reheated under high vacuum and an almost identical result was obtained to that found previously, ie. a small amount of

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yellow distillate, containing no zirconium, was collected from 380° upwards and a black non-volatile residue remained. A schematic summary of these reactions is presented in table VIII.

TABLE VIII

Poly-bis-(quinolin-8-oxy)-zirconophenylsiloxane reaction summary

$$Zr (NMe_2)_2(OC_9H_6N)_2 + Ph_2Si(OH)_2$$

insoluble (20%)   soluble (80%)

yellow solid   yellow solid

substantially $Zr(OC_9H_6N)_4$ Zr/Si :: 1.0/1.24

                                                                       Si-O-Si and Zr-O-Si; no Zr-O-Zr.

total reaction product
heated to 320°/0.1 mm   heat to 340°/0.1 mm

yellow-brown solid, m.p. 320°.   yellow-brown solid m.p. 340°

Zr/Si :: 1.0/0.98   Zr/Si :: 1.0/1.24; hydrolytically

Zr-O-Si, some Si-O-Si and Zr-O-Zr.   stable; soluble benzene, acetone,

hydrolytically stable; soluble D.M.F.   T.H.F. and D.M.F.; insoluble pet.

sparingly soluble benzene, acetone,   ether, hexane, ether and ethanol.

ether and ethanol.

insoluble pet. ether, hexane

                                                                       heat above 340°

heat in air

m.p. 320°; decomp. starts 370°,   yellow distillate, b.p. 370-500°/0.1mm

brittle fibres drawn from melt.   contains no zirconium; Si-O-Si and

black solid residue after 1½ hours   Si-Ph only present.

at 400°.   black residue, 30% weight loss, Zr-O-Si

                                                                       and Zr-O-Zr.

The results obtained here with zirconium are somewhat different than those obtained for titanium. In these compounds the maximum covalency of zirconium, being eight, is not satisfied by intramolecular co-ordination from the quinolin-8-oxy ligands, consequently we have in effect the same situation that is present with the polymers of titanium and aluminum containing trialkylsiloxy ligands. Rearrangement to the fully substituted tetra-ligand derivative takes place, and the mechanism in this case is no doubt similar to that proposed for the other system. The larger size of the zirconium atom (atomic radii : Zr, 1.48 Å Ti, 1.36 Å, Al, 1.26 Å) no doubt eliminates any steric difficulties that might arise from protection by the bulky quinolin-8-oxy groups.

The thermal stability of the soluble product which is no doubt cross-linked, is comparable to that of the titanium analogue, which is probably linear. It is noteworthy that the zirconium compound gives only volatile silicone decomposition products, whereas with titanium volatile titanium decomposition products are obtained.

3. Aluminum

The analagous reaction between bis-dimethylamino-mono-quinolin-8-oxy-aluminum and diphenylsilanediol should proceed as follows:

$$+ \ 2 \ n \ Me_2NH$$

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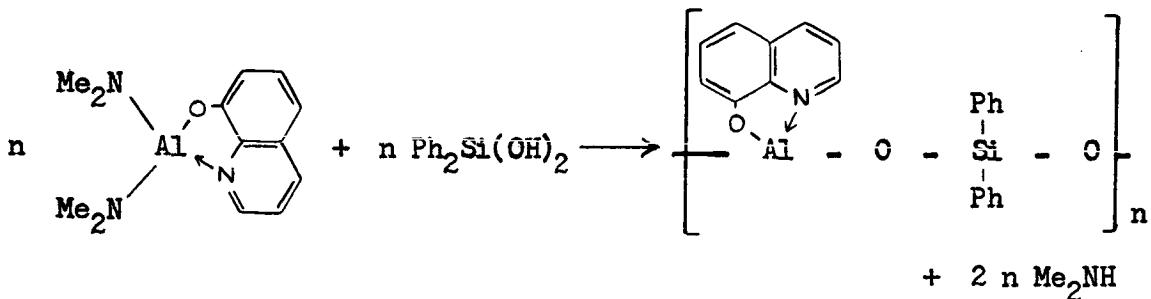
In this reaction too, two reaction procedures were carried out. In the first the diol was added as a solid over 10 minutes, resulting in the almost immediate precipitation of a yellow solid. After refluxing the mixture for several hours the solvent was removed and the total product heated to 320° under high vacuum; fusion did not take place and a bright yellow solid was obtained in quantitative yield and with metal and silicon analysis correct for the polymer written above. The presence or absence of Si-O-Si linkages could not be determined from the infrared spectrum because the very strong Al-O-Si absorption band at 1050 cm^{-1} masks all other absorption in this region; however there was increased absorption at 745 cm^{-1} which suggested the presence of Al-O-Al linkages.

The product was hydrolytically stable, sparingly soluble in acetone, benzene and D.M.F. and insoluble in hexane, ether and ethanol. On heating in air a slow colour change to brown occurred at 330°, and fusion with total decomposition occurred at 390°. This is in contrast to the titanium and zirconium analogues which fused without apparent decomposition about 320° and decomposed about 370°. The lower organic content of the aluminum polymer no doubt contributed to the higher melting point but one might expect this also to raise the decomposition temperature. However the thermal stability of the Al-O-Si and Al-quinolin-8-oxy bonds appears to be lower than the corresponding titanium and zirconium ones (cf. the stabilities of the corresponding model compounds $M(OSiPh_3)_2$ $(OC_9H_6N)_x$ and this obviously compensates this increase.

The second reaction procedure was that used previously with titanium and zirconium and involved the dropwise addition of the diol in T.H.F. solution at room temperature to the solution of the intermediate, which had previously

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been refluxed to remove dimethylamine. Soluble and insoluble products were again formed; the latter, a bright yellow solid, was shown on analysis to contain no silicon and appeared to be substantially $Al (OC_9H_6N)_3$ contaminated with $\{ Al (OC_9H_6N)-O\}_n$ and the infrared spectrum confirmed this. The soluble portion, also a yellow solid, had an Al/Si atomic ratio of 1.0/1.43; the infrared spectrum showed a strong broad band at 1055 cm^{-1} due to Al-O-Si linkages which of course masked any Si-O-Si that is probably present, there was no indication of any Al-O-Al bands causing increased absorption in the 740 cm^{-1} region.

On heating the soluble portion under high vacuum no change was observed to 245° at which temperature fusion occurred. A yellow-brown liquid, soon solidifying, started to distil at 280° and continued slowly as the temperature was raised to 400° over $1\frac{1}{2}$ hours; a black decomposed residue remained. The distillate constituted about 50% of the total starting weight and on analysis was found to have a Al/Si ratio of 1.0/2.51.

A schemic summary of the aluminum reactions is presented in table IX.

TABLE IX

Poly-quinolin-8-oxy-alimino-phenylsiloxane reaction summary.

$$Al\ (OC_9H_6N)\ (NMe_2)_2\quad +\quad Ph_2Si(OH)_2$$

insoluble (31%)   soluble (69%)

bright yellow solid   yellow solid

$Al(OC_9H_6N)_3 + (Al(OC_9H_6N)-O)_n$ Al/Si :: 1.0/1.43.

<u></u>   heat under vacuum

                                                                  m.p. 245°

total reaction product   yellow-brown distillate

heated to 320°   from 280°-400°/0.1 mm

                                                                  Al/Si :: 1.0/2.51

                                                                  black decomp. residue.

bright yellow solid m.p. >320°

Al/Si :: 1.0/1.02.

hydrolytically stable,sparingly

soluble acetone, benzene & D.M.F.

insoluble hexane, pet. ether, ether

& ethanol

heat in air

Slow colour change to brown 330°

fusion with total decomp. at 390°.

These results are somewhat similar to those obtained for zirconium which is perhaps not unexpected as aluminum in these compounds does not have its covalency maximum satisfied by intramolecular co-ordination and therefore is prone to rearrangement.

The thermal stability of the soluble portion again confirms the apparent lower stability of aluminum compounds compared to the titanium and zirconium analogues.

4. Vanadium

The proposed reaction between V^{IV} $(OC_9H_6N)_2$ $(NMe_2)_2$ and diphenylsilane-diol was as follows:
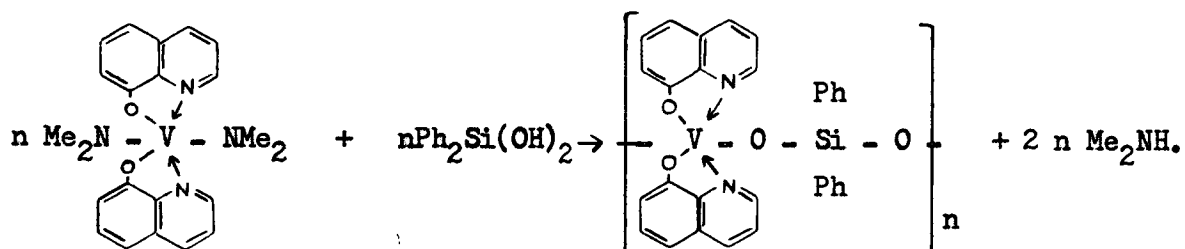
The procedure involving the dropwise addition of the diol in T.H.F. solution to the intermediate was used for this reaction, and after refluxing the mixture for several hours, two products of approximately equal weight were obtained, an insoluble dark green solid and a soluble green brown solid. The former contained no silicon and the analysis and infrared spectrum indicated it to be a quinolin-8-oxy-vanadoxane compound, whereas the latter had a V/Si atomic ratio of 1.0/2.33 and the infrared spectrum indicated the presence of V-O-Si, Si-O-Si, Si-Ph and quinolin-8-oxy bands, but no V-O-V bands.

On heating the precipitated solid under high vacuum it was found to distil at its melting point (380°) at 0.1 mm pressure without appreciable decomposition. The infrared spectrum was identical to that of the unheated

product. This would indicate that the compound was of comparatively low molecular weight and suggested structures are shown below:
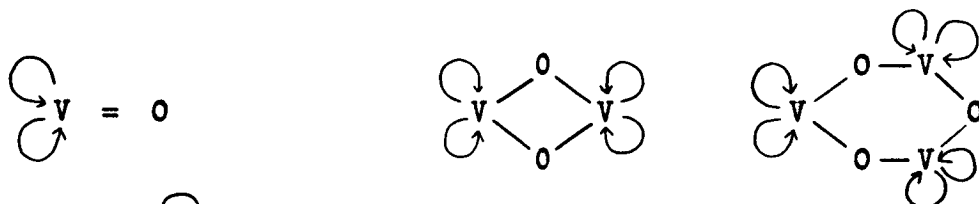
Where Q represents the quinolin-8-oxy-group. The soluble portion was heated under high vacuum. Fusion occurred at 160° and a small quantity of dark green liquid started to distill from $215^\circ/0.1$ mm upwards. The temperature was slowly raised to 400° over a period of two hours at which stage a black non-volatile residue remained and the distillation was complete. The distillate had solidified to a dark green solid and constituted about 9% of the total weight at the start; analysis indicated a V/Si ratio of 1.0/11.9 and the infrared spectrum contained strong bands attributable to Si-O-Si and Si-Ph linkages and a very weak V-O-Si band.

A black non-volatile and apparently decomposed residue remained which was not examined; the weight loss was 24%.

The reaction is presented schematically in table X.

TABLE X

Poly-bis-(quinolin-8-oxy-)vanado-phenylsiloxane reaction summary

$$V(OC_9H_6N)_2(NMe_2)_2 \quad + \quad Ph_2Si(OH)_2$$

insoluble (60%)   soluble (40%)

insoluble (60%)	soluble (40%)
dark green solid	green brown solid
$\{ V(OC_9H_6N)_2 - O \}_n$	V/Si :: 1.0/2.33
	V-O-Si and Si-O-Si
heat under vacuum.	heat under vacuum.
dark green solid	
m.p. 380°, b.p. 380°/0.1 mm	
distills substantially	m.p. 160°
unchanged.	small quantity of dark green
	distillate 215°-400°/0.1 mm.
	V/Si :: 1.0/11.9. Strong
	Si-O-Si; black decomp. residue
	(24% wt. loss).

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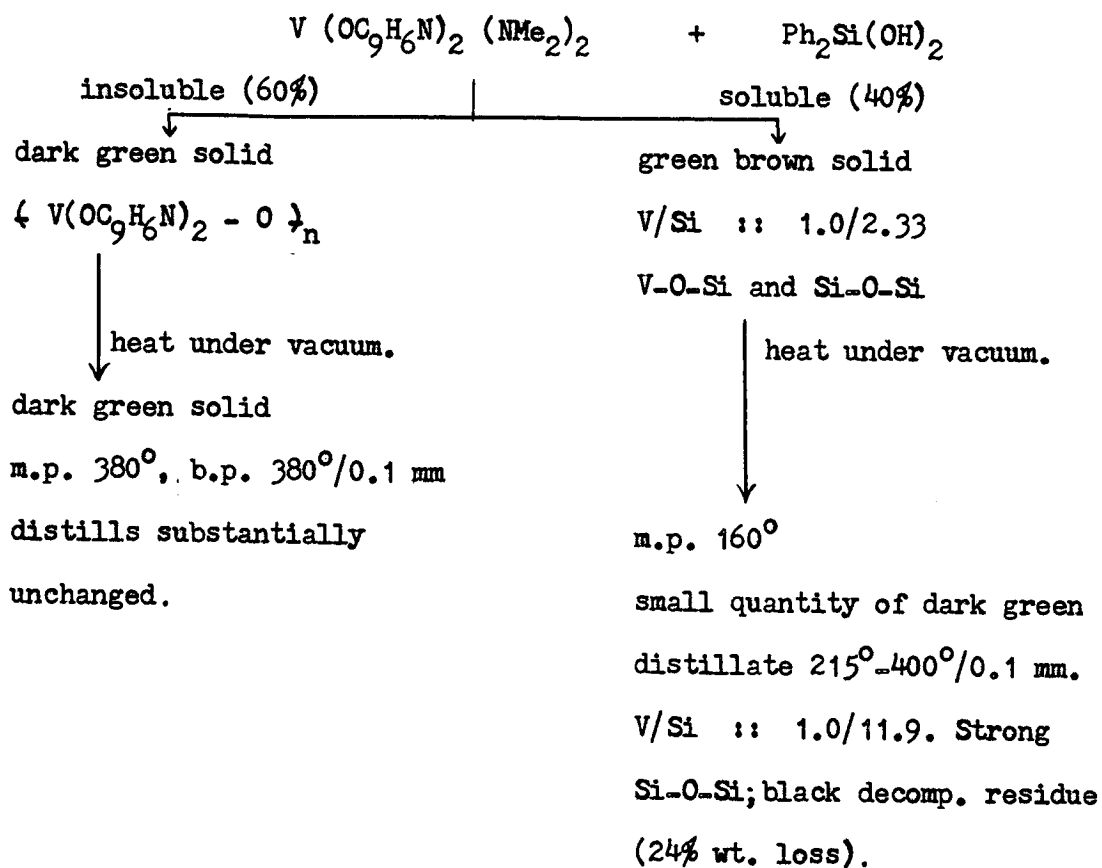
One might have expected the results obtained from this reaction to be similar to those obtained from the analagous reaction with titanium in view of the chemical similarity between titanium and tetravalent vanadium. However we have already seen that the small size of the vanadium atom reduces the reactivity of the intermediate and complete substitution of dimethylamino-groups by triphenylsilanol does not take place. Assuming similar steric factors are present in the polymerization reaction, the incompleteness of the latter will allow time for by-product formation. There is a possibility that self-condensation of the diol takes place during the reflux period giving water; the resulting hydrolysis of the vanadium intermediate then explains the formation of the insoluble vanadoxane during the reaction.

5. Tantalum

The proposed reaction between the tris-quinolin-8-oxy-tantalum dimethyl-amino intermediate and diphenylsilanediol was as follows:

$$
n \ \overset{NMe_2}{Ta} - \underset{Me}{\overset{|}{N}} - \overset{Me_2N}{Ta} \ + \ 2 \ n \ Ph_2Si(OH)_2 \longrightarrow \left[\overset{Ph}{\underset{Ph}{Ta - O - Si - O}} \right]_{2n}
$$

$$
+ \ 2 \ n \ Me_2NH \ + \ n \ MeNH_2.
$$
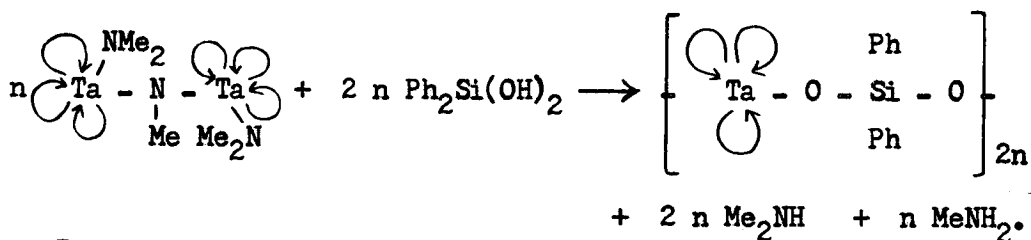
Where ⬡ represents quinolin-8-oxy.

The slow addition of the diol procedure was used in this case. Reaction appeared to be very slow and the mixture was refluxed for five hours and left over a weekend at room temperature. Soluble and insoluble products were again obtained and filtration of the reaction mixture gave a yellow solid, which on analysis contained no silicon and with a tantalum value correct for tris-(quinolin-8-oxy) - tantaloxane $\{Ta \ (OC_9H_6N)_3 - O \}_n$; the infrared spectrum confirmed this. This constituted about 29% of the total product,

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and contained about 37% of the total quinolin-8-oxy ligand present in the system.

The soluble portion making up the balance of the product was a brown solid with a Ta/Si ratio of 1.0/2.61. The infrared spectrum showed the presence of Ta-O-Si and Si-O-Si bands but no Ta-O-Ta bands.

On heating the precipitate under high vacuum, no change was observed to 340°. At this temperature a small amount of 8-hydroxyquinoline distilled off; on raising the temperature to 360° fairly rapid decomposition to a black non-volatile residue took place and no further 8-hydroxyquinoline was liberated. The residue was not examined, but consisted no doubt of a cross-linked tantaloxane admixed with charred decomposition products of the quinolin-8-oxy ligand.

On heating the soluble portion under high vacuum, 8-hydroxyquinoline started slowly to distill off at 70° and this became rapid at 115°. The yield obtained corresponded to 60% of the total amount of ligand present in the original sample.

The nature of this decomposition is of interest. We have seen that the thermal decomposition of the tantalum- (quinolin-8-oxy) bond in a tantaloxane does not give 8-hydroxyquinoline and so in this case a proton must be abstracted from the phenyl groups in the compound, as this is the only other source of hydrogen present. This would seem rather unlikely in view of the low temperature involved but there seems to be no other possible explanation.

A schematic summary of this whole synthesis is presented in table XI.

TABLE XI

Poly-tris-(quinolin-8-oxy)-tantalophenylsiloxane reaction summary.

$$\text{Ta }(OC_9H_6N)_3 (NMe_2)_2 \text{ (?)} \quad + \quad Ph_2Si(OH)_2$$

insoluble (29%) | soluble (71%)

yellow solid   brown solid

substantially $\langle$ Ta $(OC_9H_6N)_3-O\rangle_n$ Ta/Si :: 1.0/2.61

heat under vacuum   heat under vacuum

8-hydroxyquinoline off at 340°   8-hydroxyquinoline off from

(trace only) fairly rapid decomp-   70°-115°/0.1 mm in quantity

osition to black non-volatile residue   corresponding to 60% of total

at 360°/0.1 mm.   present. Dark brown residue.
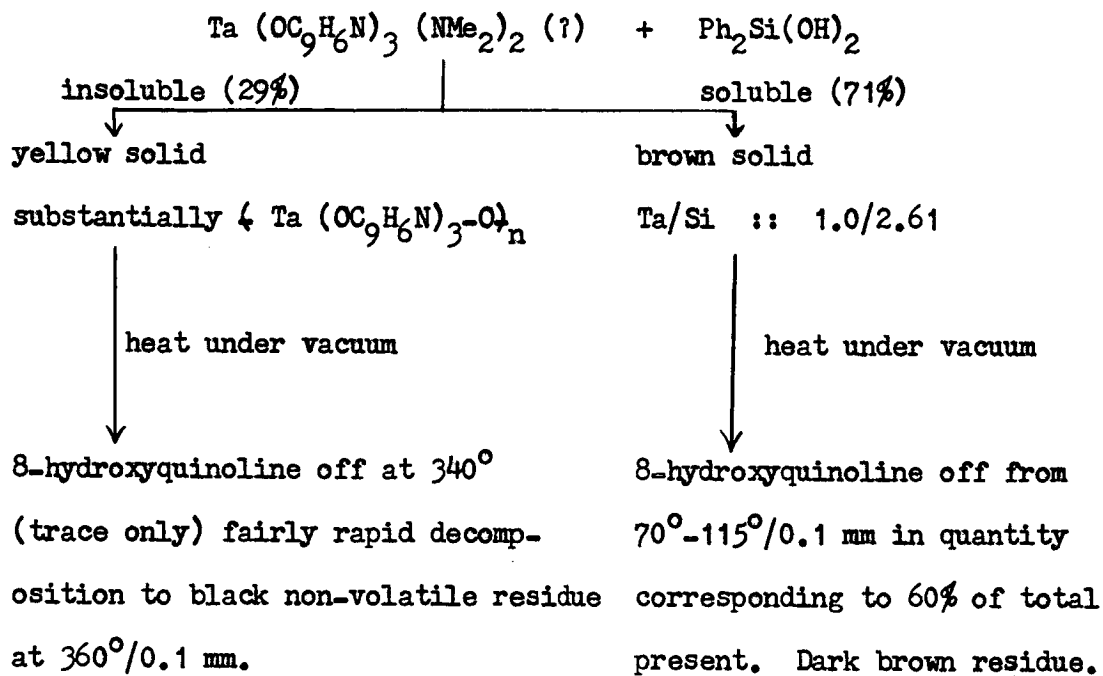
In view of these results it is apparent that three quinolin-8-oxy ligands'
around the tantalum atom exert considerable steric hindrance to reactivity and
also result in low thermal stability. The results are in accord with those
obtained in the preparation of the model compound $Ta(OSiPh_3)_2 (OC_9H_6N)_3$.

The slowness of the reaction between the tantalum intermediate and the
diol allows considerable time for any side reactions to develop. The mech-
anisms for the formation of the two products (soluble & insoluble) are not
clear; it is unlikely that they are similar to those observed in the corr-
esponding reactions with aluminum and zirconium as one would expect the
reaction with tantalum to proceed in much the same way as that with titan-
ium because the covalency expansion of both these metals to the maximum is
satisfied by intramolecular co-ordination in each case. As the tantalum
atom is about the same size as the titanium atom (atomic radii: Ta, 1.34 Å
Ti, 1.36 Å) one can only attribute the difference to steric factors.

6. Conclusions

The results obtained with the quinolin-8-oxy ligands have been dis-
appointing. Only with titanium was the required product containing the
alternating -M-O-Si-O- backbone chain obtained. The failures with vanadium
and tantalum were attributed to steric factors and those with aluminum and
zirconium to incomplete saturation of the covalency expansion of the metal
atoms by intramolecular co-ordination leading to rearrangement at low temp-
eratures.

The thermal stabilities of the titanium polymer, presumably linear, and
the zirconium soluble polymer, presumably cross-linked, were comparable and
reasonably good. Those of the aluminum, vanadium and tantalum soluble poly-
mers were rather low; these results were in agreement with the relative

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stabilities of the corresponding model compounds.

It would appear that any future work should be limited to the use of bidentate ligands on titanium and tridentate ligands on zirconium. The chances of success with the other elements seem to be slight.

c) Poly-bis-(quinolin-8-oxy)- titano- alkylsiloxanes

For the preparation of poly-organometallosiloxanes containing alkyl groups attached to silicon, the normal synthetic procedure used throughout this contract will involve the use of dialkylsilanediols. In view of the instability of the latter reagents, a possible alternative synthetic route to these polymers was sought. It was found, and was reported earlier, that the reaction between trimethylacetoxysilane and $Ti(NMe_2)_4$ gave $Ti(OSiMe_3)_4$. A preliminary reaction was therefore carried out between dimethyldiacetoxy-silane and $Ti(NMe_2)_2 (OC_9H_6N)_2$ in T.H.F. and theoretically this should give a linear polymer:

$$n\ Me_2Si\ (OAc)_2\ +\ n\ Me_2N - Ti - NMe_2 \rightarrow \left[Ti - O - Si - O \right]_n\ +\ 2nMe_2NAc$$
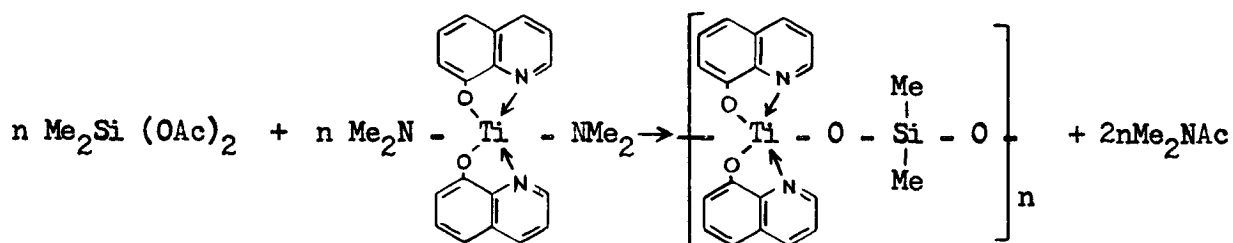
After refluxing the reaction mixture for several hours, soluble and insoluble products were obtained. The insoluble portion removed by filtration, constituted about 5% of the total yield, and the infrared spectrum showed that it was substantially a quinolin-8-oxy-titanoxane and contained very little silicon.

The soluble portion constituting the balance of the product was an orange solid product which had a Ti/Si atomic ratio of 1.0/0.98 with the individual values slightly lower than theoretical for the chain polymer written above. The infrared spectrum contained a broad Ti-O-Si band at 920 cm^{-1}-970 cm^{-1}, a weak Si-O-Si band at 1045 cm^{-1} and weak bands in the 1600 cm^{-1} region which could be attributed to acetate. There was no evidence for the presence of Ti-O-Ti linkage.

This was heated to its fusion point (190°) under high vacuum for two hours, a brittle reddish-brown solid was obtained on cooling and about 8% weight loss was observed. The analytical value for titanium and silicon approximated to the theoretical for the polymer and the atomic ratio Ti/Si was 1.0/0.96. The infrared spectrum was basically unchanged, a sharper Ti-O-Si band was present as well as bands attributable to acetate and there was a slight increase in Si-O-Si absorption.

This product was soluble in benzene and D.M.F., sparingly soluble in acetone, ethanol and T.H.F. and insoluble in ether, hexane and pet. ether. It was highly water repellent but slight hydrolysis occurred on boiling in dilute HCl. Films could be formed by evaporation of a D.M.F. or benzene solution.

These results were quite promising and obviously this reaction bears further investigation. This will be carried out if the contract is renewed.

A preliminary reaction was also carried out involving diethylsilanediol and $Ti(OC_9H_6N)_2(NMe_2)_2$:

$$n\ Et_2Si(OH)_2 + n\ Me_2N - Ti - NMe_2 \rightarrow \left[Ti - O - Si(Et)(Et) - O \right]_n + 2\ nMe_2NH$$
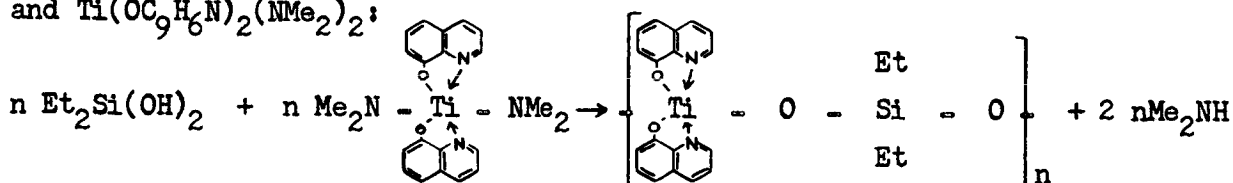
Because of the ease of self-condensation of the diol, under the influence of heat or possibly dimethylamine, giving water, reaction conditions were carefully controlled. The free amine was boiled from the solution after the preparation of the intermediate, and the diol was then added dropwise in ether solution to the vigorously stirred solution of the intermediate cooled to 0°. A yellow precipitate formed and this was filtered off after the mixture had been refluxed for several hours; this constituted 69% of the product and analysis indicated it had a Ti/Si atomic ratio of 1.0/0.61. The

infrared spectrum was similar to that of the model compound $Ti(OSiEt_3)_2$ $(OC_9H_6N)_2$ but contained in addition enhanced absorption at 740 cm^{-1} and 820 cm^{-1} attributable to Ti-O-Ti linkage. There was no evidence of Si-O-Si absorption in the 1000-1100 cm^{-1} region.

The yellow soluble portion made up the balance of the product and had a Ti/Si atomic ratio of 1.0/2.16. The infrared spectrum was also similar to that of the model compound but contained in addition strong Si-O-Si absorption at 1050-1085 cm^{-1}; in this case there was no evidence for the presence of Ti-O-Ti linkage.

On heating the precipitate under high vacuum no change was observed to 250°. At this temperature a trace of yellow distillate appeared, but not until 380° did an appreciable quantity distill; the temperature was slowly raised to 460° by which time distillation had stopped and a brown solid residue remained, this residue did not melt at any time during the heating process. The residue was found to contain no silicon and the analysis approximated to a titanoxane of the following type $\{ Ti (OC_9H_6N)_2-O\}_n$; the infrared spectrum confirmed this. The distillate of course had very much increased silicone content (Ti/Si ratio 1.0/1.90) and the infrared spectrum showed the presence of Si-O-Si, Ti-O-Si and Ti-O-Ti bands.

A logical explanation for these results is that, in spite of the precautions taken during the reaction, self-condensation of the diol is taking place. Siloxane linkages are then formed during this condensation and the water liberated is hydrolyzing the titanium intermediate giving rise to titanoxane linkages. This combination of homo- and co-polymerization will then give rise to a variety of polymer structures; these are arbitrarily separated by solubility into an insoluble fraction containing Ti-O-Si and

Ti-O-Ti linkages only, and a soluble fraction containing Ti-O-Si and Si-O-Si linkages only.

In view of this the polymerization reaction involving diacetoxysilanes would seem to be the most promising line of study for the synthesis of poly-organotitano-alkylsiloxanes containing the alternating -M-O-Si-O- backbone.

The properties of the polymers described in this section are presented in table XII.

TABLE XII

Properties of poly-bis-(quinolin-8-oxy)-titano-alkylsiloxanes

Polymer	physical properties	thermal stability
$\left[\begin{array}{c} \text{Me} \\ -\text{Ti} - \text{O} - \text{Si} - \text{O} \\ \text{Me} \end{array}\right]_n$	reddish-brown solid m.p. slight hydrol. in dil. HCl. soluble D.M.F., benzene; spar. soluble acetone, ether, T.H.F. insoluble ether, hexane, pet. ether.	--
$\left[\begin{array}{c} -\text{Ti} - \text{O} \end{array}\right]_{1.0n}\left[\begin{array}{c} \text{Et} \\ -\text{Si} - \text{O} \\ \text{Et} \end{array}\right]_{0.61n}$	yellow solid. slight hydrol. in dil. HCl & NaOH soluble D.M.F., T.H.F. spar. soluble benzene, ethanol, ether acetone. insoluble pet. ether, hexane	trace yellow distillate at $250^\circ/0.1$ mm, considerable at $380^\circ/0.1$ mm. Ti/Si ratio $1.0/1.90$. brown residue non-volatile to $460^\circ/0.1$ mm, contains no silicon, approximates to $(\text{Ti}(\text{OC}_9\text{H}_6\text{N})_2\text{-O})_n$
$\left[\begin{array}{c} -\text{Ti} - \text{O} \end{array}\right]_{1.0n}\left[\begin{array}{c} \text{Et} \\ -\text{Si} - \text{O} \\ \text{Et} \end{array}\right]_{2.16n}$	yellow solid, soluble D.M.F., T.H.F. benzene acetone. spar. soluble ether, ethanol, insoluble pet. ether, hexane. slight hydrol. in dil. HCl and NaOH	--

Note $\bigcirc$ represents quinolin-8-oxy

all compounds were highly water-repellent

d) Poly-quinolin-8-oxy-metalloxanes

These polymers were all prepared by the hydrolysis and subsequent heat treatment of bis-dialkylamino-quinolin-8-oxy-metal intermediates:
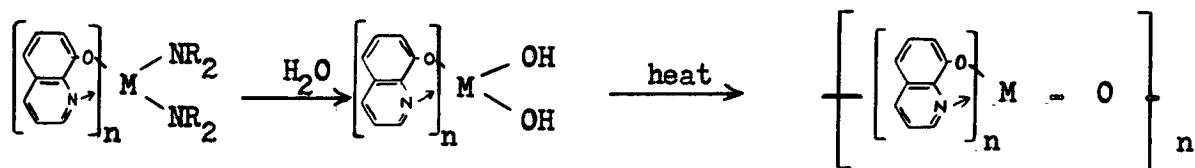
Heat is required to cause complete condensation of the metal-hydroxyl groups. This is analagous to the preparation of the silicones from silane diols except that an acid catalyst is not required.

1. Titanium

The hydrolysis of $Ti(NMe_2)_2(OC_9H_6N)_2$ in T.H.F. solution with excess water resulted in an insoluble bright yellow solid which was filtered off and heated at $100^\circ/0.1$ mm for one hour. The analysis and infrared spectrum were in accord with the expected structure ie. $(Ti(OC_9H_6N)_2-O)_n$.

The product was unaffected by boiling water or boiling dilute alkali but was soluble in dilute HCl. It was sparingly soluble in benzene, ethanol and acetone and insoluble in ether and hexane. On heating in air the colour changed to orange from about 300° and decomposition without fusion occurred at about 430°. On heating under high vacuum no change was observed to $470^\circ/$ 0.1 mm at which temperature decomposition without fusion occur.

Rust (34) reports the preparation of this compound by the hydrolysis of bis-(isopropoxy) -bis-quinolin-8-oxy-titanium and he obtained a yellow acetone soluble product which did not melt below 300° but turned brown at about 280°.

The possibility of the titanium intermediate existing in geometrical isomeric forms with the trans-form favoring the formation of linear polymers

and the cis-form cyclic polymers has already been mentioned. In this case the absence of volatility at $470^{\circ}/0.1$ mm perhaps suggests that we have here a high molecular weight linear polymer rather than a low molecular weight cyclic product which would be volatile. However this does not necessarily mean that the trans-from of the intermediate was exclusively present, as there is a possibility that rearrangement of cyclic to linear polymers can take place under the influence of heat. This is especially so if the rings are strained as they might well be under the steric influence of the bulky quinolin-8-oxy ligands.

2. Zirconium

In like manner hydrolysis of bis-diethylamino-bis-quinolin-8-oxy-zirconium gave a bright yellow insoluble solid which had analysis and infrared spectrum in accord with the proposed structure $\{Zr(OC_9H_6N)_2\text{-}O\}_n$.

The physical properties of this product were identical with the titanium analogue and the thermal stability, both in air and under vacuum, similar. However it did melt to a red liquid at about 420°. Here again one might suspect that this was a linear polymer.

3. Vanadium

The water hydrolysis of a bis-dialkylamino-bis-quinolin-8-oxy-vanadium compound was not carried out, however the isolation of $\{V(OC_9H_6N)_2\text{-}O\}_n$ has been described earlier in the section on poly-quinolin-8-oxy-metallophenyl-siloxanes. In contrast to the titanium and zirconium analogues there seems no doubt that this is either monomeric (n=1) or a small ring compound (n=2 or 3) and the proposed structures have been described.

4. Aluminum

The hydrolysis of mono-quinolin-8-oxy-bis-dimethylamino-aluminum gave a

bright yellow insoluble solid which was heated to $300°/0.1$ mm to complete
the condensation. The hydrolytic stability and solubility of this compound
were similar to that of the corresponding titanium derivative, and the analysis
and infrared spectrum were in accord with the proposed structure $\{$ Al (OC_9H_6N)
$-O\}_n$. Decomposition in air started at $400°$ and became rapid at $450°$, fusion
did not take place.

Aluminum in the four covalent state, as it is in this case, has a tetra-
hedral configuration; consequently the O-Al-O band angle is theoretically
about $108°$. This compares with the O-Ti-O angle of theoretically $90°$ in the
cis-form and $180°$ in the trans-form of the octahedral titanium analogue. We
should then expect the tendency for aluminoxanes to form cyclic compounds to
be slightly less than that for titanoxanes in the cis-configuration. The
evidence in this case seems to point to the fact that a linear polymer is
present.

5. Tantalum

The hydrolysis of the tris-quinolin-8-oxy-tantalum intermediate gave an
insoluble yellow precipitate which was heated under high vacuum in the usual
manner. From $150°$ upwards 8-hydroxyquinoline started to distill off and the
temperature was slowly raised until this ceased $(340°)$. The residue corres-
ponded approximately to $(Ta (OC_9H_6N) O_2)_n$ and had all the expected properties
of a cross-linked polymer ie. very stable chemically and thermally and almost
completely insoluble in all solvents.

The isolation of $\{$ Ta $(OC_9H_6N)_3-O\}_n$, which is presumably linear, has
been described previously in this report and it is interesting to note that
when this was heated under vacuum only a trace of 8-hydroxy-quinoline was
liberated from $340°$ upwards and ultimately decomposition took place at $360°$.

It then follows that the 8-hydroxyquinoline liberated in the hydrolysis re-action must be formed by the hydrolytic and not thermal cleavage of tantalum-(quinolin-8-oxy) bonds. Although the latter are not hydrolyzed in boiling water, the in situ liberation of water at 150° from the condensation of hydroxyl groups obviously creates more vigorous hydrolytic conditions.

6. Conclusions

The nature and thermal stabilities and the solubilities of the poly-quinolin-8-oxy-metalloxane polymers are listed in tables XIII and XIV re-spectively.

TABLE XIII

Nature and thermal stabilities of poly-quinolin-8-oxy-metalloxanes

Compound	nature	m.p.	thermal stability
$\left[\,\text{Ti} - \text{O}\,\right]_n$	orange-yellow solid	-	slow decomp. $470^\circ/0.1$ mm decomp. 460° in air
$\left[\,\text{Zr} - \text{O}\,\right]_n$	yellow solid	420°	stable $480^\circ/0.1$ mm-decomp. 460° in air
$\left[\,\text{Al} - \text{O}\,\right]_n$	bright yellow solid	-	starts slowly at 400° in air rapid at 450°
$\text{V} = \text{O} ?$	dark green solid	380°	distils at $380^\circ/0.1$ mm without appreciable decomp.
$\left[\,\text{Ta} - \text{O}\,\right]_n$	yellow solid	-	8-hydroxyquinoline given off from $340^\circ/0.1$ mm. Decomp. $360^\circ/0.1$ mm to black residue
$\left[\,\text{Ta} \overset{\text{O}}{\underset{\text{O}}{<}}\,\right]_n$	pale yellow solid	-	stable 500° in air stable $500^\circ/0.1$ mm.

Note   All temperatures are approximate

Decomposition points are visual

⟲ represents quinolin-8-oxy- group

TABLE XIV

Hydrolytic stabilities and solubilities of poly-quinolin-8-oxy-metalloxanes

Compound	dil. HCl	dil. NaOH	org. solvents
[Ti - O]$_n$	soluble hot	unchanged on boiling	slightly soluble benzene, acetone, ethanol, D.M.F. insoluble ether, hexane.
[Zr - O]$_n$	soluble hot	unchanged on boiling	slightly soluble benzene, acetone, ether, ethanol, D.M.F., insoluble hexane.
[Al - O]$_n$	unaffected on boiling, soluble in cold conc. HCl	unchanged on boiling	slightly soluble benzene, acetone, ethanol, D.M.F. insoluble ether, hexane.
V = O ?	soluble on warming giving blue-green solution	hydrolysis on warming giving red-brown precipitate	soluble D.M.F., acetone slightly soluble benzene, ethanol, insoluble ether, hexane.
[Ta - O]$_n$	soluble hot	unchanged on boiling	soluble D.M.F., slightly soluble ethanol, acetone, insoluble ether, benzene, hexane
[Ta(O)]$_n$	unchanged on boiling	unchanged on boiling	slightly soluble D.M.F., insoluble benzene, hexane, acetone, ether, ethanol.

Note   represents quinolin-8-oxy- group

All compounds were highly water-repellent and unaffected in boiling water.

The high thermal stabilities and lack of solubility are immediately apparent. The -M-O-M-O- backbone structure in these polymers is extremely polar and is that which is present in the purely inorganic metal oxides; the modifying nature of the quinolin-8-oxy ligands is obviously not sufficient to give this structure any elasticity and it retains its inorganic oxide-type properties.

E) INFRARED SPECTRA

Infrared spectra were measured on a Perkin Elmer model 421 spectro-
photometer. This instrument has interchangable optics and uses a double
grating unit for the range 2.5 - 17 microns and a cesium bromide prism unit
for the range 17-35 microns.

Samples were prepared in potassium bromide pellets in the usual manner
and the spectra are tabulated from 1600 cm^{-1} to 300 cm^{-1}.

Table XV lists the characteristic frequencies for metal-oxygen and metal-
nitrogen linkages and Table XVI those for 8-hydroxyquinoline and triphenyl-
silanol. These frequencies occur regularly in the succeeding tables of
spectra of model compounds and polymers.

The interpretations were carried out with the help of the following
references (66) (67) (68). Those in the cesium bromide range must be con-
sidered provisional because of the lack of our experience and of published
data in this range.

Abreviations used in the tables are as follows:

s   strong

ms   medium-strong

m   medium

mw   medium- weak

w   weak

vw   very weak

br   broad

sh   shoulder

TABLE XV

Characteristic frequencies of metal-oxygen and metal-nitrogen linkages

Linkage	Frequency (cm^{-1})	
Ti - O - Si	916	
Zr - O - Si	930	
Al - O - Si	1055	tendency to shift to higher frequencies in polymers.
V - O - Si (V^{IV}compds.)	880	
V - O - Si (vanadyl compds.)	900	
Ta - O - Si	895	
Si - O - Si	1030-1080	
Ti - O	818, 725-742, 513-534	
Zr - O	819, 735, 508-510	
Al - O	544, 513-519, 414-417	
V - O	819, 747, 507-530	
V = O	1000	
Ta - O	820, 740, 513-529	
Si - O	1105, 509	
Ti ←N	612-630	
Zr ←N	609-619	
Al ←N	638-641	
V ←N	631	
Ta ←N	620-624	

Note   All bands are strong.

TABLE XVI

Infrared spectra and interpretation of 8-hydroxyquinoline and triphenylsilanol

Ph_3SiOH		8-Hydroxyquinoline	
Wavelength	Interpret	Wavelength	Interpret
1585 mw	C=C ring vibration	1588 vw	C=C, C=N ring vibration
1563 w	C=C ring vibration	1576 m	C=C, C=N ring vibration
1482 mw	C=C ring vibration	1555 shw	C=C, C=N ring vibration
1427 s	Si-Ph	1500 s	C=N, C=C ring vibration
1418 shm		1468 s	C=C, C=N ring vibration
1378 brw		1455 shw	
1330 w		1430 m	
1300 w		1405 w	
1258 w		1395 m	
1184 w	Si-Ph	1376 s	
1153 vw		1350 shm	
1116 s	Si-Ph	1338 shmw	
1105 ms	Si-O	1281 s	
1067 w	Si-Ph	1270 s	
1023 w	Si-Ph	1240 w	
994 m	Si-Ph	1220 s	
850 s	Si-OH	1202 s	C-H deformation
830 s	Si-OH	1198 s	C-H deformation
735 ms	C-H out-of-plane	1169 m	
710 s	C-H out-of-plane	1161 ms	C-H deformation
695 s	C-H out-of-plane	1132 w	

Ph$_3$SiOH		8-Hydroxyquinoline	
Wavelength	Interpret	Wavelength	Interpret
509 s	Si-O	1089 m	
471 m		1053 mw	
440 m		1022 vw	
427 m	assoc. Ph ring	969 w	
367 w		891 w	
310 w		860 vw	
305 w	assoc. Ph ring	814 s	C-H out-of-plane
300 mw	assoc. Ph ring	801 m	C-H out-of-plane
		778 s	C-H out-of-plane
		739 s	C-H out-of-plane
		706 s	C-H out-of-plane
		695 shm	C-H out-of-plane
		632 m	
		572 m	
		540 m	
		513 mw	
		488 mw	
		468 ms	
		463 ms	
		421 m	assoc. Ph ring
		303 m	assoc. Ph ring

TABLE XVII

Infrared spectra of tetrakis-triphenylsiloxy-titanium and poly-bis-
(triphenylsiloxy)-titanophenylsiloxane

Ti(OSiPh$_3$)$_4$	Polymer soluble	Polymer insoluble	Insoluble heated
1582 mw	1585 mw	1582 mw	1581 mw
1560 vw	1560 vw	1560 w	1560 w
1545 vw	1547 vw		
		1492 vw	1492 vw
1480 mw	1481 w	1480 mw	1480 m
	1447 vw		
1425 s	1425 s	1425 s	1424 s
1415 shw	1417 shw	1416 shw	1415 shw
1375 vw	1370 br vw	1375 br w	1378 vw
1328 vw	1328 vw	1328 w	1328 vw
1300 vw	1302 vw	1300 w	1298 vw
1255 vw	1257 w	1257 w	1255 w
1182 w	1181 w	1181 w	1180 mw
1150 sh vw	1152 shw	1150 shw	1150 shmw
1112 s	1120 shs	1112 s	1110 s
1100 m	1111 s	1100 m	1099 ms
1061 m	1080-1058 brms	1061 w	1060 w
	1030 m		
1023 w	1020 sh m	1022 mw	1021 w
	1009 ms		
992 m	990 ms	993 m	992 m
916 br s	915 br s	920 br s	915 br s
			797 w
743 mw	738 m	742 m	741 m
734 mw		734 m	731 m

TABLE XVII (CON'T)

Ti(OSiPh$_3$)$_4$	Polymer soluble	Polymer insoluble	Insoluble heated
709 s	710 s	710 s	709 s
694 s	692 s	695 s	691 s
617 w	672 m		615 w
597 w			599 w
	526 s		
513 s	513 s	513 s	511 s
453 m	484 s	450 m	452 m
431 m			433 m
	392 w		
330 m	328 w	330 m	328 s
307 m	308 m	306 m	
300 m	300 w	300 w	

TABLE XVIII

Infrared spectra of tris-triphenylsiloxy-aluminum and poly-triphenylsiloxy-aluminophenylsiloxane

Al $(OSiPh_3)_3$	$\{Al\ (OSiPh_3)-O-SiPh_2-O\}_n$
1582 mw	1584 w
1560 vw	
1480 mw	1480 w
1461 w	1462 w
1425 s	1425 s
1393 vw	
1379 vw	1380 vw
1329 vw	
1300 w	1318 vw
1256 w	1256 w
1182 w	1182 w
1152 shw	1150 shmw
1109 s	1109 s
1082 m	
1055 s	1050 br s
1020 ms	1020 ms
992 m	992 m
888 w	
740 ms	740 m
705 s	705 s

TABLE XVIII (CON'T)

$Al(OSiPh_3)_3$	$\{Al(OSiPh_3)\text{-}O\text{-}SiPh_2\text{-}O\}_n$
695 s	696 s
666 m	
637 w	
615 w	
513 s	515 s
467 m	488 m
445 m	
429 m	
352 m	
318 m	
309 m	310 m
300 m	300 mw

TABLE XIX

Infrared spectra of other triphenylsiloxy metal derivatives.

$Zr(OSiPh_3)_4$	$Ta(OSiPh_3)_5$	$V(OSiPh_3)_4$	$VO(OSiPh_3)_3$
1582 mw	1584 mw	1582 mw	1580 mw
1561 sh vw	1560 vw	1561 vw	1558 vw
1480 mw	1480 mw	1480 m	1478 mw
1426 s	1425 s	1426 s	1424 s
1380 vw	1375 vw	1380 vw	1372 vw
1328 vw	1329 vw	1329 w	1326 vw
1300 vw	1300 vw	1300 w	1298 vw
1256 w	1258 vw	1258 w	1255 vw
1182 w	1183 w	1181 w	1181 w
1152 vw	1152 sh w	1152 vw	1150 vw
1110 s	1110 s	1112 s	1110 s
1100 m	1100 sh m	1100 m	1098 m
1060 vw	1060 w	1060 w	1060 vw
1025 w	1022 w	1023 w	1022 w
			1000 s
993 m	993 mw	992 m	992 m
930 vs	895 vs	880 vs	900 vs
738 m	735 m	732 m	735 m
707 s	707 s	710 s	707 s
696 s	692 s	694 s	692 s

TABLE XIX (CON'T)

Zr(OSiPh$_3$)$_4$	Ta(OSiPh$_3$)$_5$	V(OSiPh$_3$)$_4$	VO(OSiPh$_3$)$_3$
621 w	621 w	617 w	617 w
		595 w	595 w
540 sh m	541 sh m		540 w
513 s	513 s	513 s	507 s
	478 m		
451 m	448 m		456 m
435 m	435 m	433 m	440 sh m
			348 m
317 m	317 s	318 m	
308 m		306 m	306 m
300 m		300 m	300 m

TABLE XX

Infrared spectra of bis-triphenylsiloxy-mono-quinolin-8-oxy-aluminum
and poly-mono-(quinolin-8-oxy) aluminophenylsiloxane

$Al(OSiPh_3)_2(OC_9H_6N)$	Polymer insol.	Polymer sol.
1604 w	1594 s	1598 mw
1582 w	.	1575 mw
1560 vw	1568 s	
1549 vw	1550 sh m	1543 vw
1535 br vw		
1495 s	1488 s	1490 ms
1480 w		
1467 m	1456 s	1460 ms
1422 s	1418 m	1420 ms
1415 sh w		
1392 sh w		
1379 ms	1370 s	1375 ms
1320 m	1320 s	1320 m
1270 w	1275 ms	1270 vw
1260 w		1252 w
1240 vw		
1225 vw	1220 ms	1220 vw
1211 vw		
1180 w		1175 sh w
1171 vw	1162 w	
1150 vw		
1109 s	1104 s	1108 s
1054 br s	1055 sh w	
	1045 m	
	1032 sh m	
1020 m	1023 m	
991 m		990 v br s
910 vw	902 m	

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TABLE XX (CON'T)

Al(OSiPh$_3$)$_2$(OC$_9$H$_6$N)	Polymer insol.	Polymer sol.
820 mw		815 w
802 w	798 ms	798 vw
781 mw	780 ms	778 w
761 m		
738 ms	738 s	735 m
704 s	700 br w	
693 s		692 s
641 w	638 ms	
611 w		
581 w	591 w	598 br w
564 w	573 m	555 m
	540 br s	
515 s	513 ms	515 s
	500 shw	
478 m	465 m	476 m
450 w	452 s	
437 w		426 m
	414 s	
	398 sh m	
385 w	389 sh m	377 w
	353 m	
	337 ms	339 w
310 mw		

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TABLE XXI

Infrared spectra of bis-triphenylsiloxy-bis-quinolin-8-oxy-titanium and

poly bis(quinolin-8-oxy) titanophenylsiloxane

Ti(OSiPh$_3$)$_2$(OC$_9$H$_6$N)$_2$	Polymer insol.	Polymer sol.	Polymer insol. heated
1596 w	1595 w	1598 w	1595 w
1584 w	1581 w	1582 w	1581 w
1570 m	1569 ms	1570 ms	1569 ms
1494 s	1491 s	1495 s	1491 s
1481 w			
1467 s	1462 s	1464 s	1462 s
1426 s	1422 m	1424 m	1422 m
1389 w	1387 m	1387 m	1385 sh m
1371 s	1370 s	1370 s	1370 s
1319 s	1318 s	1318 s	1316 s
1275 m			
1268 ms	1265 ms	1267 s	1266 ms
1237 w	1230 w	1231 mw	1230 w
1221 vw	1220 w	1222 w	1220 sh w
1211 vw	1207 vw	1209 vw	1205 vw
1186 w	1182 vw	1180 vw	1180 vw
1170 vw	1165 vw	1168 w	1168 w
1150 vw			
1111 vw	1116 m	1115 s	1115 sh ms
1102 s	1101 s	1102 s	1100 s
1048 w	1043 w	1090-1045 m	1090-1045 m
1027 m	1021 m	1022 m	1021 m
1000 s	1000 sh s	999 s	996 s
982 s	980 s	976 br s	975 br s
905 s	932 s	902 sh m	901 m
855 mw			
820 m	818 m	819 s	818 s
803 m	801 m	801 m	800 m
788 m			

TABLE XXI (CON'T)

$Ti(OSiPh_3)_2(OC_9H_6N)_2$	Polymer insol.	Polymer sol.	Polymer insol. heated
778 m	780 m	781 m	780 m
760 mw			
749 s			
740 s	742 s	740 s	739 s
707 s	710 m	710 s	709 ms
695 s	694 ms	695 s	693 ms
641 m			
633 s	629 s	627 s	627 s
625 m			
		614 s	614 s
	597 m		
572 w	585 w	582 w	582 w
555 m	559 m	555 m	555 m
536 s	532 s	532 s	532 s
513 s	521 s	517 s	517 s
	500 s	494 m	495 s
455 m	462 s	465 m	465 m
448 m	448 m	445 m	442 m
441 m	435 w		
425 m			
395 m	397 m	397 s	397 s
	376 s	383 s	382 s
360 m		357 m	357 m
345 s	340 s	341 m	340 m
315 s		324 m	323 m

TABLE XXII

Infrared spectra of bis-triphenylsiloxy-bis-quinolin-8-oxy-zirconium and poly-bis(quinolin-8-oxy) zirconophenylsiloxane

$Zr(OSiPh_3)_2(OC_9H_6N)_2$	Polymer insol.	Polymer sol.
1602 mw	1600 m	1603 mw
1585 w	1582 sh w	1585 sh mw
1572 m	1571 sh s	1575 m
	1568 s	
	1554 shw	
	1545 w	
1495 s	1490 s	1495 s
1480 w		
1466 s	1462 s	1466 s
	1455 s	
1426 s	1418 m	1425 m
1380 m		
1372 s	1370 s	1375 s
1330 s		
1326 s	1315 s	1319 s
1300 w		
1272 sh w	1270 s	1270 m
1268 m		
1257 sh w		1234 mw
1222 w	1224 m	1222 w
1208 w	1203 w	1205 w
1182 w		1176 w
1170 w	1169 w	
1150 w	1127 vw	1150 w
1110 s		1115 sh s
1103 s	1103 s	1107 s
1060 w		
1048 w	1050 w	1040 ms
1026 m	1024 w	1020 ms
1000 s		

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TABLE XXII (CON'T)

$Zr(OSiPh_3)_2(OC_9H_6N)_2$	Polymer insol.	Polymer sol.
990 s	970 vw	990 s
		938 s
928 s		925 s
	905 w	
	879 w	
	868 w	
821 m	819 s	820 m
801 m	800 ms	802 mw
786 m	786 s	
780 m	780 s	781 m
760 mw		
745 s		
738 s	735 s	739 s
707 s		710 ms
695 s		696 ms
		683 mw
670 w		664 w
	646 mw	
635 w	636 mw	634 w
619 m	615 sh ms	615 m
	610 ms	
	598 m	595 m
	553 m	542 m
527 sh m		520 s
515 s	511 s	
495 sh m	489 s	492 m
	465 m	455 m
435 br m	444 m	
		419 m
382 m	380 s	381 m

TABLE XXIII

Infrared spectra of bis-triphenylsiloxy-mono-quinolin-8-oxy-vanadate and poly-bis-(quinolin-8-oxy) vanadophenylsiloxane

$VO(OSiPh_3)_2(OC_9H_6N)$	Polymer insol.	Polymer sol.
1600 w	1598 m	
1581 w	1580 m	1584 mw
1568 w	1570 ms	1568 mw
	1540 sh w	1546 w
1492 s	1492 s	1492 s
1480 w		
1475 w		
1462 s	1460 s	1461 s
1424 s	1421 w	1425 s
1415 sh w		
1390 m	1385 sh m	
1374 m	1370 s	1371 ms
1330 w		
1319 m	1317 s	1318 ms
1271 m	1267 s	1270 m
1259 m		1260 sh mw
1231 w	1231 m	1230 vw
1181 w		1181 vw
1170 vw	1168 w	
1150 w	1140 w	1151 sh w
1112 s		1120 s
1100 s	1104 s	1112 s
1060 w	1048 w	
1025 m		1031 ms
1000 ms		1009 s
995 ms	988 mw	990 ms
966 ms	978 m	

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TABLE XXIII (CON'T)

VO(OSiPh$_3$)$_2$(OC$_9$H$_6$N)	Polymer insol.	Polymer sol.
950 s	952 vw	
	941 w	930 br ms
902 br s	908 br vw	
820 mw	819 s	819 w
818 mw		
802 w	800 ms	800 vw
781 w	780 s	780 w
775 w		
750 s	747 s	
742 s	738 s	739 m
709 s	710 sh m	715 ms
696 s		693 s
680 m		671 m
664 w	641 ms	
648 m	631 ms	635 m
620 w	613 m	
594 w		
585 vw	582 w	
565 w	564 w	565 vw
537 m	541 mw	
527 m	528 s	530 s
513 s	516 m	
461 m	495 w	
444 w		
439 w		435 w
424 w		
403 m	398 m	398 m
	382 w	365 m
	348 m	357 m
	340 ms	347 m

TABLE XXIV

Infrared spectra of bis-triphenylsiloxy-tris-quinolin-8-oxy tantalum and
poly-tris(quinolin-8-oxy)tantalophenylsiloxane

Ta(OSiPh$_3$)$_2$(OC$_9$H$_6$N)$_3$	Polymer soluble	Polymer insoluble
1604 mw	1605 w	1602 m
1582 m	1584 w	1586 m
1570 ms	1571 m	1570 s
1498 s	1498 s	1496 s
1480 m		
1465 s	1468 s	1462 s
1423 s	1424 m	1420 m
1405 sh m	1402 w	
1398 m	1395 w	1395 m
1371 s	1375 s	1372 s
	1335 w	
1320 s	1321 ms	1319 s
1310 sh m		
1270 ms	1270 m	1269 s
1260 sh m	1259 m	
1230 m		1231 m
1220 m	1220 mw	1225 sh m
1202 w	1200 w	1220 ms
1182 w	1190 w	
1170 w	1160 w	1170 mw
1150 w		
1108 s	1118 s	1125 sh w
1100 sh m	1108 s	1104 s
	1087 m	
1050 w	1050 w	1050 mw
1025 mw	1025 w	1030 mw
1005 sh w		1022 mw
994 mw	995 w	

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TABLE XXIV (CON'T)

$Ta(OSiPh_3)_2(OC_9H_6N)_3$	Polymer soluble	Polymer insoluble
	980 w	963 w
	950 s	955 w
900 br s	911 m	908 s
	885 s	891 ms
		838 m
819 ms	818 m	820 ms
802 m	800 w	800 m
781 ms	781 m	786 m
	745 ms	752 ms
742 s		740 s
704 s	710 ms	703 w
693 s	692 ms	
672 w		670 w
663 w		
630 sh mw		628 m
624 m	624 m	
615 sh mw		612 m
585 w		582 w
572 w		572 w
524 ms		520 s
508 s		504 mw
455 w		496 m
435 w		387 w

TABLE XXV

Infrared spectrum of bis-triethylsiloxy-bis-quinolin-8-oxy-titanium and poly-bis-(quinolin-8-oxy)titanoethylsiloxane

$Ti(OSiEt_3)_2(OC_9H_6N)_2$	Polymer insoluble	Polymer soluble
1592 w	1598 m	1595 m
1565 m	1568 s	1569 ms
1490 s	1490 s	1492 s
1461 s	1462 s	1462 s
1452 sh m		
1419 w	1420 mw	1418 w
1400 w		1408 w
1385 w	1385 sh m	1387 w
1372 ms	1372 sh s	1374 ms
1368 ms	1370 s	1370 ms
1319 s	1317 s	1319 s
1266 m	1268 ms	1267 m
1230 mw	1230 m	1231m
1220 mw	1208 w	1210 w
1166 w	1157 w	1168 w
1127 vw	1130 w	
1100 ms	1102 s	1101 s
1042 w	1046 w	1085-1050 s
1010 m	1026 mw	1000 sh s
960 br s	950 br s	965 br s
882 br s		875 br s
822 sh m		
819 m	820 s	819 m

TABLE XXV (CON' T)

Ti(OSiEt$_3$)$_2$(OC$_9$H$_6$N)$_2$	Polymer insoluble	Polymer soluble
800 w	801 ms	801 mw
785 mw	782 ms	782 m
755 sh m		
742 s	740 s	740 s
738 s	729 s	
719 ms	691 mw	705 m
635 w		637 m
622 m		625 ms
591 w		610 m
555 sh m		546 sh m
534 s		529 s
		510 sh m
481 m		
422 w		417 w
380 br s		380 br s
		362 m
336 m		334 m

TABLE XXVI

Infrared spectra of quinolin-8-oxy-derivatives of zirconium and aluminum.

$Al(OC_9H_6N)_3$	$\{Al(OC_9H_6N)_2\text{-}O\}_n$	$Zr(OC_9H_6N)_4$	$\{Zr(OC_9H_6N)_2\text{-}O\}_n$
1598 s	1601 m	1600 m	1600 m
1570 s	1587 m	1570 s	1578 s
			1544 w
1494 s	1495 s	1491 s	1490 s
1462 s	1465 s	1460 s	1462 s
			1456 s
1419 m	1422 w	1420 m	1418 m
1375 s	1380 s	1372 s	1370 s
1325 s	1327 s	1313 s	1312 s
1279 m	1280 m	1271 s	1270 s
		1234 m	
1222 m	1225 m	1221 m	1224 m
1209 w	1210 vw	1205 w	1204 w
1168 w	1170 vw	1168 w	1169 w
			1165 w
1129 sh w		1129 vw	1127 w
1108 s	1110 s	1104 s	1103 s
1046 mw	1050 w	1048 w	1050 mw
1030 m	1029 w	1023 w	1022 mw
		969 vw	
905 m		904 vw	905 w
856 w		859 vw	865 w
818 ms	820 m	817 s	819 ms
800 m	800 m	800 m	800 m
	784 m	786 ms	
781 ms		780 s	780 ms
741 s	745 s	745 sh m	750 ms

TABLE XXVI (CON'T)

$Al(OC_9H_6N)_3$	$\{Al(OC_9H_6N)_2\text{-}O\}_n$	$Zr(OC_9H_6N)_4$	$\{Zr(OC_9H_6N)_2\text{-}O\}_n$
		735 s	735 s
641 ms	641 s		646 m
		638 mw	637 m
		609 m	610 ms
569 m	572 m		
	544 s	555 w	555 m
	519 m	510 s	508 s
	495 w	490 s	
	465 w		
	452 m		
437 mw	441 w	437 w	
	417 s		
404 s			
392 s	392 m	380 m	
360 m	358 m		360 s
342 sh mw			332 s
305 sh mw	300 m		
291 m			

TABLE XXVII

Infrared spectra of poly-quinolin-8-oxy-metalloxanes containing

titanium and tantalum

{Ti(OC$_9$H$_6$N)$_2$-O}$_n$	{Ta(OC$_9$H$_6$N)-O$_2$}$_n$
1598 m	1602 mw
1570 ms	1576 m
1492 s	1498 s
1464 s	1468 s
1420 m	1420 mw
1372 s	1378 s
1318 s	1322 s
1270 ms	1270 m
1231 mw	1236 w
1222 sh w	1222 w
1205 sh w	
1168 w	1169 w
1129 w	1130 w
1100 s	1108 ms
1045 w	1050 w
1023 w	1025 w
818 s	820 s
808 s	
797 s	800 ms
	780 ms
	740 s
725 s	
635 sh m	
625 ms	620 ms

TABLE XXVII (CON'T)

$\{Ti(OC_9H_6N)_2-O\}_n$	$\{Ta(OC_9H_6N)-O_2\}_n$
612 ms	
588 sh w	
559 m	562 m
532 ms	529 s
519 s	
494 ms	498 m
	465 w
435 br w	438 w
398 m	394 w
384 mw	
312 br s	304 m

F) SUMMARY OF RESULTS AND CONCLUSIONS

The results from the years work can be summarized as follows:

1. The reaction between bis-dialkylamino-metal derivatives and diphenyl-silanediol appears to be satisfactory for the preparation of poly-organo-metallophenylsiloxane polymers but the chemical properties of the products cause complications.

2. Trialkylsiloxy ligands attached to titanium or aluminum in metallo-phenylsiloxane polymers are unsatisfactory. Rearrangement takes place at low temperatures with the formation of monomers, of the type $M(OSiR_3)_x$, and a cross-linked residue.

3. The mechanism of this rearrangement probably involves covalency expansion of the metal atom in one polymer chain through co-ordination from an oxygen atom from a neighboring chain. This is followed by cleavage of the chain and cross-linking.

4. A stage is reached when the extent of cross-linking is sufficient to sterically shield the metal atom from further covalency expansion and rearrangement stops. In general about 50% of the theoretical quantity of monomer is formed.

5. The steric shielding of triphenylsiloxy ligands is almost sufficient to eliminate rearrangement. Both poly-bis(triphenylsiloxy)titanophenyl-siloxane, $(Ti (OSiPh_3)_2-O-SiPh_2-O)_n$, and poly-triphenylsiloxy-aluminophenyl-siloxane, $(Al (OSiPh_3)_2 -O-SiPh_2-O)_n$, were obtained. The former was stable to $450^\circ/0.1$ mm and the latter decomposed at about $300^\circ/0.1$ mm without giving $Al (OSiPh_3)_3$.

6. The tendency of these polymers to rearrange should be reduced by the use of chelating ligands which either partially or completely satisfy coval-

ency exansion of the metal by intramolecular co-ordination.

7. This is the case with the quinolin-8-oxy ligand attached to titanium in a metallophenylsiloxane. The maximum covalency of six for titanium is satisfied and degradation does not take place until about $350°$.

8. Similar results should be obtained with vanadium^{IV} and tantalum as the covalency maxima of these elements can be satisfied by quinolin-8-oxy ligands. However steric complications arise because of the small size of these atoms.

9. With zirconium and aluminum the covalency maxima are not satisfied by quinolin-8-oxy ligands and the results obtained are similar to those for trialkylsiloxy ligands attached to titanium and aluminum,ie.rearrangement taken place at low temperature.

10. In a preliminary reaction with diethylsilanediol and $Ti(OC_9H_6N)_2(NMe_2)_2$ complications arose because of the instability of the diol. In spite of special reaction conditions self-condensation of the diol appeared to take place with the liberation of water. This gave rise to a product containing Si-O-Si and Ti-O-Ti linkages, the latter being formed by the water hydrolysis of the titanium intermediate.

11. An alternative synthetic procedure for poly-organometalloalkylsiloxanes which does not involve dialkylsilanediols shows promise; this is the reaction between dialkyldiacetoxysilanes and bis-dialkylamino-metal derivatives; an N:N dialkylacetamide is the by-product.

12. Poly-quinolin-8-oxy-metalloxanes of titanium, zirconium, vanadium, tantalum and aluminum may be prepared by the hydrolysis and subsequent heat treatment of bis-dialkylamino-quinolin-8-oxy-metal derivatives. In all cases except vanadium and tantalum these polymers were infusible and non-volatile

and appear to be linear; a cross-linked polymer was obtained with tantalum
and an insoluble but volatile compound with vanadium which was probably
monomeric or dimeric.

G) EXPERIMENTAL

1. General

The extreme moisture sensitivity of the dialkylamino-metal derivatives necessitated special precautions to avoid hydrolysis. All-glass apparatus was used throughout and was dried in an oven at ca. 120° prior to use. Reactions were carried out in the absence of air under an atmosphere of dry nitrogen.

2. Analysis

Basic nitrogen was estimated by hydrolysis of a sample in dilute sodium hydroxide solution and distillation of the liberated amine, which is a strong base, into excess standard acid solution. This was followed by back titration against standard alkali.

Metals in combination with nitrogen alone were estimated by careful hydrolysis of a sample in a platinum crucible with water, evaporation under an infrared lamp and subsequent ignition to the metal oxide on a Meker burner.

Silicon and metal in combination were estimated as follows: a sample, (ca 0.5 g) was added to concentrated sulphuric acid (ca 15 ml) containing ammonium sulphate (ca 10 g) and the mixture was refluxed until all traces of carbon had disappeared (1-3 hours). After cooling, water (150 ml) was added; the metal remained in solution as the sulphate and the silicon was precipitated as silica. The latter was filtered off, ignited and weighed. In the case of titanium and vanadium the total filtrate was then passed through a Jones Reductor into excess ferric alum solution and the metal was then estimated by titration of this solution against standard ceric ammonium sulphate solution using ferroin as indicator.

With zirconium, aluminum and tantalum this method for metal analysis

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was not applicable and a separate metal estimation was carried out. This involved decomposition of a sample in a platinum crucible with concentrated sulphuric and nitric acids, this was followed by evaporation to dryness under an infrared lamp and ignition on a Meker burner. This determined the total oxide, $SiO_2 + M_2O_x$, and the metal was then determined by difference, the silicon content having previously been estimated.

Microanalysis for carbon, hydrogen and nitrogen was carried out by the Microanalytical Laboratory, Max-Planck Institute, Mulheim, Germany.

3. Reagents

Benzene was azeotropically dried using ethanol and stored over sodium wire.

Tetrahydrofuran was distilled from lithium aluminum hydride and stored over sodium wire.

Ether and petroleum ether (b.p. 30°-60°) were dried over sodium and used without further purification.

Triphenylsilanol and diphenylsilanediol were pure grade obtained from the Fine Chemicals Department of this Company and were recrystallized from benzene-heptane and methyl ethyl ketone respectively and dried under high vacuum at 50° prior to use.

Trimethylsilanol was prepared by the method of Sommer et al (64) involving the hydrolysis of trimethylfluorosilane. This compound was fractionally distilled and was obtained as a colourless liquid b.p. 165°-166°/1 atmos.

Diethylsilanediol was prepared by the method of George et al (69) involving the hydrolysis of diethyldichlorosilane. This was obtained as a colourless crystalline solid m.p. 95° from pentane-ether.

Because of the ease of self-condensation of the last three reagents to

disiloxanes and water they were used immediately after isolation.

Trimethylacetoxysilane and dimethyldiacetoxysilane were prepared by the method of Schuyten et al (65) involving the reaction between the corresponding chlorosilanes and sodium acetate in ether; they were obtained as colourless hydrolyzable liquids b.p. 102°-103°/1 atmos. and b.p. 165°-66°/1 atmos. respectively.

8-hydroxyquinoline was reagent grade and was recrystallized from aqueous ethanol and dried under high vacuum at room temperature prior to use.

The dialkylamino-metal derivatives of titanium (56), zirconium (56), vanadium (57) and tantalum (58) were prepared by the method of Bradley and Thomas involving the reaction between the metal chloride and lithium dialkyl-amide in ether. These are listed in table XXVIII.

TABLE XXVIII

Compound	nature	m.p.	b.p.
Ti $(NMe_2)_4$	orange liquid	-	55°/0.1 mm
Ti $(NEt_2)_4$	orange liquid	-	110°/0.1 mm
Zr $(NMe_2)_4$	colourless solid		
Zr $(NEt_2)_4$	pale green liquid	-	110°/0.1 mm
V $(NMe_2)_4$	dark green solid	ca 40°	55°/0.1 mm
V $(NEt_2)_4$	dark green liquid	-	110°/0.1 mm
Ta $(NMe_2)_5$	yellow red solid	-	sublimes 100°/ 0.1 mm

Tris-dimethylamino-aluminum was prepared by the method of Ruff (59) involving the reaction between lithium aluminum tetradimethylamide and aluminum chloride in ether. This was obtained as a colourless solid m.p. ca. 85°, b.p 90°/0.1 mm. Reaction of this compound with aluminum chloride

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in a 2:1 molar ratio in ether gave bis-dimethylaminoaluminum chloride as a white solid m.p. ca 50°, b.p. 90°/0.1 mm. This method is also due to Ruff (59).

In view of the extreme moisture sensitivity of these dialkylamino-derivatives they were always distilled or sublimed, usually straight into the reaction flask, immediately prior to use.

4. Preparation of polymer intermediates

a) Dialkylamino-metal derivatives and bis-dialkylamino-titanium dichlorides

1. Bis-dimethylamino-titanium dichloride

Titanium tetrachloride (25.3 g : 0.133 mole) in pet. ether (150 ml) was added dropwise to a stirred solution of tetrakis-dimethylamino-titanium (30.0 g : 0.133 mole) in ether (150 ml). An exothermic reaction occurred and a brown precipitate was formed; the mixture was refluxed for one hour and the solvent then evaporated to give a brown solid product (55.0 g: 100% yield). Found: Ti, 23.4%. $TiCl_2(NMe_2)_2$ requires Ti, 23.2%.

2. Bis-diethylamino-titanium dichloride

In like manner titanium tetrachloride (8.20 g: 0.0432 mole) and tetrakis-diethylamino-titanium (14.5 g : 0.0432 mole) gave a liquid product which was distilled under high vacuum to give a deep red liquid product (16.9 g : 75% yield) b.p. 100°/0.1 mm. Found: Ti, 18.1%, basic N, 10.7%. $TiCl_2(NEt_2)_2$ requires Ti, 18.2%; basic N, 10.67%.

3. Reaction between triethylaluminum and diethylamine in hexane

Diethylamine (45 g) was added dropwise to triethylaluminum (ca 16 g) in hexane (120 ml) with stirring. An exothermic reaction took place and a gas was evolved. The colourless solution was then refluxed for 15 minutes, the

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solvent evaporated and the residue distilled under high vacuum to give a
colourless liquid product (25.0 g : ca 95% yield based on aluminum content)
b.p. $90^{o}/0.1$ mm. Found : Al, 15.5%. $Et_3Al_2(NEt_2)_3$ requires Al, 15.1%.

This product (22.0 g) was refluxed with a further quantity of diethyl-
amine (30 ml) for two hours, the amine was then evaporated and the residue
distilled under high vacuum to give a colourless liquid product (21.5 g)
b.p. $90^{o}/0.1$ mm. Found : Al, 15.7%.

4. Reaction between aluminum chloride and lithium diethylamide in ether.

Aluminum chloride (28.0 g : 0.210 mole) was added over 30 minutes to a
stirred solution of lithium diethylamide (0.66 gm-equiv.) in ether (600 ml).
An exothermic reaction ensued and the mixture was stirred at room temperature
for 4 hours, left overnight and the solvent then evaporated. Distillation
of the residue under high vacuum gave a yellow viscous liquid (21.0 g :
50% yield based on aluminum content) b.p. 140°-$180^{o}/0.1$ mm. Found : Al, 13.4%,
basic N, 16.9%; Cl, zero; Ratio Al/N 1.0/2.43. $Al(NEt_2)_3$ requires Al, 11.1%;
basic N, 17.3%. $(Et_2N)_2AlNEtAl(NEt_2)_2$ requires Al, 14.0%; basic N, 18.2%.

5. Reaction between lithium aluminum tetradiethylamide and aluminum
chloride in tetrahydrofuran.

Diethylamine (90 ml) was added dropwise over two hours to a stirred
solution of lithium aluminum hydride (8.00 g : 0.211 mole) in tetrahydrofuran
(80 ml). Hydrogen was liberated and evolution ceased just before the end of
the addition. The solution was stirred for two hours and aluminum chloride
(9.00 g: 0.0675 mole) in tetrahydrofuran (50 ml) then added dropwise. An
exothermic reaction occurred and the mixture was refluxed for 90 minutes;
the solvent was evaporated and the residue distilled under high vacuum to
give a pale yellow liquid product (25.0 g) b.p. $135^{o}/0.1$ mm. Found: Al, 15.6%;

Cl, zero.

6. **Reaction between vanadium oxytrichloride and lithium dimethylamide in ether.**

Vanadium oxytrichloride (48.7 g : 0.281 mole) in pet. ether (50 ml) was added dropwise over 40 minutes to a stirred and cooled solution of lithium dimethylamide (0.91 gm-equiv.) in ether (700 ml). The initially green mixture soon became red-brown and was refluxed for two hours, left overnight and the ether then evaporated and replaced with pet. ether. The mixture was filtered and the filtrate evaporated. The residue was heated under high vacuum and a deep green low melting solid distilled (18.0 g : 28% yield based on vanadium content) m.p. ca 40°, b.p. $50^\circ/0.1$ mm. Found: V, 22.2%; valency, 4.01, 4.04. $V(NMe_2)_4$ requires V, 22.4%.

7. **Reaction between vanadium oxytrichloride and lithium diethylamide in ether.**

In like manner vanadium oxytrichloride (50.0 g : 0.289 mole) and lithium dimethylamide (1.04 gm-equiv.) gave a dark green-brown liquid distillate (12.8 g : 13% yield based on vanadium content) b.p. $110^\circ/0.1$ mm. Found: V, 15.0%; basic N, 16.6%; valency, 4.05; Cl, zero. $V(NEt_2)_4$ requires V, 15.01%; basic N, 16.51%.

8. **Reaction between gaseous oxygen and tetrakis-diethylamino-vanadium[IV] in heptane.**

Oxygen was slowly bubbled through a solution of tetrakis-diethylamino-vanadium[IV] (11.4 g) in heptane (80 ml). The solution became very warm and turned deep red; passage of the gas was continued until the temperature had fallen to room temperature (ca 2 hours). Evaporation of the solvent and distillation of the residue under high vacuum gave a deep red liquid (0.44 g)

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b.p. 90-120°/0.1 mm. Found: V, 15.2%. V(NEt$_2$)$_4$ requires V, 15.01%.

b) Bis-dialkylamino-trialkyl(aryl)siloxy-metal derivatives

1. Bis-dimethylamino-bis-trimethylsiloxy-titanium

Sodium trimethylsilanolate (8.00 g : 0.0714 mole), prepared from sodium metal and trimethylsilanol in ether and purified by sublimation, in ether (30 ml) was added dropwise over 10 minutes to a stirred solution of bis-dimethylamino-titanium dichloride (6.71 g : 0.0324 mole) in benzene (100 ml). An exothermic reaction took place, a white precipitate was formed and the colour changed from brown to orange. The mixture was stirred for a further 30 minutes, the solvents then evaporated and the residue distilled under high vacuum to give an orange liquid product (8.00 g : 78% yield) b.p. 60°/0.1 mm. Found : Ti, 15.5%; Si, 17.5%; Cl, zero. Ti(OSiMe$_3$)$_2$ requires Ti, 15.23%; Si, 17.87%.

2. Bis-diethylamino-bis-triethylsiloxy-titanium

In like manner sodium triethylsilanolate, prepared from sodium metal and triethylsilanol (9.30 g : 0.103 mole),and bis-diethylamino-titanium dichloride (9.06 g : 0.0344 mole) gave a product which was distilled under high vacuum to give a yellow liquid (11.8 g : 76% yield) b.p. 140°/0.1 mm. Found: Ti, 10.6%; Si, 12.3%; Cl, zero. Ti(NEt$_2$)$_2$(OSiEt$_3$)$_2$ requires Ti, 10.5%; Si, 12.3%.

3. Bis-diethylamino-bis-triphenylsiloxy-titanium

In like manner sodium triphenylsilanolate, prepared from sodium metal and triphenylsilanol (14.5 g : 0.0525 mole), and bis-diethylamino-titanium dichloride (6.90 g : 0.0262 mole) gave a mixture which was filtered under nitrogen. Evaporation of the solvent from the filtrate gave an orange-yellow viscous liquid (13.8 g : 71% yield). Found: Ti, 6.52%, Si, 7.38%, Cl, slight trace. Ti(OSiPh$_3$)$_2$(NEt$_2$)$_2$ requires Ti, 6.45%; Si, 7.56%.

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Attempted distillation under high vacuum gave a few drops of liquid distillate at ca. $300°/0.1$ mm, which was not identified, and an apparently decomposed black residue.

4. Bis-dimethylamino-mono-trimethylsiloxy-aluminum

In like manner sidium trimethylsilanolate (10.0 g : 0.0893 mole) and bis-dimethylamino-aluminum chloride (12.8 g : 0.0853 mole) gave a crude mixture which was distilled under high vacuum to give a colourless liquid product (13.8 g : 79% yield) b.p. $105°/0.1$ mm. Found: Al. 13.0%; Si. 13.9%; Cl. zero. $Al(OSiMe_3)(NMe_2)_2$ requires Al, 13.20%; Si, 13.74%.

5. Bis-dimethylamino-mono-triphenylsiloxy-aluminum

In like manner sodium triphenylsilanolate (19.0 g : 0.0636 mole) and bis-dimethylamino-aluminum chloride (9.48 g : 0.0632 mole) gave a crude mixture which was filtered and the filtrate evaporated to give a pale yellow solid (24.0 g : 98% yield). Found: Al, 6.60%; Si, 7.22%; Cl, slight trace. $Al(OSiPh_3)(NMe_2)_2$ requires Al, 6.68%; Si, 7.19%.

A sample (21.0 g) was heated under high vacuum. Fusion occurred at $50°$, and a small quantity of liquid distillate was collected at $250°-280°/0.1$ mm (2.20 g). Found: Al, 16.6%. $Al(NMe_2)_3$ requires Al, 16.95%.

A light brown glossy residue remained (17.0 g). Found: Al, 6.64%; Si, 8.08%; ratio Al/Si :: 1.0/1.2.

This residue was reheated and an orange liquid solidifying to a light brown solid distilled at $300°-400°/0.1$ mm (4.20 g). Found: Al, zero; Si,9.56%. $Ph_3SiOSiPh_3$ requires Si, 10.4%.

6. Reaction between tetrakis-dimethylamino-titanium and hexamethyl-disiloxane.

Tetrakis-dimethylamino-titanium (11.7 g) was refluxed in hexamethyldi-

siloxane (80 ml) under a short fractionating column. The solution became dark but no change was observed in the column head temperature (100°, b.p. of hexamethyldisiloxane) during 8 hours reflux. The hexamethyldisiloxane was removed under reduced pressure and the residue distilled under high vacuum to give an orange liquid product (10.7 g) b.p. $55^{\circ}/0.1$ mm Found : Ti, 21.5%. $Ti(NMe_2)_4$ requires Ti, 21.36%.

7. Reaction between tetrakis-triphenylsiloxy-titanium and tetrakis diethylamino-titanium in benzene.

Tetrakis-diethylamino-titanium (0.98 g : 0.00291 mole) and tetrakis-triphenylsiloxy-titanium (3.35 g: 0.00291 mole) were refluxed in benzene (60 ml) for 10 hours. There was no indication of the siloxy compound going into solution during this time; the mixture was left at room temperature overnight, the solid then removed by decantation and the decantate evaporated, the resulting thick liquid residue was distilled under high vacuum to give a red liquid (0.60 g) b.p. $110^{\circ}/0.1$ mm/ Found: Ti, 14.0%. $Ti(NEt_2)_4$ requires Ti, 14.24%.

The insoluble solid was washed with benzene (20 ml) and then dried under high vacuum (3.10 g). Found: Ti, 4.35%; Si, 9.60%; basic N, zero. $Ti(OSiPh_3)_4$ requires Ti, 4.17%; Si, 9.76%.

8. Reaction between tetrakis-triethylsiloxy-titanium and tetrakis-diethylamino-titanium in benzene

Tetrakis-diethylamino-titanium (2.71 g : 0.00806 mole) and tetrakis-triethylsiloxy-titanium (4.62 g : 0.00806 mole) were refluxed in benzene (60 ml) for 2 hours. The solvent was then evaporated and the residue distilled under high vacuum into two fractions.

1st. fraction. Orange liquid (3.64 g) b.p. $130-135^{\circ}/0.1$ mm. Found: Ti, 12.8%; Si, 6.78%; basic N, 11.3%; Ratio, Ti/N/Si :: 1.0/3.01/0.90.

Ti $(NEt_2)_3(OSiEt_3)$ requires Ti, 12.1%; Si, 7.08%; basic N, 10.6%.

2nd. fraction. Yellow low melting solid (3.12 g) b.p. $135°-150°/0.1$ mm. Found: Ti, 9.30%; Si, 16.2%; basic N, 2.61%; Ratio Ti/N/Si :: 1.0/0.96/2.98. $Ti(OSiEt_3)_3(NEt_2)$ requires Ti, 9.33%; Si, 16.4%; basic N, 2.73%.

9. Reaction between triethylsilanol and tetrakis-diethylamino-titanium in pet. ether.

Triethylsilanol (4.35 g : 0.0330 mole) in pet. ether (40 ml) was added dropwise over 20 minutes to a stirred solution of tetrakis-diethylamino-titanium (5.53 g : 0.0165 mole) in pet. ether (100 ml). The yellow-orange solution was left overnight at room temperature, the solvent then evaporated and the residue distilled under high vacuum to give an orange liquid (7.00 g : 93% yield) b.p. $140°/0.1$ mm. Found : Ti, 11.2%; Si, 12.5%; basic N, 6.70%; Ratio Ti/N/Si :: 1.0/2.04/1.90. $Ti(NEt_2)_2(OSiEt_3)_2$ requires Ti, 10.53%; Si, 12.37%; basic N, 6.16%.

10. Reaction between triphenylsilanol and tetrakis-diethylamino-titanium in benzene.

Triphenylsilanol (7.60 g : 0.0276 mole) in benzene (100 ml) was added dropwise over 1 hour to a vigorously stirred solution of tetrakis-diethyl-amino-titanium (4.64 g : 0.0138 mole) in benzene (80 ml). A small amount of solid was precipitated during the reaction. The mixture was allowed to stand overnight, the solid removed by decantation and the decantate evapor-ated to give an orange pasty solid (10.6 g : theoretical 10.2 g).

Pet. ether (120 ml) was then added giving a yellow solid precipitate and an orange solution. The latter was decanted off & the solid dried under high vacuum (6.00 g). Found : Ti, 5.66%; Si, 8.45%; basic N, 2.34%; Ratio Ti/Si/N:: 1.0/2.56/1.41.

The orange decantate was evaporated to give an orange pasty solid (4.5 g). Found : Ti, 7.00%; Si, 6.87%; basic N, 4.68%; Ratio Ti/Si/N :: 1.0/1.68/2.29.

c) Bis-dialkylamino-quinolin-8-oxy-metal derivatives

1. Bis-dimethylamino-bis-quinolin-8-oxy-titanium.

8-hydroxyquinoline (14.4 g : 0.0992 mole) in benzene (80 ml) was added dropwise over 30 minutes to a stirred solution of tetrakis-dimethylamino-titanium (11.1 g : 0.0496 mole) in benzene (100 ml). The resultant red solution was left overnight at room temperature and the solvent then evaporated to give a light orange solid (20.3 g : 99% yield). Found: Ti, 11.4%; basic N, 6.50%. $Ti(OC_9H_6N)_2(NMe_2)_2$ requires Ti, 11.29%; basic N, 6.60%.

A sample heated to $150°/0.1$ mm gave a trace of liquid distillate and a black apparently decomposed residue.

2. Bis-diethylamino-bis-quinolin-8-oxy-titanium.

In like manner 8-hydroxyquinoline (7.50 g : 0.0517 mole) and tetrakis-diethylamino-titanium (8.74 g : 0.0259 mole) gave an orange-red solid product (12.5 g : 100% yield). Found: Ti, 9.87%; basic N, 5.81%. $Ti(NEt_2)_2(OC_9H_6N)_2$ requires Ti, 9.97%; basic N, 5.83%.

A sample was crystallised from benzene to give small red crystals. Found: Ti, 9.90%; basic N, 5.80%.

A sample (7.12 g) was heated under high vacuum, an orange liquid (1.02 g) distilled at $120°/0.1$ mm. Found: Ti, 14.1%. $Ti(NEt_2)_4$ requires Ti, 14.24%.

3. Bis-dimethylamino-bis-quinolin-8-oxy-zirconium.

In like manner 8-hydroxyquinoline (8.30 g : 0.0572 mole) and tetrakis-dimethylamino-zirconium (7.64 g : 0.0286 mole) gave a bright yellow solid product (13.3 g : 100% yield). Found: Zr, 19.7%; basic N, 5.87%. $Zr(NMe_2)_2(OC_9H_6N)_2$ requires Zr, 19.5%; basic N, 5.99%.

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A sample was crystallised from benzene to give small yellow crystals. Found: Zr, 19.6%; basic N, 5.95%.

4. Bis-dimethylamino-mono-quinolin-8-oxy-aluminum.

In like manner 8-hydroxyquinoline (4.64 g : 0.0320 mole) and tris-di-methylamino-aluminum (5.08 g : 0.0320 mole) gave a benzene insoluble bright yellow solid product (8.20 g : 99% yield). Found : Al, 10.2%; basic N, 10.8%. $Al(OC_9H_6N)(NMe_2)_2$ requires Al, 10.40%; basic N, 10.80%.

A sample (3.22 g) was heated under high vacuum, a white sublimate appeared from 120°-200°/0.1 mm (0.62 g). Found : Al, 14.1%. A yellow residue remained.

5. Bis-diethylamino-bis-quinolin-8-oxy-vanadium^{IV}.

In like manner 8-hydroxyquinoline (5.64 g : 0.0388 mole) and tetrakis-diethylamino-vanadium^{IV} (6.58 g : 0.0194 mole) gave a benzene soluble dark brown solid (9.48 g : 100% yield). Found : V, 10.3%; basic N, 5.67%; Ratio V/N :: 1.0/2.00; Valency, 4.02, 4.04. $V(NEt_2)_2(OC_9H_6N)_2$ requires V, 10.54%; basic N, 5.79%.

6. Reaction between 8-hydroxyquinoline and pentakis-dimethylamino-tantalum in benzene.

In like manner 8-hydroxyquinoline (4.72 g : 0.0325 mole) and pentakis-dimethylamino-tantalum (4.35 g : 0.0108 mole) gave a benzene soluble dark maroon solid product (8.38 g). Found : Ta, 23.5%; basic N, 2.68%; Ratio Ta/N :: 1.0/1.47.

7. Reaction between tetrakis-quinolin-8-oxy-zirconium and tetrakis-diethylamino-zirconium in benzene.

Tetrakis-diethylamino-zirconium (3.15 g : 0.00830 mole) and tetrakis-quinolin-8-oxy-zirconium (5.54 g : 0.00830 mole) were refluxed in benzene (100 ml) for five hours. No apparent reaction ensued and the $Zr(OC_9H_6N)_4$

remained insoluble throughout. The mixture was cooled and the solid decanted off, washed with benzene (50 ml) and dried at $300°/0.1$ mm. The infrared spectrum of this product was identical with an authentic sample of $Zr(OC_9H_6N)_4$.

d) Miscellaneous reactions.

1. Preparation of tris-dimethylamino-mono-cyclopentadienyl-titanium.

Cyclopentadiene (16.0 g : excess) in ether (20 ml) was added dropwise to a stirred and cooled solution of tetrakis-dimethylamino-titanium (25.5 g) in ether (120 ml). An exothermic reaction took place and the solution became deep red; left overnight at room temperature and the solvent then evaporated to give a deep red solid product (30.1 g). This was distilled under high vacuum to give a deep red liquid distillate soon crystallizing (25.3 g : 91% yield) m.p. ca. $60°$, b.p. $110°/0.1$ mm. Found : Ti, 19.7%; $Ti(NMe_2)_3(C_5H_5)$ requires Ti, 19.5%.

2. Reaction between cyclopentadienylsodium and bis-diethylamino-titanium dichloride.

Cyclopentadienylsodium (0.24 gm-equiv; prepared from cyclopentadiene and sodium metal sand) in tetrahydrofuran (100 ml) was added dropwise over 15 minutes to a stirred solution of bis-diethylaminotitanium dichloride (31.0 g: 0.118 mole) in pet. ether (80 ml). The resulting reddish-brown mixture was left overnight at room temperature, then filtered and the solvents evaporated from the filtrate to give a deep red pasty solid (20.0 g : 42% yield). This was distilled under high vacuum to give a deep red liquid (3.30 g) b.p. $140°-160°/0.1$ mm. Found : Ti, 15.6%. $Ti(NEt_2)_2(C_5H_5)_2$ requires Ti, 14.86%.

A black decomposed residue remained which contained a considerable quantity of lower valent titanium.

3. Reaction between acetylacetone and tetrakis-dimethylamino-titanium in benzene.

Acetylacetone (7.91 g : 0.0791 mole), purified by fractional distill-ation, in benzene (20 ml) was added dropwise to a stirred solution of tetra-kis-dimethylamino-titanium (8.86 g : 0.0395 mole) in benzene (100 ml) over 30 minutes. The solution immediately became deep red and considerable heat was evolved. Stirred for a further 45 minutes, solvent removed under reduced pressure and the resultant thick red liquid product heated at $50^{\circ}/0.1$ mm for 2 hours (11.5 g: theory 13.2 g).

Heated under high vacuum; a pale yellow low melting solid (2.43 g) distilled at $95^{\circ}-110^{\circ}/0.1$ mm. Found: Ti, zero; basic N, 3.99%.

4. Reaction between acetylsalicylic acid and tetrakis-dimethylamino-titanium in benzene.

Acetylsalicylic acid (14.3 g : 0.0794 mole) suspended in benzene (70 ml) was added slowly to a stirred solution of tetrakis-dimethylamino-titanium (8.92 g : 0.0397 mole) in benzene (110 ml). An exothermic reaction ensued and a "sticky" yellow precipitate was formed during this time. Refluxed 45 minutes during which time the precipitate melted and formed an immiscible layer. The latter was removed by decantation after cooling and dried under high vacuum to give a fine yellow powdered solid (13.4 g: theory 19.8 g). Found : Ti, 13.9%; basic N, 4.32%; Ratio Ti/N :: 1.0/1.06. $Ti(NMe_2)_2$ $(C_9H_7O_4)_2$ requires Ti, 9.70%; basic N, 5.70%.

5. Preparation of model compounds.

a) Trialkyl(aryl)siloxy- derivatives

1. Tetrakis-trimethylsiloxy-titanium.

Trimethylacetoxysilane(13.0 g : 0.01985 mole) in benzene (20 ml) was added to tetrakis-dimethylamino-titanium (5.31 g : 0.0239 mole) in benzene (100 ml). No immediate reaction ensued but after several minutes a red colour developed and the solution became very warm. Refluxed for two hours during which time the colour changed to pale yellow; left overnight at room temperature, solvent then evaporated and the residue distilled under high vacuum to give a colourless liquid product (4.26 g : 47% yield) b.p. 60°/ 0.1 mm. Found : Ti, 11.8%. Ti(OSiMe$_3$)$_4$ requires Ti, 11.84%.

2. Tetrakis-triethylsiloxy-titanium

Triethylsilanol (10.0 g : 0.0757 mole) in pet. ether (40 ml) was added dropwise to a stirred solution of tetrakis-diethylamino-titanium (4.94 g : 0.0147 mole) in pet. ether (100 ml) over 10 minutes. An exothermic reaction took place and the resulting solution was left overnight at room temperature. The solvent was then evaporated and the residue distilled under high vacuum to give a very pale yellow solid (7.20 g : 85% yield) b.p. 150°/0.1 mm, m.p. ca 110°. Found : Ti, 8.41%; Si, 19.5%. Ti(OSiEt$_3$)$_4$ requires Ti, 8.36%; Si, 19.59%.

3. Tetrakis-triphenylsiloxy-titanium.

Triphenylsilanol (18.0 g : 0.0651 mole) was added to a stirred solution of tetrakis-diethylamino-titanium (4.26 g : 0.0127 mole) in benzene (180 ml). An exothermic reaction took place and a white solid was precipitated; the mixture was stirred at room temperature for one hour, left overnight then filtered. The filtered solid was washed with benzene, then dried at 100°/0.1mm

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for 10 minutes (14.1 g: 97% yield). Found : Ti, 4.18%; Si, 9.72%. Ti(OSiPh$_3$)$_4$ requires Ti, 4.17%; Si, 9.76%.

This product was found to sublime without decomposition at approximately 390°/0.05 mm and melt with decomposition at approximately 490° in air.

4. Tetrakis-triphenylsiloxy-zirconium

In like manner triphenylsilanol (19.0 g : 0.0688 mole) and tetrakis-diethylamino-zirconium (6.50 g : 0.0171 mole) gave a white insoluble solid (17.8 g : 87% yield). Found : Zr, 7.71%; Si, 9.40%. Zr(OSiPh$_3$)$_4$ requires Zr, 7.65%; Si, 9.42%.

The sublimation point for this product was about 400°/0.05 mm without decomposition and the melting point about 450° in air with decomposition.

5. Tris-triphenylsiloxy-aluminum

In like manner triphenylsilanol (20.0 g : 0.0724 mole) and tris-dimethyl-amino-aluminum (3.71 g : 0.0233 mole) gave a white insoluble solid (15.0 g : 75% yield.). Found : Al, 3.14%, Si, 9.91%. Al(OSiPh$_3$)$_3$ requires Al, 3.16%; Si, 9.88%.

This compound melted at 193°-5° and the approximate distillation point was 300°/0.1 mm without decomposition. The decomposition point in air was about 350°.

6. Tetrakis-triphenylsiloxy-vanadium^{IV}

In like manner triphenylsilanol (21.0 g : 0.0761 mole) and tetrakis-diethylamino-vanadium^{IV} (6.29 g : 0.0185 mole) gave a pale blue insoluble solid (15.4 g : 72% yield). Found : V, 4.31%; Si, 9.65%. V(OSiPh$_3$)$_4$ requires V, 4.42%; Si, 9.75%. A sample of this product melted with rapid and complete decomposition at about 360°/0.1 mm.

7. Pentakis-triphenylsiloxy-tantalum

In like manner triphenylsilanol (11.3 g : 0.0413 mole) and pentakis-dimethylamino-tantalum (3.27 g : 0.00815 mole) gave a product that was soluble in hot benzene but partially crystallized on cooling. Most of the benzene was evaporated and ether (100 ml) added; the white solid precipitate was then filtered off and dried at 200°/0.1 mm for 30 minutes (11.0 g : 87% yield). Found : Ta, 11.5%; Si, 9.05%. Ta(OSiPh$_3$)$_5$ requires Ta, 11.61%; Si, 9.01%.

This compound (17.2 g) was heated at 0.1 mm pressure. No change occurred to 420°, at this temperature fusion to a light brown liquid took place and a yellow liquid distilled. The residue remained liquid for 60 minutes at 420°-440° and the distillate was collected during this time; the latter soon solidified to a light brown solid. After a further 30 minutes the residue had solidified to a dark brown solid (9.77 g). Found : Ta, 18.5%; Si, 12.1%; Ratio Ta/Si :: 1.0/4.20.

Distillate (6.00g). Found : Ta, 3.66%; Si, 6.17%; Ratio Ta/Si :: 1.0/10.9.

8. Tris-triphenylsiloxy-vanadate

Isopropylvanadate (4.11 g : 0.0168 mole) and triphenylsilanol (15.0 g : 0.0543 mole) were refluxed in benzene (150 ml) under a short fractionating column. The isopropyl alcohol-benzene binary azeotrope appeared immediately at the column head and was removed during 30 minutes reflux; benzene was then removed slowly over a further 45 minutes. The solvent was then evapor-ated, replaced with ether (100 ml) and the mixture filtered. The resulting white solid was dried at 180°/0.1 mm for 60 minutes (12.0 g : 80% yield). Found : V, 5.72%; Si, 9.49%. VO(OSiPh$_3$)$_3$ requires V, 5.70%; Si, 9.43%.

This compound had a melting point of 213°-15° and distilled without

decomposition at about $330^\circ/0.1$ mm. Decomposition occurred suddenly at about 400° in air.

b) (Quinolin-8-oxy) (triphenylsiloxy) - metal derivatives.

1. Bis-quinolin-8-oxy-bis-triphenylsiloxy-titanium

8-hydroxyquinoline (5.54 g : 0.0385 mole) in benzene (40 ml) was added dropwise over 15 minutes to a stirred solution of tetrakis-diethylamino-titanium (6.42 g : 0.0191 mole) in benzene (80 ml). The mixture was stirred for 15 minutes after the addition and triphenylsilanol (10.5 g : 0.0381 mole) in benzene (50 ml) then added dropwise over 15 minutes. The resultant orange solution was left overnight at room temperature and turned yellow during this time. The solvent was evaporated to give a bright yellow solid (16.2 g : 97% yield) m.p. 182°-90°. Found : Ti, 5.78%. Si, 6.40%. $Ti(OSiPh_3)_2(OC_9H_6N)_2$ requires Ti, 5.40%; Si, 6.33%.

A sample was crystallized from benzene-hexane and gave a bright yellow crystalline solid m.p. 187°-90°. Found : Ti, 5.42%; Si, 6.31%.

The product could be distilled without decomposition at approximately $330^\circ/0.1$ mm and decomposed in air at about 460°.

2. Bis-quinolin-8-oxy-bis-triphenylsiloxy-zirconium

In like manner 8-hydroxyquinoline (9.92 g : 0.0680 mole), tetrakis-diethylamino-zirconium (12.8 g : 0.0340 mole) and triphenylsilanol (18.7 g : 0.0680 mole) gave a bright yellow crystalline solid from benzene (10.0 g : 32% yield) m.p. 202°-05°. Found : Zr, 9.87%; Si, 5.99%. Evaporation of the mother liquor to low bulk and the addition of hexane gave a granular yellow solid precipitate which was filtered off and dried under high vacuum (19.0 g : 61% yield) m.p. 198°-201°. Found Zr, 9.83%; Si, 6.00%. $Zr(OSiPh_3)_2(OC_9H_6N)_2$ requires Zr, 9.80%; Si, 6.04%.

The first crystalline product distilled without decomposition at about 340°/0.05 mm and had a decomposition temperature of about 490° in air.

3. Mono-quinolin-8-oxy-bis-triphenylsiloxy-aluminum. I

In like manner 8-hydroxyquinoline (6.05 g : 0.0417 mole) tris-dimethyl-amino-aluminum (6.63 g : 0.0417 mole) and triphenylsilanol (23.0 g :0.0834 mole) gave a bright yellow solid product after removal of the solvent from the reaction mixture and this was heated to its fusion point (210°) at 0.1 mm pressure for 5 minutes. On cooling a brittle yellow solid resulted (29.8 g : 99% yield) m.p. 210°. Found : Al, 3.76%, Si, 7.80%. $Al(OSiPh_3)_2(OC_9H_6N)$ requires Al, 3.74%; Si, 7.78%.

The compound distilled with considerable decomposition at about 380°-410°/0.1 mm.

4. Tris-quinolin-8-oxy-bis-triphenylsiloxy-tantalum

In like manner 8-hydroxyquinoline (7.75 g : 0.0534 mole) pentakis-di-methylamino-tantalum (7.15 g : 0.0178 mole) and triphenylsilanol (9.85 g : 0.0357 mole) gave a bright yellow solid product on evaporation of the reaction mixture, this was heated to its fusion point (120°) under high vacuum for 5 minutes (20.2 g : 98% yield). Found : Ta, 15.4%; Si, 4.95%. $Ta(OSiPh_3)_2(OC_9H_6N)_3$ requires Ta, 15.54%; Si, 4.83%.

On heating a sample under high vacuum, 8-hydroxyquinoline sublimed from 135° and rapid decomposition occurred at 145°.

5. Mono-quinolin-8-oxy-bis-triphenylsiloxy-aluminum. II

8-hydroxyquinoline (0.73 g : 0.00503 mole) and tris-triphenylsiloxy-aluminum (4.28 g : 0.00503 mole) were heated in benzene (70 ml) to the boil-ing point. An immediate yellow coloration developed; after cooling, ether (50 ml) was added and the mixture filtered to give a yellow solid product

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which was heated to the fusion point (210°) under high vacuum for 5 minutes
(3.34 g : 92%). Found: Al, 3.78%; Si, 7.77%. Al(OSiPh$_3$)$_2$(OC$_9$H$_6$N) requires
Al, 3.74%; Si, 7.78%.

6. Mono-quinolin-8-oxy-bis-triphenylsiloxy-vanadate.

In like manner 8-hydroxyquinoline (1.19 g : 0.00819 mole) and tris-
triphenylsiloxy-vanadate (7.32 g : 0.00819 mole) gave a dark green cryst-
alline solid after filtration from benzene-ether (5.37 g : 86% yield) m.p.
180°-81°. Found: V, 6.70%; Si, 7.33%. VO(OSiPh$_3$)$_2$(OC$_9$H$_6$N) requires V, 6,69%;
Si, 7.37%.

The distillation temperature was about 320°/0.05 mm without decomposition
and the decomposition point was about 330° in air.

7. Reaction between triphenylsilanol and bis-diethylamino-bis-quinolin-
   8-oxy-vanadium^{IV}

8-hydroxyquinoline (4.25 g : 0.0293 mole) in benzene (80 ml) was added
dropwise over 20 minutes to a stirred solution of tetrakis-diethylamino-
vanadium^{IV} (4.96 g : 0.0146 mole) in benzene (80 ml). The mixture was stirred
for a further 20 minutes after the addition then triphenylsilanol (8.07 g :
0.0293 mole) was added over 5 minutes. A slightly exothermic reaction took
place; the mixture was refluxed for one hour and the solvent then evaporated
to give a dark greenish-brown solid (14.0 g : theory 13.0 g). Ether (150 ml)
was added and the mixture filtered to give a khaki powdered solid (9.00 g).
Found : V, 7.83%; Si, 3.96%; Ratio V/Si :: 1.0/0.92. V(OSiPh$_3$)$_2$(OC$_9$H$_6$N)$_2$
requires V, 5.72%; Si, 6.31%.

c) Other model compounds

1. Bis-quinolin-8-oxy-bis-triethysiloxy-titanium. I

Triethylsilanol (2.96 g : 0.0224 mole) in bnezene (40 ml) was added

dropwise over 30 minutes to a stirred solution of tetrakis-diethylamino-titanium (3.76 g : 0.0112 mole) in benzene (100 ml). The yellow solution was stirred at room temperature for a further 30 minutes then 8-hydroxy-quinoline ((3.24 g : 0.0224 mole) in benzene (40 ml) added dropwise. The colour changed from yellow to orange-red then back to yellow after the addition. Evaporation of the solvent gave a thick yellow liquid soon solid-ifying to a yellow solid (6.47 g : 97% yield). m.p. $132^{\circ}-5^{\circ}$. Found: Ti, 8.03%; Si, 9.21%. $Ti(OSiEt_3)_2(OC_9H_6N)_2$ requires Ti, 8.00%; Si, 9.38%.

2. Bis-quinolin-8-oxy-bis-triethylsiloxy-titanium II

8-hydroxyquinoline (3.13 g : 0.0216 mole) in benzene (50 ml) was added dropwise to a stirred solution of tetrakis-diethylamino-titanium (3.62 g : 0.0108 mole) in benzene (80 ml). The deep red solution was stirred for 30 minutes then triethylsilanol (2.90 g : 0.0218 mole) in benzene (30 ml) added dropwise over 30 minutes. The colour changed to yellow and the solution was allowed to stand for a further 30 minutes. Evaporation of the solid gave a thick yellow liquid soon solidifying to a yellow solid (6.40 g : 99% yield). Found: Ti, 8.47%; Si, 9.35%.

Distilled (4.07 g) under high vacuum giving an orange distillate solid-ifying to a yellow solid (3.50 g) m.p. $133^{\circ}-5^{\circ}$, b.p. ca. $240^{\circ}/0.1$ mm. Found : Ti, 8.09%; Si, 9.50%; C, 60.14%; H, 7.10%; N, 4.68%. $Ti(OSiEt_3)_2(OC_9H_6N)_2$ requires Ti, 8.00%; Si, 9.38%; C, 60.18%; H, 7.07%; N, 4.68%.

3. Bis-quinolin-8-oxy-bis-triethylsiloxy-zirconium

In like manner 8-hydroxyquinoline (4.52 g : 0.0312 mole), tetrakis-diethylamino-zirconium (5.90 g : 0.0156 mole) and triethylsilanol (4.12 g : 0.0312 mole) gave a yellow solid product which was distilled under high vacuum to give an orange distillate soon solidifying to a yellow solid

(8.00 g : 80% yield) m.p. 139°-41°, b.p. ca 240°/0.1 mm. Found : Zr, 14.0%;
Si, 8.79%. $Zr(OSiEt_3)_2(OC_9H_6N)_2$ requires Zr, 14.05%; Si, 8.75%.

4. Tris-quinolin-8-oxy-aluminum

8-hydroxyquinoline (9.40 g : 0.0648 mole) in benzene (100 ml) was added
over 10 minutes to a stirred solution of tris-dimethylamino-aluminum (3.41 g :
0.0214 mole) in benzene (80 ml). An exothermic reaction took place and a
yellow precipitate was formed; refluxed for 1 hour, left overnight then
filtered. The bright yellow solid product was dried at 200°/0.1 mm for 15
minutes (9.00 g : 92% yield) m.p. ca 350°. Found : Al, 5.85%; basic N, zero.
$Al(OC_9H_6N)_3$ requires Al, 5.87%.

5. Tetrakis-quinolin-8-oxy-zirconium

In like manner 8-hydroxyquinoline (16.5 g : 0.114 mole) and tetrakis-
diethylamino-zirconium (10.7 g : 0.0282 mole) gave a bright yellow insoluble
product which was dried at 340°/0.1 mm for 30 minutes (17.0 g : 90% yield)
m.p. ca 420°. Found : Zr, 13.7%; basic N, zero; C, 64.1% H, 3.63%; N, 8.36%.
$Zr(OC_9H_6N)_4$ requires Zr, 13.66%; C, 64.74%; H, 3.62%; N, 8.39%.

6. Preparation of polymers

a) Poly-trialkyl(aryl)siloxy-metallo-phenylsiloxanes

1. Poly-bis-(trimethylsiloxy)-titano-phenylsiloxane

Diphenylsilanediol (9.45 g : 0.0437 mole) was added over 10 minutes to
a stirred solution of bis-trimethylsiloxy-bis-dimethylamino-titanium (13.7 g:
0.0437 mole) in ether (180 ml). A small amount of heat was evolved and a
clear pale yellow solution resulted. Removal of the solvent under reduced
pressure gave a hetrogenous product consisting of an opague gel dispersed in
a pale yellow liquid (19.2 g : 99% yield).

On heating under high vacuum a colourless liquid distillate was obtained

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(4.70 g : 53% yield based on -OSiMe$_3$ content of original product) b.p. 50-200°/0.1 mm. Found : Ti, 11.5%; Si, 26.4%. Ti(OSiMe$_3$)$_4$ requires Ti, 11.84%; Si, 27.77%.

A gummy brown residue remained. Found : Ti, 10.8%; Si, 17.4%; Ratio Ti/Si :: 1.0/2.74. This (5.70 g) was further heated under high vacuum and a dark liquid distillate was obtained (2.50 g) b.p. 200°-500°/0.1 mm. Found: Ti, 4.26%; Si, 19.3%; Ratio Ti/Si :: 1.0/7.8.

2. Poly-bis-(triethylsiloxy)-titano-phenylsiloxane

Diphenylsilanediol (11.9 g : 0.0550 mole) was added over one hour to a stirred solution of bis-triethylsiloxy-bis-diethylamino-titanium (25.0 g : 0.0550 mole) in benzene (250 ml). The resultant pale green solution was refluxed for 2 hours, left overnight and the solvent then evaporated to give a viscous brown liquid product which was heated to 100°/0.1 mm for 10 minutes (29.0 g : 100% yield).

A sample (27.0 g) was heated under high vacuum and a colourless liquid, soon solidifying to a waxy solid, distilled (7.00 g : 45% yield based on total -OSiEt$_3$ content of original product). The infrared spectrum of this distillate was identical with that of an authentic sample of Ti(OSiEt$_3$)$_4$.

3. Poly-bis-(triphenylsiloxy)-titano-phenylsiloxane

Diphenylsilanediol (9.30 g : 0.0430 mole) was added over 15 minutes to a stirred solution of bis-triphenylsiloxy-bis-diethylamino-titanium (31.9 g : 0.0430 mole) in benzene (250 ml). A white precipitate formed soon after the addition and, after refluxing the mixture for several hours, this was filtered off and dried at 60°/0.1 mm for two hours (26.3 g : 77% yield). Found : Ti, 5.12%; Si, 9.82%; Ratio Ti/Si :: 1.0/3.27. {Ti(OSiPh$_3$)$_2$-O-SiPh$_2$-O}$_n$ requires Ti, 5.89%; Si, 10.37%.

The filtrate was evaporated and the pale yellow powdered residue dried at $50^{\circ}/0.1$ mm for two hours (7.90 g : 23% yield). Found : Ti, 5.10%; Si, 11.3%; Ratio Ti/Si :: 1.0/3.82.

The filtered solid (15.1 g) was heated to $450^{\circ}/0.1$ mm for 75 minutes; a white sublimate was removed from 380° upwards (2.36 g). Found : Ti, 4.03%; Si, 10.0%. $Ti(OSiPh_3)_4$ requires Ti, 4.16%; Si, 9.77%. On cooling a pale yellow powdered solid remained (12.6 g). Found : Ti, 5.65%; Ai, 10.3%; Ratio Ti/Si :: 1.0/3.09.

4. Poly-trimethylsiloxy-alumino-phenylsiloxane

Diphenylsilanediol (12.2 g : 0.0565 mole) was added over 5 minutes to a stirred solution of mono-trimethylsiloxy-bis-dimethylamino-aluminum (11.4 g: 0.0565 mole) in benzene (180 ml). An exothermic reaction took place and the resultant clear solution was refluxed for one hour then left overnight at room temperature. Evaporation of the solvent gave a light brown solid product which was heated to its fusion point (120°) at 0.1 mm pressure for 10 minutes until gaseous evolution had ceased. On cooling a brown brittle solid product was obtained (18.4 g : 100% yield). Found : Al, 8.00%; Si, 17.1%; Ratio Al/Si :: 1.0/2.06. $\{Al(OSiMe_3)-O-SiPh_2-O\}_n$ requires Al, 8.16%; Si, 17.00%.

Heated (16.0 g) under high vacuum. A white sublimate formed from $180^{\circ}-240^{\circ}/0.1$ mm (2.41 g). Found : Al, 9.31%; Si, 27.4%. $Al(OSiMe_3)_3$ requires Al, 9.17%; Si, 28.6%.

The residue was heated further; a few drops of liquid distillate were collected at $320^{\circ}-360^{\circ}/0.1$ mm and the residue slowly solidified to a light brown solid (9.67 g). Found : Al, 9.85%; Si, 13.8%; Ratio Al/Si :: 1.0/1.35.

5. Poly-triphenylsiloxy-alumino-phenylsiloxane

Diphenylsilanediol (13.4 g : 0.0620 mole) was added to a stirred solution

of mono-triphenylsiloxy-bis-dimethylamino-aluminum (24.2 g : 0.0620 mole).

Exothermic reaction and clear yellow solution formed. Refluxed for one hour,

left overnight and the solvent then evaporated to give a brown solid which

was heated at its fusion point (200°) at 0.1 mm pressure until gaseous evo-

lution ceased (30 minutes). On cooling a brittle light brown solid was ob-

tained (30.5 g : 95% yield) Found: Al, 5.17%; Si, 10.8%; Ratio Al/Si :: 1.0/

2.01. $(Al(OSiPh_3)-O-SiPh_2-)_n$ requires Al, 5.22%; Si, 10.87%.

Heated (20.0 g) under high vacuum. A very viscous brown liquid distillate

was obtained at 300°-400°/0.1 mm (4.00 g). Found : Al, zero; Si, 11.3%.

$(Ph_3Si)_2O$ requires Si, 10.5%.

A light brown powdery residue, insoluble in commom organic solvents,

remained (11.3 g). Found : Al, 8.95%; Si, 10.3%; Ratio Al/Si :: 1.0/1.11.

b)   Poly-quinolin-8-oxy-metallo-phenylsiloxanes

1.   Poly-bis-(quinolin-8-oxy)-titanophenylsiloxane I

8-hydroxyquinoline (5.74 g : 0.0396 mole) in benzene (70 ml) was added

dropwise over 20 minutes to a stirred solution of tetrakis-diethylamino-ti-

tanium (6.64 g : 0.0198 mole) in benzene (70 ml). The red solution was

stirred for two hours and diphenylsilanediol (4.27 g : 0.0198 mole) then

added over 10 minutes. A clear red solution had formed immediately after

the addition but on continued stirring this changed to yellow and a yellow

solid was precipitated. The mixture was refluxed for one hour, left over-

night then filtered and the bright yellow solid precipitate dried under

high vacuum at room temperature (10.0 g : 95% yield). Found : Ti, 8.32%;

Si, 4.54%; Ratio Ti/Si :: 1.0/0.93.

Heated (1.91 g) under 0.1 mm. No change to 320°at which temperature

fusion occurred and gaseous products were liberated. After 10 minutes cooled

to give brittle hard orange-brown solid (1.69 g). Found : Ti, 9.18%; Si, 5.33%. Ratio Ti/Si :: 1.0/0.99. $\{Ti(OC_9H_6N)_2-O-SiPh_2-O\}_n$ requires Ti, 8.70%, Si, 5.10%.

2. Poly-bis-(quinolin-8-oxy)titanophenylsiloxane II

In like manner 8-hydroxyquinoline (13.8 g : 0.0962 mole) tetrakis-di-ethylamino-titanium (16.0 g : 0.0476 mole) and diphenylsilanediol (9.85 g : 0.0476 mole) gave a yellow product which was heated to its fusion point (310°) at 0.1 mm until gaseous evolution ceased (30 minutes). On cooling a brittle orange-brown solid product was obtained (26.0 g : 100% yield). Found : Ti, 8.75%; Si, 5.06% ; C, 64.4%; H, 3.94%; N, 5.19%. $\{Ti(OC_9H_6N)_2-O-SiPh_2-O\}$ requires Ti, 8.70%; Si, 5.10%; C, 65.45%; H, 4.03%; N, 5.09%

A sample (8.38 g) was reheated under high vacuum and a red distillate was collected from 350°-400°/0.1 mm (2.13 g). Found : Ti, 3.48%; Si, 6.05%; Ratio Ti/Si :: 1.0/2.97. A black decomposed residue remained (5.76 g).

3. Poly-bis-(quinolin-8-oxy)-titano-phenylsiloxane III

8-hydroxyquinoline (9.48 g : 0.0654 mole) in T.H.F. (50 ml) was added dropwise to a stirred solution of tetrakis-dimethylamino-titanium (7.33 g : 0.0327 mole) in T.H.F. (100 ml) over 20 minutes. The deep red solution was refluxed for 20 minutes to remove dimethylamine and diphenylsilanediol (7.07 g: 0.0327 mole) in T.H.F. (50 ml) then added dropwise over 40 minutes to the cooled and vigorously stirred solution. A yellow precipitate started to separate when about 2/3 of the diol had been added. The mixture was refluxed for 5 hours, left overnight and filtered; the bright yellow solid was dried at 100°/0.1 mm for 10 minutes (15.5 g : 80% yield). Found : Ti, 8.21%; Si, 4.56%; Ratio Ti/Si :: 1.0/0.95.

The filtrate was evaporated to give an orange-yellow solid (3.90 g : 20% yield). Found : Ti, 7.26%; Si, 5.94%; Ratio Ti/Si :: 1.0/1.39.

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A sample of the precipitate (12.4 g) was heated to its fusion point under high vacuum ($350°/0.1$ mm) for 10 minutes. Cooled to give brittle light brown solid (11.4 g). Found : Ti, 8.90%; Si, 4.97%; Ratio Ti/Si :: 1.0/0.95. A sample of this product (7.68 g) was boiled in T.H.F. (100 ml) for 5 minutes, cooled and filtered to give a bright yellow solid (0.50 g). The solvent was evaporated from the filtrate and the residue heated to its fusion point under high vacuum ($200°/0.1$ mm) for 5 minutes. Cooled to give a red-brown solid (7.10 g) Found : Ti, 8.72%; Si, 5.14%; Ratio Ti/Si :: 1.0/1.00.

4. Poly-bis-(quinolin-8-oxy)-zircono-phenylsiloxane I

8-hydroxyquinoline (23.1 g : 0.159 mole) in benzene (150 ml) was added dropwise to a stirred solution of tetrakis-diethylamino-zirconium (30.1 g : 0.0795 mole) in benzene (200 ml) over 30 minutes. The yellow crystalline solid in a yellow solution was stirred for a further 30 minutes and diphenyl-silanediol (17.2 g : 0.0795 mole) added over 10 minutes. A bright yellow precipitate in a yellow solution resulted and this was refluxed for one hour, left overnight and the solvent evaporated. The yellow solid residue was then heated to its fusion point ($320°$) under high vacuum until gaseous evolution ceased (30 minutes). On cooling a brittle yellow-brown solid was obtained (42.0 g : 90% yield). Found : Zr, 16.8%, Si, 5.04%; Ratio Zr/Si :: 1.0/0.98. $(Zr(OC_9H_6N)_2-O-SiPh_2-O)_n$ requires Zr, 15.36%; Si, 4.73%.

5. Poly-bis-(quinolin-8-oxy)-zircono-phenylsiloxane II

8-hydroxyquinoline (10.56 g : 0.0728 mole) in T.H.F (50 ml) was added dropwise over 30 minutes to a stirred and cooled solution of tetrakis-dimethyl-amino-zirconium (9.72 g : 0.0364 mole) in T.H.F. (80 ml). The mixture was refluxed for 10 minutes after the addition, cooled and diphenylsilanediol (7.85 g : 0.0364 mole) in T.H.F (50 ml) added dropwise over 50 minutes.

A yellow precipitate formed just before the end of the addition and,after refluxing the mixture for 6 hours,this was filtered off and dried at $140^\circ/$ 0.1 mm for 10 minutes (5.32 g : 25% of total product). Found : Zr, 14.0%; Si, zero. $Zr(OC_9H_6N)_n$ requires Zr, 13.66%.

The filtrate was evaporated to give a yellow solid which was dried at $150^\circ/0.1$ mm for 10 minutes (16.2 g : 75% of total product). Found : Zr, 16.1%; Si, 6.15%; Ratio Zr/Si :: 1.0/1.24.

A sample (11.9 g) was heated to its fusion point (340°) at 0.1 mm pressure and kept at this temperature for one hour. Cooled to give brittle brownish-yellow solid (11.2 g). Found : Zr, 16.4%; Si, 6.60%; Ratio Zr/Si :: 1.0/1.30.

A sample (4.99 g) was heated at $330^\circ/0.05$ mm for 45 minutes, weight loss 0.03 g. Reheated under high vacuum trace of yellow distillate from 380° and decomposed black non-volatile residue after one hour at $380^\circ-400^\circ$.

6. Poly-quinolin-8-oxy-alumino-phenylsiloxane I

8-hydroxyquinoline (10.7 g : 0.0738 mole) in benzene (100 ml) was added dropwise over one hour to a stirred solution of tris-dimethylamino-aluminum (11.7 g : 0.0738 mole) in benzene (200 ml). Stirred for a further 30 minutes then diphenylsilanediol (0.0738 mole) added over 10 minutes. At the end of the addition the yellow precipitated intermediate had almost dissolved but another yellow precipitate formed almost immediately. The mixture was refluxed for 2 hours, left overnight and the solvent then evaporated; the residue was heated to $320^\circ/0.1$ mm for 10 minutes and on cooling a bright yellow solid resulted (28.3 g : 100% yield). Found: Al, 6.89%; Si, 7.34%; Ratio Al/Si :: 1.0/1.02. $\{Al(OC_9H_6N)-O-SiPh_2-O\}_n$ requires Al, 7.00%; Si, 7.29%.

A sample was heated in air. Darkening started at 330° and fusion with

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total decomposition to a black residue occurred at 390°.

7. Poly-quinolin-8-oxy-alumino-phenylsiloxane II

8-hydroxyquinoline (7.77 g : 0.0536 mole) in T.H.F. (50 ml) was added dropwise to a stirred solution of tris-dimethylamino-aluminum (8.52 g : 0.0536 mole) in T.H.F. (80 ml) over 50 minutes. The mixture was refluxed for 30 minutes, cooled and diphenylsilanediol (11.58 g : 0.0536 mole) in T.H.F. (50 ml) added dropwise over 75 minutes to the vigorously stirred mixture. A bright yellow precipitate resulted and after refluxing for 3 hours this was filtered off and dried at $60^\circ/0.1$ mm for one hour (7.05 g : 31% yield of total product). Found : Al, 7.24%; Si, zero. $Al(OC_9H_6N)_3$ requires Al, 5.87%. $\{Al(OC_9H_6N)-O\}_n$ requires Al, 14.42%.

The filtrate was evaporated to give a yellow solid which was dried at $60^\circ/0.1$ mm for one hour (15.8 g : 69% of total product). Found : Al, 6.12%; Si, 9.10%; Ratio Al/Si :: 1.0/1.43.

A sample (4.50 g) was heated under high vacuum. Yellow brown distillate from $280^\circ/0.1$ mm (2.10 g). Found: Al, 4.96%; Si, 13.0%; Ratio Al/Si :: 1.0/2.51.

8. Poly-bis-(quinolin-8-oxy)-vanado-phenylsiloxane

8-hydroxyquinoline (17.7 g : 0.122 mole) in T.H.F. (80 ml) was added dropwise over 45 minutes to a solution of tetrakis-dimethylamino-vanadium^{IV} (13.9 g : 0.0610 mole) in T.H.F. (80 ml). The deep green solution was re-fluxed for 15 minutes to remove dimethylamine then diphenylsilanediol (13.2g: 0.0610 mole) in T.H.F. (60 ml) added dropwise to the refluxing solution over 60 minutes; a precipitate started to form about half way through the addition and after refluxing for a further 2 hours this was filtered off to give a dark green solid (18.0 g : 60% of total product). Found: V, 13.7%; Si, zero.

$\{V(OC_9H_6N)_n-O\}_n$ requires V, 14.3%.

A sample (12.2 g) was heated under high vacuum and distilled as a dark green liquid at its melting point (10.8 g) b.p. 380°/0.1 mm. Found : V, 13.5%.

The filtrate from the reaction was evaporated to give a green-brown solid (15.1 g : 40% of total product). Found : V, 8.00%; Si, 10.3%; Ratio V/Si :: 1.0/2.33. A sample (7.57 g) of this was heated under high vacuum; fusion occurred at 160° and a dark green distillate appeared at 215°/0.1 mm, this was collected slowly while the temperature rose to 400° (0.65 g : 9% yield). Found : V, 1.85%; Si, 12.2%; Ratio V/Si :: 1.0/11.9.

A black non-volatile residue remained (5.79 g).

c) Poly-bis-(quinolin-8-oxy)titano-alkylsiloxanes

1. Poly-bis-(quinolin-8-oxy)-titanomethylsiloxane

8-hydroxyquinoline (10.95 g : 0.0755 mole) in T.H.F. (50 ml) was added dropwise to a stirred solution of tetrakis-dimethylamino-titanium (8.46 g : 0.0377 mole) in T.H.F. (80 ml) over 30 minutes. Dimethyldiacetoxysilane (6.64 g : 0.0377 mole) in T.H.F. (50 ml) was then added dropwise to this mixture over 60 minutes. The solution remained deep red for 30 minutes after the addition but a yellow solid then started to separate out; the latter was removed by filtration, after the mixture had been refluxed for 5 hours, and dried at 50°/0.1 mm for 30 minutes (0.94 g : 5.2% of total product).

The filtrate was evaporated to give an orange solid which was dried at 50°/0.1 mm for 30 minutes. (17.0 g : 95% of total product). Found : Ti, 9.65% Si, 5.55%; Ratio Ti/Si :: 1.0/0.98. $\{Ti(OC_9H_6N)_2-O-SiMe_2-O\}_n$ requires Ti, 11.23%; Si, 6.59%.

A sample (14.7 g) was heated to its fusion point (190°) at 0.1 mm for two hours. Cooled to give a brittle red-brown solid (13.5 g). Found : Ti,

10.6%; Si, 6.00%; Ratio Ti/Si :: 1.0/0.96.

2. Poly-bis-(quinolin-8-oxy)-titanoethylsiloxane

8-hydroxyquinoline (18.6 g : 0.128 mole) in benzene (100 ml) was added dropwise to a stirred solution of tetrakis-dimethylamino-titanium (14.4 g : 0.0641 mole) in benzene (125 ml) over 25 minutes. The mixture was refluxed for 1 hour to remove dimethylamine, cooled to 0° and diethylsilanediol (7.72 g: 0.0641 mole) in ether (100 ml) added dropwise over 1 $\frac{1}{2}$ hours to the vigorously stirred mixture with the temperature maintained at 0° to - 10° throughout. A yellow precipitate formed and, after refluxing for 3 hours, this was filtered off and dried at $100^\circ/0.1$ mm for 30 minutes (20.3 g : 69% of total product) Found : Ti, 12.4%; Si, 4.42%; Ratio Ti/Si :: 1.0/0.61.

The filtrate was evaporated to give a yellow solid which was dried at $100^\circ/0.1$ mm for 30 minutes (8.96 g : 31% of total product). Found : Ti, 8.58%; Si, 10.9%; Ratio Ti/Si :: 1.0/2.16.

A sample of the precipitate (12.2 g) was heated under high vacuum. A trace of yellow distillate appeared at 250° but not until 380° did an appreciable quantity start to distil; temperature taken to 460°, then cooled. Distillate, orange-yellow solid (1.5 g). Found : Ti, 9.65%; Si, 10.8%; Ratio Ti/Si :: 1.0/1.90.

Residue, brown solid (9.40 g). Found : Ti, 15.2%; Si, zero. $\{Ti(OC_9H_6N)_2-O\}_n$ requires Ti, 13.6%.

d) Poly-quinolin-8-oxy-metalloxanes

1. Poly-bis-(quinolin-8-oxy)-titanoxane

Water (20 ml) was added to a stirred solution of bis-dimethylamino-bis-quinolin-8-oxy-titanium (14.0 g) in T.H.F. (80 ml). A clear yellow solution resulted immediately after the addition but an orange-yellow solid soon pre-

cipitated. After refluxing for one hour the solid was filtered off and dried at $100^{\circ}/0.1$ mm for one hour. (10.9 g : 94% yield). Found : Ti, 13.5%; N, 7.71%; Ratio Ti/N :: 1.0/1.95. $(Ti(OC_9H_6N)_2-O)_n$ requires Ti, 13.6%; N, 7.97%.

2. Poly-bis-(quinolin-8-oxy)-zirconoxane

Water (35 ml) was added to a stirred solution of bis-diethylamino-bis-quinolin-8-oxy-zirconium (35.7 g) in T.H.F. (100 ml). A yellow precipitate formed immediately and this was filtered off after the mixture had been re-fluxed for one hour; dried at $100^{\circ}/0.1$ mm for 30 minutes (24.4 g : 90% yield). Found : Zr, 23.0%. $(Zr(OC_9H_6N)_2-O)_n$ requires Zr, 23.06%.

3. Poly-quinolin-8-oxy-aluminoxane

Water (10 ml) was added to a stirred solution of mono-quinolin-8-oxy-bis-dimethylamino-aluminum (17.7 g) in T.H.F. (120 ml). A yellow precipitate formed and this was filtered off after refluxing the mixture for one hour; dried at $300^{\circ}/0.1$ mm for 75 minutes (12.0 g : 94% yield). Found : Al, 14.3%. $(Al(OC_9H_6N)-O)_n$ requires Al, 14.41%.

4. Poly-quinolin-8-oxy-tantaloxane

Water (20 ml) was added to a stirred solution of tris-quinolin-8-oxy-bis-dimethylamino-tantalum (18.9 g) in T.H.F. (150 ml). The resultant yellow precipitate was filtered off after one hour reflux, and dried at $340^{\circ}/0.1$ mm. A considerable quantity of 8-hydroxyquinoline distilled out from 150° and the heating was continued until this ceased (ca. 30 minutes). A pale yellow powder was obtained (8.00 g : 87% yield). Found : Ta, 48.2%. $(Ta(OC_9H_6N)O_2)_n$ requires Ta, 50.6%.

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