# METAL ALKOXIDES AND DIALKYLAMIDES

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## I. Introduction

Since the metal alkoxides $M(OR)_x$ were first comprehensively reviewed in 1960 (*1*), considerable progress has been maintained and the next major review in 1967 (*2*) quoted over three hundred references. The most significant advances have involved the chemistry of the transition metal alkoxides (*3*) with the emphasis on the ligand field aspects of the alkoxo group (e.g., electronic spectra, magnetism, etc.) and on X-ray crystallographic and NMR structural determinations. Industrial applications (*4*) have been concerned with metal alkoxides as components of soluble Ziegler–Natta catalysts for olefin polymerization and also as sources for the production of pure metal oxides.

The metal dialkylamides $M(NR_2)_x$ are of special interest in that they contain covalent metal–nitrogen bonds and occupy a position between the metal alkoxides and the metal alkyls. The field has not been fully reviewed hitherto. However, excellent reviews have recently appeared on titanium dialkylamides (*5*) and the reactivity of metal–dialkylamido bonds (*6*). A concise review of recent work on transition metal dialkylamides has also been given (*6*). It is clear that this is a rapidly developing field and that metal dialkylamides are synthetic reagents showing considerable versatility.

## II. Metal Alkoxides

In this chapter we shall restrict discussion to the fully substituted alkoxides $M(OR)_x$, with an occasional reference to metal oxide alkoxides $MO_y(OR)_{(x-2y)}$, bearing in mind that the latter class of compounds was recently reviewed (*7*). This excludes from consideration a considerable range of metal compounds containing alkoxo groups, in addition to one or more other types of ligand, viz., $M(OR)_xX_yL_z$ (where X = anionic ligand and L = neutral ligand). In most of these compounds the alkoxo groups play only a subsidiary role in determining the nature of the molecule, whereas in the alkoxides $M(OR)_x$ the alkoxo group is unambiguously the key ligand.

The methods of preparation of metal alkoxides are well established (*1*, *2*, *4*) and have recently been reviewed (*8*). It is considered unnecessary to treat this aspect under a separate heading. Similarly, the basic physical and chemical properties of the metal alkoxides are also firmly established (*1*, *2*, *4*) and these do not require separate consideration other than in a brief restatement in this introduction. Thus, we may deal with the metal alkoxides in a different fashion from previous reviews and concentrate on areas of recent development of the subject.

To summarize rather briefly, the chief chemical properties of metal alkoxides are their characteristic ease of hydrolysis (except for a few notable exceptions) and reactivity with hydroxylic molecules. Physical properties involve a balance between the tendency of the metal to expand its coordination number by utilizing the bridging property of alkoxo groups and the opposition to this by the steric effect of the alkyl group. This results in a wide spectrum of properties ranging from insoluble, nonvolatile, polymeric solids to volatile, monomeric liquids. Some notable progress has been made in the elucidation of the structures of the intermediate oligomeric compounds $[M(OR)_x]_n$.

### A. ALKALI METAL ALKOXIDES

With the current resurgence of interest in the chemistry of the alkali metals it is timely to review the present status of the alkali metal alkoxides. The common assumption that all alkali metal compounds are ionic has been critically reexamined and it is noteworthy that several years ago the covalent nature of alkali metal zirconium alkoxides $MZr_2(OR)_9$ (M = Li, Na, or K) was reported (*9*). Wheatley (*10*) determined the crystal structure of LiOMe and showed it to be an infinite two-dimensional polymer with a layer structure. The environment of the lithium atoms

(Li–O = 1.95 Å) was a squashed tetrahedron (OLiO = 101.7° and 131.1°), while the oxygens were each bonded to four lithiums and a methyl group in a tetragonal-pyramidal configuration with the methyl group taking the apical position. In classical terms the $CH_3O^-$ oxygen has only three pairs of electrons for coordination to four lithium ions, therefore the covalency must involve delocalized bonding typical of electron-deficient structures. Bains (*11*) showed that lithium alkoxides become more soluble (in nonpolar solvents), less polymeric, and more volatile in the following order $LiOEt < LiOPr^i < LiOBu^t$. Thus, the *tert*-butoxide sublimed at 110°/0.1 mm and it was tetrameric in benzene and hexameric in cyclohexane indicative of covalent nature. The proton NMR spectrum of $(LiOBu^t)_n$ showed a single line ($\tau = 8.473$; $CCl_4$ solution) shifted downfield from *tert*-butanol ($\tau = 8.778$) indicating either that all ligands are equivalent or that nonequivalent ligands are engaged in rapid exchange. Independent work by Golovanov *et al.* (*12*) also showed the *tert*-butoxide to be hexameric ($n = 6.4 \pm 0.7$) in cyclohexane, but a higher degree of polymerization was observed ($n = 9.4 \pm 0.9$) in benzene. In order to clarify the behavior in benzene and to check the proposal by Simonov *et al.* (*13*) that polymeric species exist in the vapor (from the similarity of the infrared spectra of the vapor at 180° and the solid) further work was carried out by Hartwell and Brown (*14*). These authors found that solutions in benzene were hexameric and that the mass spectrum at 130° gave fragment ions of the hexamer [e.g., $Li_6(OBu^t)_5(OCMe_2)^+$ and $Li_6(OBu^t)_5{}^+$]. They proposed a structure for $(LiOBu^t)_6$ based on a distorted octahedral cluster of lithiums with triple bridging *tert*-butoxo groups occupying six faces and resulting in $D_{3d}$ symmetry with three-coordinated lithium. Presumably the steric effect of the *tert*-butyl groups prevents the formation of a layer structure similar to $(LiOMe)_\infty$ in which the lithiums are four-coordinated.

X-Ray crystallographic analysis of the tetrameric *tert*-butoxides $[MOBu^t]_4$ (M = K, Rb, or Cs) has shown (*15*) a "cubane" type of structure similar to that exhibited by thallous alkoxides. In the structure (Fig. 1) a tetrahedral cluster of metal atoms is bonded by triple-bridging alkoxo groups whose oxygen atoms occupy positions outside each face of the tetrahedron. The metal is thus three-coordinated and presumably is prevented from attaining the four-coordination found in LiOMe by the steric repulsion of the *tert*-butyl groups. Broad line $^1H$ NMR studies suggested free rotation of the *tert*-butyl groups at temperatures > −20°, but at lower temperatures the rotation is frozen out. Sodium *tert*-butoxide gave crystals of lower symmetry. Weiss (*16*) has also shown that KOMe crystals are tetragonal, and the infinite polymer adopts an interesting double layer structure (Fig. 2) containing two parallel sheets

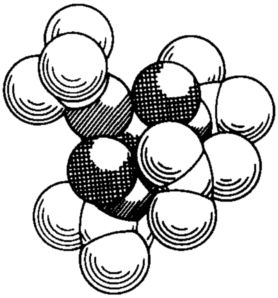


FIG. 1. The $[MOBu^t]_4$ cubane structure. Cross-hatched, M; hatched, O.

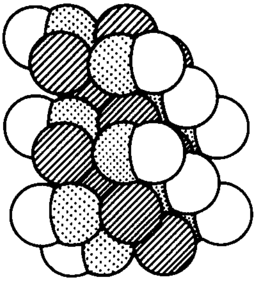


FIG. 2. The structure of [KOMe]. Hatched, K; stippled, O; plain, $CH_3$.

of potassium atoms and two sheets of oxygen atoms with the methyl groups above and below these sheets. Each potassium is five-coordinated to oxygen and each oxygen is six-coordinated (5-potassiums and 1-methyl). On the other hand, sodium methoxide (*17*) is isostructural with lithium methoxide, although partial hydrolysis [e.g., to $Na_3(OH)(OMe)_2$] leads to the more compact potassium methoxide structure.

Conductance measurements on sodium alkoxides dissolved in their parent alcohols (*18*) showed a marked decrease in the order $NaOMe > NaOEt > NaOPr^i \gg NaOBu^t$, with the latter being practically nonconducting. This confirms the covalent nature of sodium *tert*-butoxide, but it would be preferable to study these compounds in the same noninteracting solvent before attempting to compare their relative tendencies toward ionization.

Some interesting results have recently been obtained with alkali metal derivatives of fluorinated alcohols. A novel synthetic method was employed to obtain the trifluoromethoxides of the higher alkali metals (*19*).

$$MF + COF_2 \rightleftharpoons MOCF_3 \qquad (1)$$
$$(M = K, Rb, Cs)$$

The reaction is reversible, but in anhydrous acetonitrile the metal trifluoromethoxides are preferentially formed as stable solids. The reaction was reversed by heating *in vacuo* and thermolysis studies indicated the following order of stability: $CsOCF_3 > RbOCF_3 > KOCF_3$. Further work (*20*) has shown that other perfluoroalkoxides [Eqs. (2) and (3)] may be obtained by suitable choice of perfluorocarbonyl compounds.

$$\begin{gathered} MF + R_fCOF \rightleftharpoons MOCF_2R_f \\ (M = Rb, Cs;\ R_f = CF_3, C_2F_5, C_3F_7) \end{gathered} \tag{2}$$

$$\begin{gathered} MF + (CF_3)_2CO \rightleftharpoons MOCF(CF_3)_2 \\ (M = Rb, Cs) \end{gathered} \tag{3}$$

However, these perfluoroalkoxides were less stable than the trifluoromethoxides, although they were considerably more soluble in polar solvents and enabled $^{19}F$ NMR measurements to be obtained. The thermal instability of these derivatives of primary and secondary perfluoroalkoxides is probably related more to the ease of $\alpha$-fluorine elimination rather than ionic character, and a dramatic increase in stability was found by Dear *et al.* (*21*) for the derivatives of perfluoro-*tert*-butanol. For example, both the lithium and sodium compounds could be melted and distilled under atmospheric pressure [b.p. $LiOC_4F_9$, 218°; $NaOC_4F_9$, 232°] while the potassium compound (decomposes >220°) could be sublimed *in vacuo* (140°/0.2 mm). The compounds $MOC(CF_3)_3$ ($M = Li$, Na, K) were all soluble in ether, acetone, and acetonitrile and could be recrystallized from benzene. Sodium perfluoro-*tert*-butoxide gave a complex mass spectrum (65°), which included fragment ions of the tetramer species, and it crystallizes in the cubic system ($a = 18.32$ Å) with 32 molecules in the unit cell. It is tempting to speculate on the possibility that the structure may involve tetrameric units having the cubane structure exhibited by the *tert*-butoxides. In concluding this section on alkali metal alkoxides it is relevant to note that an X-ray crystal analysis (*22*) has confirmed the tetrameric structure of thallium(I) alkoxides since the methoxide has a distorted "cubane" configuration. Raman and infrared spectra have been obtained for $Tl_4(OR)_4$ ($R = Et, Pr^n$) and a normal coordinate analysis has been carried out for the $Tl_4(OC)_4$ core of the structure (*23*). The high intensity of the lowest frequency Raman bands was indicative of metal–metal bonding and a metal–metal stretching force constant of 0.26 mdyne/Å was deduced.

## B. Alkoxides of Beryllium, Magnesium, Zinc, and the Alkaline Earths

Although the alkyl metal(II) alkoxides, RMOR′, studied by Coates and co-workers do not come strictly within the terms of reference of this chapter, their interesting chemistry and relevance to the alkoxides justifies some comment. Of particular interest are the tetrameric species such as $[\mathrm{MeBeOPr}^i]_4$ (*24*), $[\mathrm{EtMgOBu}^t]_4$ (*25*), $[\mathrm{MeZnOMe}]_4$ (*26*), and $[\mathrm{MeCdOEt}]_4$ (*27*), which are all believed to have the "cubane" structure (Fig. 3) found by X-ray crystal analysis of $[\mathrm{MeZnOMe}]_4$ (*28*). The structure is clearly determined by the triple-bridging alkoxo groups which occupy the four faces of the metal atom tetrahedron. The relationship of these structures to those of the tetrameric alkali metal and thallium(I) alkoxides is striking. It is also noteworthy that in these compounds the Group II metals are attaining four-coordination.

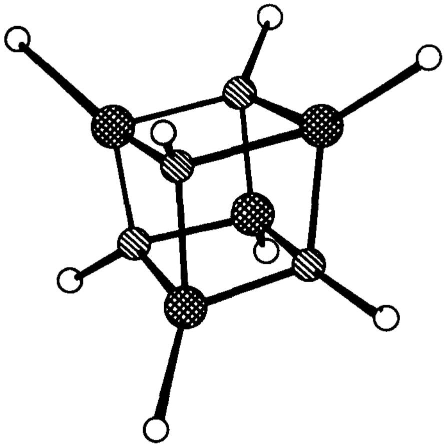
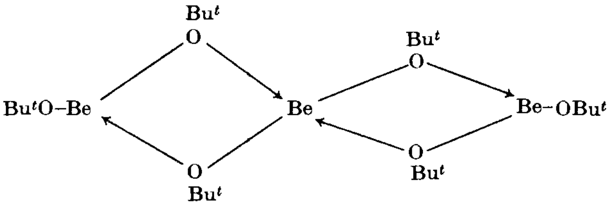


FIG. 3. The $[\mathrm{MeZnOMe}]_4$ cubane structure. Cross-hatched, Zn; hatched, O; plain, $CH_3$.

Beryllium alkoxides $\mathrm{Be(OR)_2}$ of the lower aliphatic alcohols are insoluble, nonvolatile compounds, which are probably infinite polymers with tetrahedrally coordinated beryllium. Mehrotra (*2*, *29*) found that alcoholysis of beryllium alkoxides was very slow. The methoxide and ethoxide have been included in an infrared study of Group II alkoxides (*30*). Splitting of the $\nu_{\mathrm{CO}}$ band was taken to indicate appreciable covalent character in the BeO bonds. Steric hindrance of bulky alkyl groups has a profound effect on intermolecular bonding (*1*), and Coates and Fishwick (*24*) found that di-*tert*-butoxyberyllium prepared by the interesting route [Eq. (4)] was a trimer $Be_3(OBu^t)_6$. The compound (m.p. 112°) was soluble

$$Me_2Be \xrightarrow[\text{or}\ Me_2CO]{Bu^tOH} (MeBeOBu^t)_4 \xrightarrow{Me_2CO} Be_3(OBu^t)_6 \quad (4)$$

in hydrocarbon solvents and could be sublimed *in vacuo* ($100°/10^{-3}$ mm). Its $^1H$ NMR spectrum in benzene gave a single line ($\tau = 8.56$), but in perdeuteriomethylcyclohexane there were two lines ($\tau = 8.60, 8.75$) in a 2:1 ratio and the spectrum was unchanged from 33°–100°. A similar spectrum ($\tau = 8.62, 8.78$; 2:1) was given in carbon tetrachloride and the data are consistent with structure (I) involving a tetrahedrally coordinated beryllium in the middle with two three-coordinated berylliums



(I)

at the ends. In view of the preference for the tetrameric cubane structure by RBeOR′ species (*24*), it would not have been surprising if $Be(OBu^t)_2$ had adopted a similar structure with four bridging and four terminal alkoxo groups. However, it appears that such a structure is prevented by steric hindrance, and it is noteworthy that $(Bu^tBeOBu^t)_2$ is dimeric. Using the more bulky triethylcarbinol produced the dimeric derivative $Be_2(OCEt_3)_4$, which was more volatile (sublimes at $50°–60°/10^{-3}$ mm) and no doubt contains three-coordinated beryllium. Its $^1H$ NMR spectrum showed only one type of alkoxide species and it appears that rapid exchange takes place between terminal and bridging ligands in contrast to behavior of species (I).

The lower aliphatic alkoxides of magnesium $Mg(OR)_2$ are also insoluble and nonvolatile. Infrared studies have been carried out on the methoxide and ethoxide (*30–32*) and interpreted as indicating a considerable degree of covalency in the MgO bonds compared with alkaline earth alkoxides which appear to be more ionic in character. Magnesium methoxide is sparingly soluble in methanol and an unstable solvate can readily be crystallized, but an attempt to determine the crystal structure of $Mg(OMe)_2$ was unsuccessful because the unsolvated compound was amorphous (*31*). Bryce-Smith and Wakefield (*33*) reported that $Mg(OPr^i)_2$ obtained by the action of $Pr^iOH$ on $Bu^nMgOPr^i$ was initially a porous rubbery material which on standing changed to a friable solid. Coates *et al.* (*34*) found that $Mg(OBu^t)_2$ was insoluble in ether, but it reacted with magnesium bromide to produce the dimer $Mg_2(OBu^t)_2Br_2(Et_2O)_2$ which contains four-coordinated magnesium in a structure involving *tert*-butoxo bridges.

Since zinc alkoxides $Zn(OR)_2$ are insoluble, nonvolatile compounds (including the *tert*-butoxide) various preparative methods have been devised. Using the dialkylzinc compound as a starting material, the dialkoxides have been obtained by controlled oxygenation (*35*) or by prolonged reaction with excess alcohol (*36*). Talalaeva *et al.* (*37*) also prepared $Zn(OBu^t)_2$ by means of the reaction of zinc chloride with lithium *tert*-butoxide in ether solution, whereas Mehrotra and Arora (*38*) obtained $Zn(OMe)_2$ and $Zn(OPr^i)_2$ by using the lithium alkoxide in its parent alcohol. They also prepared alkoxides by means of the alcoholysis reaction provided some soluble lithium–zinc double alkoxide was present as a catalyst. It appears, therefore, that zinc alkoxides are all highly polymeric compounds, but the coordination number of the zinc is not known.

X-Ray diffraction analysis of the alkaline earth dimethoxides $M(OMe)_2$ ($M = Ca$, Sr, Ba) revealed hexagonal layer lattices ($CdI_2$) indicative of six-coordination with all methoxo groups triple-bridging through edge-shared octahedra (*31*, *39*). The corresponding ethoxides proved to exhibit a similar structure (*40*). Infrared studies were also carried out on the methoxides and ethoxides (*30–32*), and it was concluded that the ionic character in the M–O bonds increased from Be to Ba with the alkaline earths being predominantly ionic.

### C. Aluminum and Gallium Alkoxides

Aluminum alkoxides have been known since 1876 and have found important uses, yet detailed structural knowledge was lacking until recently and there are still many unsolved problems. Physical data from the earlier literature are unreliable owing to insufficient precautions being taken to prevent hydrolysis and also to a lack of knowledge of the "aging" phenomenon (slow change of the state of aggregation) of certain alkoxides.

For example, aluminum trimethoxide is a solid which is commonly believed to be nonvolatile, but Bradley and Faktor (*41*) found that the pure compound sublimed readily at 240° in a high vacuum. Wilhoit *et al.* (*42*) reinvestigated the alleged polymorphism of aluminum triethoxide and found only one form (m.p. ~ 140°) which was sparingly soluble contrary to earlier reports. Aluminum triisopropoxide, which is the most frequently used derivative, is obtained as a liquid by distillation and may remain supercooled for a long time, although the solid eventually formed has a high melting point. A recent report (*43*) identifies three forms of solid $Al(OPr^i)_3$, a low melting material (m.p. 29.5°) produced by solidification of the liquid (previously heated to 130°–140°) at 0°, the usually obtained compound (m.p. 118°) produced by cooling the liquid at room temperature or by crystallization from isopropanol, and a high melting modification (m.p. ~137°) obtained by keeping the liquid at 60°–65°.

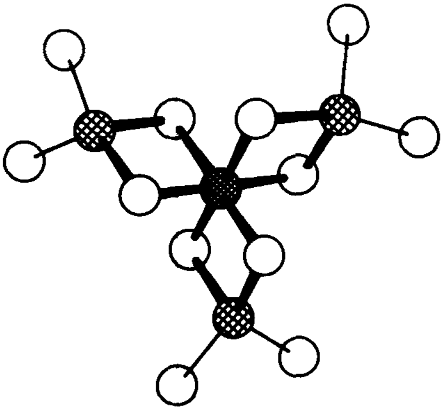


FIG. 4. The structure of $[Al(OR)_3]_4$. Fine cross-hatched, Al (octahedral); hatched, Al (tetrahedral); plain, OR.

The sec-butoxide appears to be the only commonly used alkoxide of aluminum which is a liquid at room temperatures.

Mehrotra (*44*, *45*) made a systematic study of a wide range of aluminum alkoxides and established that straight-chain alkoxides were tetramers $Al_4(OR)_{12}$, the freshly distilled isopropoxide was a trimer which slowly transformed to a tetramer, and the *tert*-butoxide was a dimer $Al_2(OBu^t)_6$. Fieggen (*43*) found that the low melting aluminum isopropoxide was trimeric and the higher melting forms were tetrameric. Cyclic structures involving tetrahedral aluminum were first proposed for the trimers and tetramers, but it was suggested by Bradley (*46*), in order to explain the "aging" phenomenon, that the tetramer might involve a unique structure (Fig. 4) with a central octahedral aluminum and three peripheral tetrahedral aluminum atoms.

The structure (Fig. 4) was confirmed for solutions of the tetramer by Shiner *et al.* (*47*) using $^1H$ NMR, which gave three doublets for the $CH_3$ protons in a 1 : 1 : 2 ratio, because the methyl groups in the bridging isopropoxo groups are nonequivalent. Kleinschmidt (*48*) obtained a $^{27}Al$ NMR spectrum of the tetramer. A broad peak and a sharper peak were found in the ratio 3 : 1, which also agrees with the proposed structure, since the central octahedral aluminum which experiences a higher symmetry electric field than the tetrahedral aluminums should give the sharper signal. Recent $^1H$ NMR work by Oliver and Worrall (*49*) has convincingly shown that the asymmetric central aluminum in the tetrameric $Al_4(OCH_2R)_{12}$ ($R = C_6H_5$, 4-Cl–$C_6H_4$) causes nonequivalence of the methylene protons with consequent appearance of an AB quartet ($J_{AB} = 11$ Hz). In both compounds the methylenes in the bridging groups gave well-defined quartets ($\delta_{AB} = 22.5$ and 21.3 Hz, respectively) at 60 MHz, but the terminal groups gave unresolved singlets. However, at 220 MHz the terminal group methylenes also gave AB quartets ($\delta_{AB} = 0.5$ and 6 Hz converted to 60 MHz equivalents). The larger $\delta_{AB}$ values for the bridging group methylenes were ascribed to their closer proximity to the asymmetric center.

Conclusive evidence that tetrameric $Al_4(OPr^i)_{12}$ maintains its integrity in the vapor phase was reported by Fieggen *et al.* (*50*) from mass spectral studies of $Al_4(OPr^i)_{12}$ and $Al_4(OCDMe_2)_{12}$. The highest mass fragment was due to $Al_4(OPr^i)_{11}(OCHMe)^+$, but more intense peaks were found corresponding to $Al_4(OPr^i)_{11}{}^+$, $Al_4(OPr^i)_{10}(OCMe_2)^+$, $Al_4(OPr^i)_{10}(OCHMeCH_2)^+$, and $Al_4O(OPr^i)_9{}^+$. Fragment ions containing three and two aluminums were also present which could have arisen from trimer and dimer species or by fragmentation of the tetramer species. Metastable peaks corresponding to the loss of $CH_3CHO$, $CH_3CH{:}CH_2$, and $Pr_2{}^iO$ were found, and a plausible fragmentation pattern was deduced. These mass spectral data show that the initial vapor evaporated from $Al_4(OPr^i)_{12}$ at 118° contains predominantly tetrameric species, but Mehrotra (*45*) reported that vapor density measurements showed the vapor to be dimeric. It is therefore desirable to carry out further mass spectral studies to determine whether the composition of vapor depends on its thermal history (e.g. equilibrium studies). This is particularly important in interpreting thermodynamic data such as entropies of vaporization (*44, 45, 51*). By means of reaction calorimetry Wilson (*52*) has derived a value for the enthalpy of formation of tetrameric aluminum isopropoxide, $\Delta H^0{}_f[Al_4(OPr^i)_{12}](C) = -5149.5$ $kJ \cdot mole^{-1}$.

In their NMR studies Shiner *et al.* (*47*) examined the supercooled liquid aluminum isopropoxide, which they confirmed was essentially

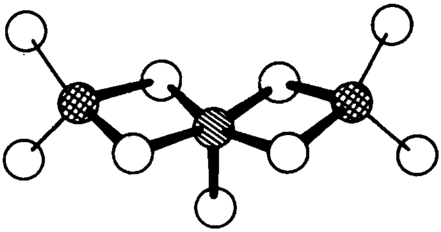
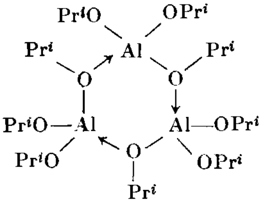


FIG. 5. A structure for $[Al(OR)_3]_3$. Hatched, Al (five-coordinated); cross-hatched, Al (tetrahedral); plain, OR.

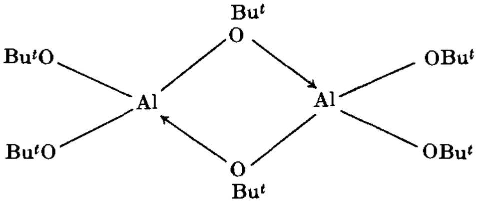
trimeric in solution. Solutions of the trimer in various solvents gave a simple spectrum showing a single isopropoxide species with a chemical shift close to that observed for the terminal groups of the tetramer. At low temperatures the trimer signals broadened and, in some cases, split into two (approximately species 1:2), in accordance with the requirements of a cyclic trimer (II). Since the addition of isopropanol demonstrated that alcoholysis of the trimer was relatively slow (separate signals for trimer and alcohol), it was concluded that the fast exchange of terminal and bridging groups in the trimer was an intramolecular process assisted by the coordinatively unsaturated nature of the four-coordinated aluminums. In the tetramer (Fig. 4) the very slow terminal-bridging exchange is understandably blocked by the presence of the central octahedral aluminum, whereas a cyclic tetramer would be expected to give rapid exchange. Shiner *et al.* (*47*) also noted that solutions of the trimer exhibited a rate of transformation to the tetramer which was much slower than in the molten trimer, and they determined the half-life of the trimer in the melt at 22° to be ca. 50 hr. They also noted that an "aged" sample of the trimer showed weak signals due to yet another species besides the tetramer.



(II)

Kleinschmidt (*48*) proposed an alternative structure for the trimer (Fig. 5) involving a central five-coordinated aluminum bridged to two four-coordinated aluminums, and Fieggen (*43*) has found $^1H$ NMR evidence for chloroform solutions of the trimer, which supports this structure.

The best established dimeric aluminum alkoxide is $Al_2(OBu^t)_6$ (*44*), whose structure (III) was confirmed by $^1H$ NMR (*47*, *53*). The mixed alkoxide $Al(OPr^i)(OBu^t)_2$ is also dimeric (*53*), and recent $^1H$ NMR studies (*54*) suggest that it has the interesting unsymmetrical structure (IV), which contains one asymmetric aluminum atom. However, the spectrum at 60 MHz is poorly resolved and could be interpreted in terms of a mixture of dimer species differing in the constitution of the bridge system. It is clearly desirable to obtain spectra at 220 MHz in more than one solvent to obtain more definitive information. The mass spectrum of this compound (*54*) gave numerous fragment ions containing two aluminum atoms, and the proposed fragmentation pattern was consistent with structure (IV).



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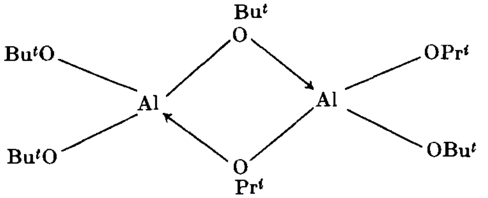


(IV)

Other dimeric species recently reported are $Al_2(OCH_2CCl_3)_6$ (*55*) and $Al_2(OCH_2CH_2Cl)_6$ (*56*) which are of interest because of the ease with which the bridge is cleaved by donor molecules (L) to form complexes $Al(OR)_3L$.

The infrared spectra have been obtained for several aluminum alkoxides [see Mehrotra (*2*) for earlier references], but they have not been particularly helpful from a structural viewpoint. Fieggen (*43*) has compared the infrared and Raman spectra of the tetrameric and trimeric forms of aluminum isopropoxide and has found that they are consistent with the proposed structures.

Aluminum alkoxides are commonly used as catalysts in the Meerwein-Ponndorf–Verley and Tishchenko reactions (*1*, *46*), and the nature of the alkoxide has an important bearing on the mechanism of the reaction. Bearing in mind the complex nature of aluminum alkoxides, Bains and Bradley (*57*) studied the kinetics of the system depicted by Eq. (5).

$$\mathrm{Me_2CO + Al_2(OPr^{i*})_2(OBu^t)_4 \rightleftharpoons Me_2{}^*CO + Al_2(OPr^i)_2(OBu^t)_4} \qquad (5)$$

The course of the reaction was followed by using $^{14}$C-labeled isopropoxo groups, but the kinetics at different temperatures proved to be unexpectedly complex and cast doubts on the accepted mechanism of the Meerwein–Ponndorf–Verley reaction. However, it had been assumed that the dimer structure involved isopropoxide bridges, but recent NMR work (*54*) suggests that structure (IV) is present with both bridging and terminal isopropoxide groups. It is also possible that more than one dimer species is present and the proportions may vary with temperature; hence, the system may not be as simple as was originally envisaged.

Even more compelling evidence refuting the accepted mechanism of the Meerwein–Ponndorf–Verley reaction was forthcoming from the $^1$H NMR studies of Shiner and Whittaker (*58*). They showed that acetone did not break down the polymeric structure of either $\mathrm{Al_3(OPr^i)_9}$ or $\mathrm{Al_4(OPr^i)_{12}}$, and there was no evidence for a monomeric activated complex $\mathrm{(Pr^iO)_3Al(Me_2CO)}$. In the reaction of acetophenone with the isopropoxides [Eqs. (6) and (7)] the rate-determining step was the alcoholysis [Eq. (7)], since the rate of formation of acetone was much

$$\mathrm{C_6H_5COCH_3} + \frac{1}{n}\mathrm{[Al(OPr^i)_3]_n} \rightarrow \frac{1}{n}\mathrm{\{Al[OCH(CH_3)C_6H_5](OPr^i)_2\}_n + Me_2CO} \qquad (6)$$

$$\mathrm{Pr^iOH} + \frac{1}{n}\mathrm{\{Al[OCH(CH_3)C_6H_5](OPr^i)_2\}_n} \rightarrow \frac{1}{n}\mathrm{[Al(OPr^i)_3]_n + C_6H_5(CH_3)CHOH} \qquad (7)$$

greater than that of α-phenylethanol. It was also demonstrated that the trimer $\mathrm{Al_3(OPr^i)_9}$ reacted much faster than the tetramer $\mathrm{Al_4(OPr^i)_{12}}$.

Recent work on the kinetics of the Tishchenko reaction of acetaldehyde with aluminum isopropoxide catalysts (*59*) showed the formation of ethyl acetate to be first-order in catalyst and first-order in acetaldehyde. Surprisingly, the rate constant for the trimer as catalyst was lower than for the tetramer, but isopropyl acetate was also formed and there may be complications owing to simultaneous Meerwein–Ponndorf–Verley reactions.

Alkoxides of gallium(III) have recently been prepared (*60*, *61*) and found to undergo the typical reactions of metal alkoxides.

Gallium trimethoxide is a white, insoluble solid which can be sublimed *in vacuo* (275°–280°/0.4 mm). Other normal alkoxides $Ga(OR)_3$ ($R = Et$, $Pr^n$, $Bu^n$) are more volatile and are tetrameric in solution like the corresponding aluminum derivatives. However, the isopropoxide, a viscous liquid (b.p. 120°/1.0 mm), surprisingly is dimeric. The crystalline dimeric *tert*-butoxide has been shown by $^1H$ NMR (*54*) to have the same structure as $Al_2(OBu^t)_6$ (III).

## D. TRANSITION METAL ALKOXIDES

Alkoxides of the transition metals have received considerable attention during the past 20 years, and the basic features of the subject have been dealt with in earlier reviews (*1*, *2*, *46*). A recent review (*3*) has concentrated on developments over the past 3–5 years, so this account will be restricted to a few highlights and it is not intended to deal with all reported work.

### *1. $d^0$ Systems*

It is convenient to deal with $d^0$ systems separately since crystal field effects are absent. Also, these alkoxides are all diamagnetic and the metals are present in their highest oxidation states.

All these compounds are very rapidly hydrolyzed. Dealing first with the metal methoxides, the following compounds are known $M(OMe)_4$ ($M = Ti$, Zn, Hf), $VO(OMe)_3$, $M(OMe)_5$ ($M = Nb$, Ta), and $W(OMe)_6$. The tetramethoxides are generally insoluble powdery solids of low volatility owing to their polymeric nature, whereas the dimeric pentamethoxides and monomeric hexamethoxide are soluble and much more volatile. A soluble tetrameric form of $Ti(OMe)_4$ was discovered by Dunn (*62*), and it was shown by X-ray crystal analysis (*63*) to have the interesting structure shown in Fig. 6. This has the same $M_4O_{16}$ framework as crystalline $Ti_4(OEt)_{16}$ (*64*) and $Ti_4(OMe)_4(OEt)_{12}$ (*65*), and this is clearly of fundamental importance to our understanding of the structural chemistry of metal alkoxides. These units are centrosymmetric and contain octahedrally coordinated titanium in a group of four edge-sharing octahedra. Within each tetrameric unit there are two alkoxo groups which are triple-bridging (i.e., $Ti_3OR$), four which are double-bridging ($Ti_2OR$), and ten nonbridging groups. The latter are disposed in groups of either two or three per titanium atom in mutually cis positions. There are two different environments for the titanium atoms. Ti(1) and Ti(1′) are bonded to three nonbridging and three bridging oxygens, whereas Ti(2) and Ti(2′) are bonded to two nonbridging and four bridging.

A detailed analysis of the bond lengths is limited by a peculiar uncertainty in the positions of methoxo groups (4) and (5), which the authors ascribed to partial hydrolysis and replacement by hydroxo groups. However, it does seem clear that a trans influence is operating in this system. Thus, ignoring groups (4) and (5), the shortest Ti–O bond lengths are found to involve the nonbridging methoxo groups [(1), (2), and (3)], which are trans to the triple-bridging methoxo groups [(8) and (8′)]: Ti(2)–O(1) = 1.79; Ti(2)–O(2) = 1.78; and Ti(1)–O(3) = 1.83 Å. Although this may be largely a $\sigma$-bonding effect, it is significant that all the valence electrons on the triple-bridging oxygens are involved in $\sigma$ bonds and cannot contribute to $\pi$ bonding, whereas the trans nonbridging oxygens have lone pairs available for $\pi$ donation to vacant titanium $d$ orbitals. Moreover this $\pi$-donation hypothesis is consistent with the wide angles: Ti(2)–$\hat{\mathrm{O}}$(1)–C(1) = 161; Ti(2)–O(2)–C(2) = 152; and Ti(1)–$\hat{\mathrm{O}}$(3)–C(3) = 140°; and the short C–O bond lengths C(1)–O(1) = 1.38; C(2)–O(2) = 1.39; and C(3)–O(3) = 1.38 Å. Since each titanium atom shares 12 electrons by virtue of $\sigma$ bonding, it needs a share of six $\pi$ electrons to achieve the 18-electron configuration. In Ti(1) this could arise if the nonbridging oxygens (3), (4), and (5) each contributed a

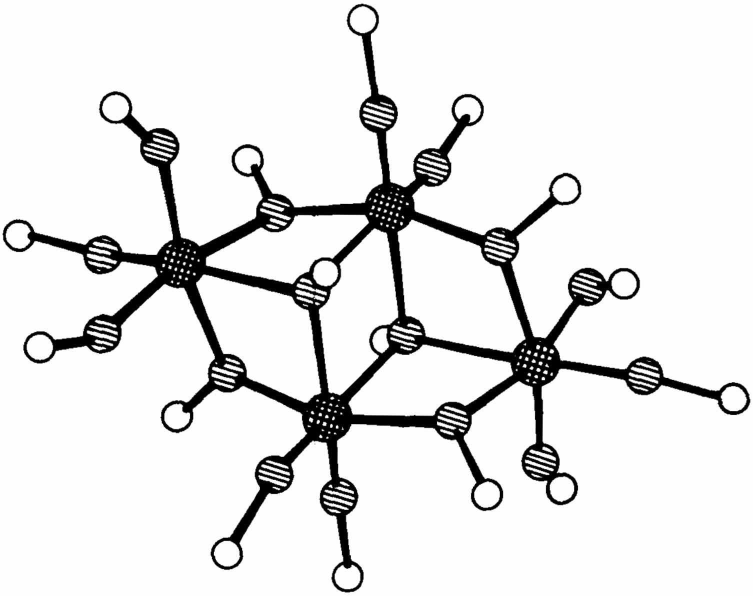


FIG. 6. The structure of $[\mathrm{Ti(OMe)_4}]_4$. Cross-hatched, Ti; hatched, O; plain, $CH_3$.

$\pi$-electron pair by interacting with the three vacant *d* orbitals. Unfortunately, only Ti(1)–O(3) is known accurately, but it is considerably shorter than the trans bond Ti(1)–O(8) (2.20 Å). In Ti(2) four $\pi$ electrons could be donated by the nonbridging oxygens (1) and (2) producing short bonds and resulting in the long bonds in the trans position, viz, Ti(2)–O(8′) = 2.15 and Ti(2)–O(8) = 2.13 Å. The other two $\pi$ electrons could be contributed by the bridging oxygens (6) and (7), which are equidistant with Ti–O = 1.96 Å [significantly shorter than the bonds between these oxygens and titanium (1)]. Consistent with this view the double-bridging oxygens have intermediate C–O bond lengths [C(6)–O(6) = 1.45 and C(7)–O(7) = 1.44 Å] compared with the short nonbridging (1.38 Å) and long triple-bridging [C(8)–O(8) = 1.50 Å] bond lengths and also intermediate Ti–Ô–C angles (117°–124°).

Thus, the $\pi$-bonding hypothesis explains not only the mutually cis configuration of nonbridging methoxo groups, but also the relative order of bond lengths and bond angles for all the ligands in the tetrameric molecule. A NMR spectrum of titanium methoxide gave four broad peaks in the ratio 1:2:3:2, which were assigned on the basis of the tetrameric structure (*66*).

Before completing the discussion of titanium tetramethoxide it should be mentioned that Winter *et al.* have shown that the insoluble form (A) has a different X-ray powder pattern from the soluble species (B) (*67*), and there are also significant differences in their infrared spectra in the C–O and Ti–O regions (*68*). It was implied that the insoluble form (A) does not contain the triple-bridging methoxo groups characteristic of the tetrameric units in (B) and, hence, would inevitably be more highly polymeric.

The crystal structure of $VO(OMe)_3$ was recently determined by Caughlan *et al.* (*69*), and it is instructive to compare it with $Ti(OMe)_4$ and consider why it has such a different structure. In fact, it is composed of dimeric units $V_2O_2(OMe)_6$ (Fig. 7), which are linked by weak bridges at O(10) and O(9′) to generate a linear polymer down the *c*-axis of the crystal. Hence, the overall structure is that of an infinite linear polymer involving edge-sharing distorted octahedra. The hypotheses used in interpreting the $Ti_4(OMe)_{16}$ structure may be applied equally well to the $[VO(OMe)_3]_\infty$ structure. Inspection of the dimer unit reveals two types of nonbridging groups, the V–O at O(7) and (O8) and the terminal methoxo groups at O(5) and O(6), and it is significant that each V=O is cis to the terminal methoxo group and trans to the very weak interdimer bridging methoxo group. With six $\sigma$ bonds and one $\pi$ bond each vanadium has a share in 14 electrons and requires four more $\pi$ electrons to achieve the 18-electron configuration. The V=O oxygen could donate a lone pair to give some triple bond character $V^{-}\equiv O^{+}$ and the other lone-pair π donation could be contributed by the terminal methoxo group. The terminal methoxo groups thus have shorter V–O distances (1.74 Å) than the weakly bridging methoxo groups [O(9) and O(10); V–O = 1.84 and 1.86 Å] which, in turn, are shorter than the intradimer bridges [O(3) and O(4); V–O = 1.96 and 2.03 Å trans to O(10) and O(9) and V–O = 2.04 and 2.05 Å trans to O(5) and O(6)], whereas the longest bonds are given by the weak interdimer bridges [O(9′) and O(10′); V–O = 2.30 and 2.25 Å] which are trans to the very short V=O bonds.

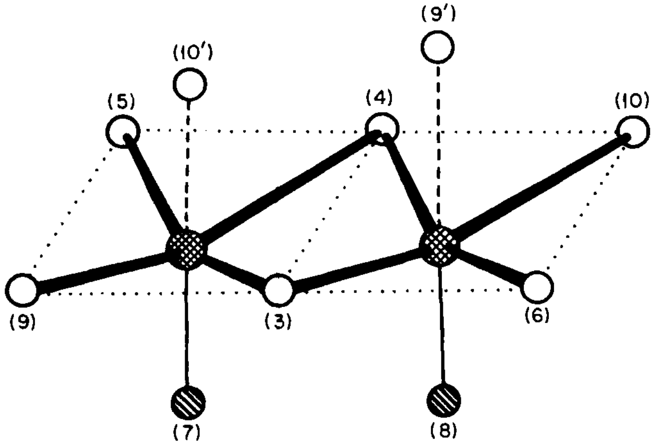


Fig. 7. The dimer unit in $[VO(OMe)_3]_a$; Cross-hatched, V; hatched, 0 in V=O group; plain, O in OMe group.

Unfortunately, there are no X-ray structures available on the dimeric methoxides $M_2(OMe)_{10}$ (M = Nb, Ta), but their structures were solved using variable temperature $^1H$ NMR measurements in solution (*70*). At low temperatures (ca. −60°) three signals were obtained in the ratio 2 : 2 : 1 corresponding to the two distinguishable types of terminal groups and the bridging group required by the structure in Fig. 8. Once again there is octahedral coordination with edge-sharing by bridging methoxo groups, and the structural relationship between this dimer and the $Ti_4(OMe)_{16}$ tetramer is evident. Applying the same arguments as before and in anticipation of an X-ray structural analysis, it is tempting to predict that the terminal methoxo groups [O(3), O(3′), O(4), and O(4′)] trans to the bridging oxygens [O(5) and O(5′)] will have slightly shorter M–O bond lengths than the other type of terminal groups which are paired off in trans positions. Thus, each metal atom shares 12 electrons

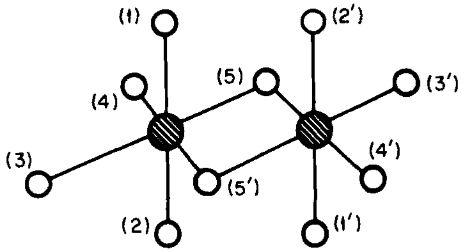


FIG. 8. The dimer $[M(OR)_5]_2$. Hatched, Nb or Ta; plain, OR.

from $\sigma$ bonding and requires six $\pi$ electrons to attain the 18-electron configuration. Assuming that the bridging oxygens form longer M–O bonds and are less effective $\pi$ donors than the terminal oxygens, then the terminal oxygens trans to them [O(3) and O(4)] will each donate a pair of electrons to a vacant *d* orbital, leaving one pair to be donated from the two trans terminal oxygens [O(1) and O(2)] into the remaining vacant *d* orbital. Since O(1) and O(2) are directly competing with each other both as $\sigma$ and $\pi$ donors, whereas O(3) and O(4) are only competing with the weaker bridging oxygens, it follows that M–O(3) and M–O(4) should be slightly shorter than M–O(1) and M–O(2), which, in turn, should be shorter than M–O(5) and M–O(5'). At higher temperatures the NMR signals of terminal methoxo group protons coalesced as intramolecular exchange occurred, and the activation energy for exchange for $Ta_2(OMe)_{10}$ was derived as $E_a = 8.6 \pm 0.5$ kcal·mole$^{-1}$ from the temperature dependence of line broadening. At still higher temperatures further broadening occurred as terminal groups exchanged with bridging groups ($E_a = 10.4 \pm 0.4$ kcal·mole$^{-1}$) and eventually the spectrum collapsed into one sharp signal. This work was independently confirmed by Riess and Pfalzgraf (*71*), who also showed by NMR measurements that the complex $Nb(OMe)_5(C_5H_5N)$ was reversibly formed in solution. The formation of weak complexes $Ta(OR)_5(C_5H_5N)$ had earlier been proposed by Bradley *et al.* (*72*) to account for the monomeric behavior of tantalum alkoxides in pyridine.

Finally we mention $W(OMe)_6$, which was obtained by methanolysis of $W(NMe_2)_6$ (*73*). It is a monomeric, white crystalline solid which sublimes *in vacuo* (50°–60°/$10^{-4}$ mm) and is undoubtedly an octahedral molecule.

Metal ethoxides have received considerable attention, and recent work has clarified the structural status of titanium ethoxide, which had been a controversial subject for some time. A major advance came with the advent of the X-ray crystal analysis by Ibers (*64*), which demonstrated the presence of tetramers (same $Ti_4O_{16}$ configuration as Fig. 6) in the solid state. The positions of the carbon atoms were not reported, but it was stated that the ethyl groups took up positions which gave a cylindrical structure to the tetrameric molecule. The titanium–oxygen bond lengths reflected the nature of the coordination of the oxygen atom, i.e., $Ti_3OEt$, 2.23; $Ti_2OEt$, 2.03; and TiOEt, 1.77 Å. The same tetrameric $Ti_4O_{16}$ framework was also found in the mixed alkoxide $[Ti(OMe)(OEt)_3]_4$ (*65*), which had Ti–O bond lengths in the range 1.6–2.4 Å and the closest Ti...Ti distances 3.3–3.5 Å. Unfortunately, the positions of the carbon atoms were not given, but it would be very interesting to know which sites were occupied by the methoxo groups. Titanium tetraethoxide has interesting physical properties. It is very soluble in organic solvents and is usually obtained as a supercooled liquid by vacuum distillation. Over a period of several months at room temperature it gradually solidifies to the tetrameric crystalline form, but in solution it is predominantly, if not entirely, trimeric. Bradley and Holloway (*74*, *75*) claimed that earlier work suggesting a decreasing degree of polymerization with decreasing concentration was erroneous because of the sensitivity of molecular weight measurements to traces of water and the difficulty in keeping benzene rigorously dry. Using exceptional precautions to avoid hydrolysis they found by cryoscopic measurements that the compound was trimeric over a wide concentration range. These results have since been confirmed by the completely independent technique of light scattering (*76*), and the problem which remains is to determine the structure of the trimer. The chief candidates are shown in Figs. 9–12. The linear structure (Fig. 9) based on face-sharing octahedral units was originally proposed by Caughlan *et al.* (*77*) and much favored by Bradley (*1*, *46*). The alternative structures (Figs. 10 and 11) were proposed by Martin and Winter (*78*). In Fig. 10 the structure involves a triangular arrangement of titanium atoms with edge-sharing trigonal prisms, while in Fig. 11 another triangular arrangement involves five-

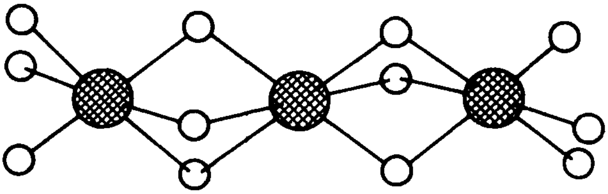


FIG. 9. A structure for $[Ti(OR)_4]_3$. Cross-hatched, Ti (octahedral); plain, OR.

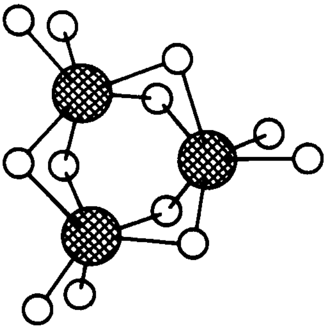


FIG. 10. A structure for $[Ti(OR)_4]_3$. Cross-hatched, Ti (trigonal-prismatic); plain, OR.

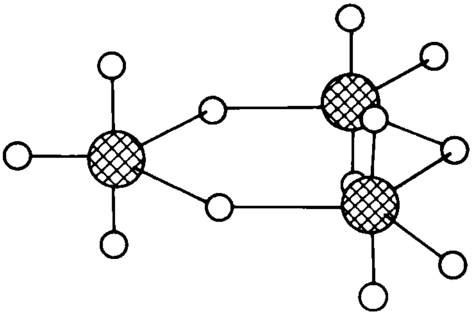


FIG. 11. A structure for $[Ti(OR)_4]_3$. Cross-hatched, Ti (trigonal-bipyramidal); plain, OR.

coordinated titanium (trigonal bipyramid) with corners sharing. Since titanium is predominantly octahedral in six-coordinated systems, Fig. 10 seems highly unlikely and, although five-coordination is a distinct possibility, it is difficult to imagine why the trimer structure (Fig. 11) would have preference over an edge-shared dimer. The structure in Fig. 12 (*66*) has a linear arrangement of titaniums with the central one octahedrally coordinated and the outer ones five-coordinated in an edge-sharing arrangement of two trigonal bipyramids and an octahedron. This is the structure which is clearly favored by the results of Russo and Nelson (*76*). They calculated values for the molecular polarizability anisotropy for the three structures [Fig. 9 ($9.0 \times 10^{-48}$ cm$^6$), Fig. 11 ($14.0 \times 10^{-48}$ cm$^6$), and Fig. 12 ($111.6 \times 10^{-48}$ cm$^6$)]. The average value obtained from six concentrations in cyclohexane (0.03–0.60 M) and three in carbon tetrachloride (0.10–0.60 M) was $111.5 \pm 2 \times 10^{-48}$ cm$^6$, so even allowing generously for errors in the calculated values there is no doubt that the structures in Figs. 9 and 11 can be eliminated. These authors also observed that below 800 $cm^{-1}$ there are no coincident bands in the infrared and Raman spectra which suggests a centrosymmetrical structure which again rules out Fig. 11. Bradley and Westlake (*79*) had earlier attempted to assign structures of metal alkoxides by determining the ratio of terminal to bridging groups from band intensities of the C–O stretching frequencies. For $Ti_3(OEt)_{12}$ they found a ratio of 2:1, which agreed with none of the structures in Figs. 9–11 which were then being considered. However, it is now seen to be in agreement with the structure in Fig. 12. Attempts have also been made to assign the $Ti_3(OEt)_{12}$ structure by $^1H$ NMR studies (*72*, *75*, *80*). Owing to the fluxional nature of the molecule the spectrum at room temperature or above shows only one quartet ($CH_2$ protons) and one triplet ($CH_3$ protons) due to rapid intramolecular exchange of terminal and bridging alkoxo groups. At lower temperatures broadening and splitting are observed, but have been interpreted in different ways. Weingarten and Van Wazer (*66*) considered that the unequal splitting of the quartet at −48° in toluene ruled out Figs. 9 and 10 and they favored the structure in Fig. 10 with the 3:1 ratio of terminal : bridging, although they did not completely rule out Fig. 12. In a more detailed variable temperature study in toluene and carbon disulfide, Bradley and Holloway (*80*) observed some additional features. In both solvents it was noted that the new peaks increased in intensity at the expense of the original peaks as the temperature was lowered, and it suggested that a new species was developing rather than that terminal-bridging peaks of one species were being resolved. Below −60° the spectra were broadened owing to viscosity effects, and it was not possible to make any definite structural assignments. Nevertheless, it was found that the ethoxide readily crystallized

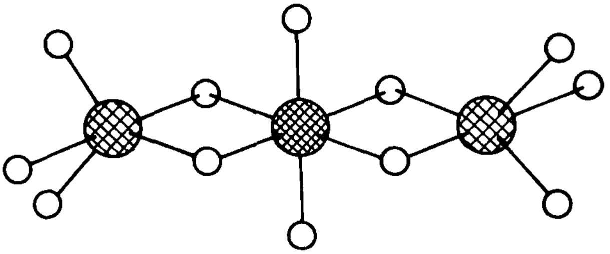


FIG. 12. A structure for $[Ti(OR)_4]_3$. Fine cross-hatched, Ti (octahedral); cross-hatched, Ti (five-co-ordinated); plain, OR.

from $CS_2$ at low temperatures, whereas the liquid trimer transforms to the solid tetramer very slowly at room temperatures. It was therefore proposed that the low-temperature NMR spectra were showing the transformation in solution of the trimer to the tetramer. Similar measurements on the trimeric *n*-propoxide and *n*-butoxide in $CS_2$ showed no splitting even down to −90°, although the lines were broadened, and this indicates very rapid terminal-bridging exchange in the trimer (*80*). This behavior is readily understood for the structure in Fig. 12 containing two five-coordinated and one six-coordinated titanium. Since the enthalpy of formation of an ethoxo bridge was estimated by various methods to be ca. $-11\ \text{kcal}\cdot\text{mole}^{-1}$ (*66*), it seems unlikely that the terminal-bridging exchange for the trimer would involve a simple bridge-dissociation mechanism.

Assuming that the trimer has the structure shown in Fig. 12, a reappraisal of the structural implications of the theory of Bradley *et al.* (*7*) for the soluble hydrolysis products of $Ti_3(OEt)_{12}$ is called for. On the basis of ebullioscopic molecular weight studies a series of polymers $[Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}]$ ($x = 0, 1, 2, 3, \ldots \infty$) was postulated based on a condensation process involving the octahedral trimers (Fig. 9) as structural units. In addition, a crystalline product corresponding to $x = 1$ $[Ti_6O_4(OEt)_{16}]$ was isolated. An X-ray crystal analysis of this compound (*81*) has shown that a heptameric unit $Ti_7O_{24}$ (Fig. 13) is present, and it is clearly patterned on the tetramer unit $Ti_4O_{16}$ of the crystalline tetraethoxide. Unfortunately the positions of the carbon atoms were not located, so the details of the structure are not known, but the proposed formula $Ti_7O_5(OEt)_{19}$ is impossible for quadrivalent titanium and the formula is presumably either $Ti_7O_4(OEt)_{20}$ or $Ti_7O_4(OH)(OEt)_{19}$. It is possible to reconcile the difference between the species in solution and in the crystal by considering that the species in solution contains some five-coordinated titanium [e.g., a species $Ti_6O_4(OEt)_{16}$ involving two five-coordinated titaniums and four octahedral titaniums can be visualized], and rearrangement occurs to give an entirely octahedral system in the crystal.

The pentaethoxides of niobium and tantalum were shown by variable temperature $^1H$ NMR studies to have the dimeric structure (Fig. 8) involving edge-sharing octahedra (*70*), and hydrolysis studies (*7*) indicated the presence of polymers in the series $M_{2(x+1)}O_{3x}(OR)_{2(2x+5)}$ based on a condensation process of dimer units. The only crystalline hydrolysis product which has so far been obtained was shown by X-ray analysis to be $Nb_8O_{10}(OEt)_{20}$ (*82*). This has the interesting cage structure shown in Fig. 14, which is based on octahedral niobium. It may be visualized as comprising two $Nb_3O_{13}$ (three edge-sharing octahedra)

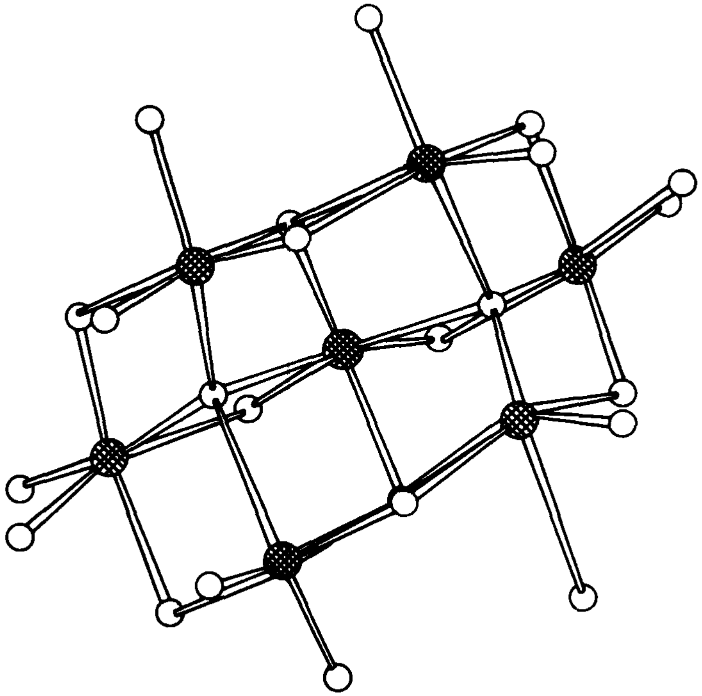


FIG. 13. The [$Ti_7O_{24}$] unit. Cross-hatched, Ti; plain, O.

units linked by two corner-sharing octahedra. It is noteworthy that there are no Nb=O bonds [compare $VO(OMe)_3$], and consequently all the oxo oxygens are in bridging positions (two triple-bridging and eight double-bridging), whereas the nonbridging ethoxo groups are arranged in cis pairs (except for the two niobiums which have only a single non-bridging group). It is significant that all the polymeric six-coordinated methoxide and ethoxide structures which are known with certainty involve edge-sharing octahedra in contrast to the adjacent face-sharing depicted for Fig. 9. It was pointed out by Russo and Nelson (*76*) that the face-sharing structure would bring the titanium atoms too close together (ca. 2.3 Å compared with Ti...Ti of 3 Å in the edge-shared structures). To conclude this section on the ethoxides we note the $^1H$ NMR and calorimetric studies on the "scrambling" reactions of $Ti(OEt)_4$ with $Ti(OR)_4$ ($R = Pr^i$, $Bu^t$), $Ti(NMe_2)_4$, and $TiCl_4$ (*66*) and also the thermochemical work from which the standard heat of formation $\Delta H_f^0[Ti(OEt)_4, (c)] = -349 \pm 1.4$ kcal·mole$^{-1}$ and the average Ti–O bond dissociation energy $\bar{D} = 101 \pm 2.1$ kcal·mole$^{-1}$ were derived (*83*). Other titanium

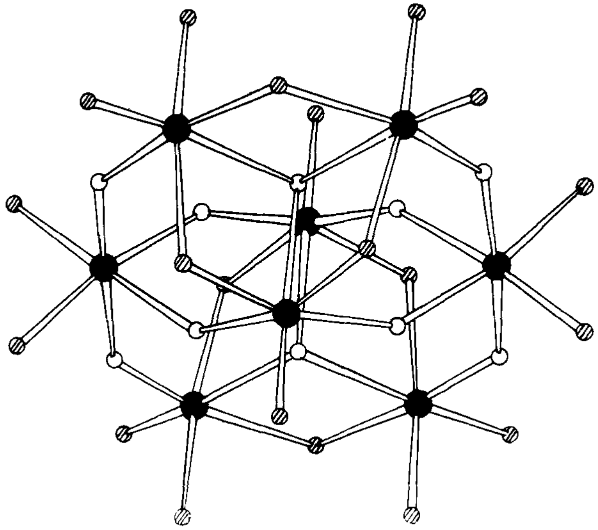


FIG. 14. The structure of [$Nb_8O_{10}(OEt)_{20}$]. Solid, Nb; plain, O; hatched, OEt.

alkoxides were similarly studied and all gave $\bar{D}$ (Ti–O) values in the range 101–109 kcal·mole$^{-1}$ (*84*).

Cryoscopic molecular weight determinations and $^1H$ NMR studies have been carried out on the metal isopropoxides (*75*, *80*). Steric hindrance of the branched alkyl groups opposes intermolecular bonding, and titanium isopropoxide is monomeric in solution and more volatile than the normal alkoxides. Nevertheless, it was shown by NMR measurements that polymerization takes place at lower temperatures. Zirconium isopropoxide ($\bar{n} = 3.57 \pm 0.08$) shows a small but significant difference in degree of polymerization from hafnium isopropoxide ($\bar{n} = 3.33 \pm 0.09$), and it appears that trimers and tetramers are present, although no change in molecular weight with concentration was detected. A single type of isopropoxo group was found in the NMR spectrum of the freshly distilled compounds indicating rapid terminal-bridging exchange in the trimer species, but "aged" samples had three additional small sets of doublets believed to be due to tetramer species. The extra peaks coalesced into the main doublet at higher temperatures. The pentaisopropoxides of niobium and tantalum gave interesting $^1H$ NMR spectra in solution (*70*). Distinct resonances were found for the monomer $M(OPr^i)_5$ (a single type of isopropoxide) and the dimer $M_2(OPr^i)_{10}$ (two types of isopropoxide in 4:1 ratio), and the variation of intensities of monomer and dimer peaks with temperature and concentration fitted the mass law relationship for an equilibrium.

$$M_2(OPr^i)_{10} \rightleftharpoons 2M(OPr^i)_5 \qquad (8)$$

At a given temperature and concentration the niobium compound had a lower dimer concentration than tantalum. From the temperature dependence of the equilibrium constant for Eq. (8), the enthalpy of the dimerization process was derived as $Nb_2(OPr^i)_{10}$, $\Delta H = 16.3$ kcal·mole$^{-1}$, and $Ta_2(OPr^i)_{10}$, $\Delta H = 17.0 \pm 1.5$ kcal·mole$^{-1}$. Addition of isopropanol caused the removal of the monomer peak which coalesced with that of the alcohol and a reduction in intensity of the dimer peaks owing to some solvation.

$$M_2(OPr^i)_{10} + 2Pr^iOH \rightleftharpoons 2M(OPr^i)_5(Pr^iOH) \qquad (9)$$

Evidently the dimer exchanges isopropoxo groups slowly with isopropanol, whereas the solvated monomer undergoes a rapid intramolecular ligand exchange and a rapid intermolecular exchange with the alcohol.

Steric hindrance is very marked in the *tert*-butoxo group, and the *tert*-butoxides of titanium, zirconium, hafnium, niobium, and tantalum are all monomeric and volatile. For the tetra-*tert*-butoxides the $^1H$ NMR studies (*75*) showed that $Ti(OBu^t)_4$ remained monomeric in solution down to −50°, whereas $M(OBu^t)_4$ (M = Zr, Hf) showed some broadening and a slight shift to low field, which indicated some polymerization at −50°. Addition of *tert*-butanol showed that exchange with $Ti(OBu^t)_4$ was slow, whereas coalescence of alkoxide and alcohol signals showed rapid exchange for $Zr(OBu^t)_4$ and $Hf(OBu^t)_4$. The penta-*tert*-butoxides $M(OBu^t)_5$ (M = Nb, Ta) remained monomeric in solution down to −100°, and intramolecular ligand exchange was too fast to allow structural identification (i.e., distinction between trigonal bipyramid and square pyramid). Addition of *tert*-butanol gave a single coalesced signal indicating rapid exchange.

To summarize this brief account of the $d^0$ alkoxides of Groups IV and V, it appears that in the polymeric species involving edge-shared octahedral structures the intramolecular exchange of alkoxo groups is relatively slow as is the intermolecular exchange with the parent alcohol. For species involving some or all of the metal atoms in lower coordination numbers the exchange processes appear to be much more rapid.

### 2. $d^n$ Systems

The $d^n$ systems ($n = 1$–$9$) are of interest because of the intervention of crystal field effects. From an important survey of the polymeric dimethoxides $M(OMe)_2$ (M = Cr, Mn, Fe, Co, Ni, Cu), in which polymeric structures involving octahedral coordination were found, Martin *et al.* (*85*) deduced from the reflectance spectra and magnetism that the methoxo group exerted a crystal field splitting similar to that of water in these high-spin systems. Infrared spectra in the M–O region (600–200 $cm^{-1}$) showed trends which could be related to ligand field effects on the M–O vibrations (*86*). It is convenient to deal with the $d^n$ metal alkoxides according to the number of *d* electrons (*n*).

$d^1$ *Metal Alkoxides.* Titanium trimethoxide was isolated as a highly reactive (to air), insoluble, yellow-green solid (*85*). It would be expected to have octahedral Ti(III), but the reflectance spectrum gave a "*d–d*" transition at 10,000 $cm^{-1}$ and the compound was diamagnetic indicating strong metal–metal interactions. Lappert and Sanger (*87*) have recently reported that triethoxotitanium(III) is a diamagnetic, dark blue-green crystalline tetramer $Ti_4(OEt)_{12}$. A number of tetraalkoxovanadium(IV) compounds have been prepared (*3*). The trimethoxo compound is a soluble trimeric derivative $V_3(OMe)_{12}$, and it is paramagnetic with $\mu_{eff}$ varying slightly with temperature (1.79 at 289°K to 1.70 at 123°K) (*88*). The data could be fitted to a model involving a distorted octahedral configuration with the $^2T_{2g}$ state split by >1000 $cm^{-1}$ leading to an orbital singlet ground state. This was confirmed by ESR studies (*89*), which showed a broad signal ($g = 1.955 \pm 0.005$) in the solid at room temperature with no hyperfine structure. However, it should be borne in mind that the actual structure of the trimer may be analogous to $Ti_3(OEt)_{12}$ (Fig. 12) with both six-coordinated and five-coordinated metal atoms. Vanadium tetraethoxide has received further study (*88*). It is a dimeric solid which obeys the Curie law with $\mu_{eff} = 1.69$ (123°–289°K). Electronic spectra showed two "*d–d*" transitions at 6000 and 14,200 $cm^{-1}$, which could be assigned to five-coordinated vanadium (trigonal-bipyramidal). The broadness of the bands suggested splitting of the $^2E''$ and $^2E'$ states by a lowering in symmetry from $D_{3h}$ to $C_{2v}$, in accordance with an edge-sharing bridged structure for the dimer $V_2(OEt)_8$. Also an ESR signal was given by the solid at room temperature ($g = 1.954$) and in solution there was a partial resolution of the $^{51}V$ hyperfine coupling (*89*). The tetra-*tert*-butoxovanadium(IV) is a bright blue, volatile, monomeric liquid, and its electronic absorption spectrum gave a broad asymmetric band which was resolved by gaussian analysis into two "*d–d*" transitions at 10,930 and 13,900 $cm^{-1}$ (*89*). Earlier work had shown that $V(OBu^t)_4$ gave at room temperature an ESR signal ($\langle g \rangle = 1.964$; $\langle a \rangle = 0.0064$ $cm^{-1}$) with $^{51}V$ hyperfine splitting, and frozen solutions (−196°) gave resolved anisotropic spectra ($g_{\parallel} = 1.940$; $g_{\perp} = 1.984$; $A_{\parallel} = 0.0125$; $A_{\perp} = 0.0036$ $cm^{-1}$) (*90*). A molecular orbital treatment gave a reduced spin–orbit coupling constant $\lambda = 156\ \text{cm}^{-1}$), and the coefficients of the wave functions suggested a moderate degree of covalency owing to participation of the *d* orbitals. These ESR data were confirmed ($\langle g \rangle = 1.962$) (*89*) and found to be in agreement with the magnetic susceptibility data ($\mu_{\text{eff}} = 1.69 \pm 0.03$ independent of temperature) (*88*) and all the data point to a distorted tetrahedral configuration ($D_{2d}$ point group) with a $^2B_1(d_{x^2-y^2}$ orbital) ground state (Fig. 15). The *d–d* transitions then correspond to $^2B_1 \rightarrow {}^2B_2$ (10,930 cm$^{-1}$) and $^2B_1 \rightarrow {}^2E$ (13,900 cm$^{-1}$). The distortion of the $d^1$ tetrahedral system ($^2E$ ground state) could be attributed to the Jahn–Teller effect, but similar distortions of $d^2$ systems have been found which cannot be so explained, and Bradley and Chisholm (*91*) prefer an explanation based on the consequences of covalent bonding. Thermochemical measurements (*92*) gave a value of $D(\text{V–O}) = 87.5$ kcal·mole$^{-1}$ for $V(OBu^t)_4$.

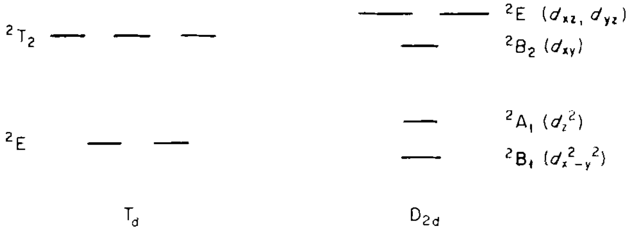


FIG. 15. Splitting of *d*-orbital energy levels.

Some alkoxo derivatives of the $d^1$ species Nb(IV) and W(V) have been isolated by Brubaker and co-workers. Ethanolic solutions of $NbCl_5$ saturated with HCl were electrolytically reduced to Nb(IV) and the red, diamagnetic, dimeric complex $Nb_2Cl_2(OEt)_6(C_5H_5N)_2$ was obtained by addition of pyridine. Treatment of this complex with NaOEt gave $Nb(OEt)_4$ as a dark red oil (b.p. ca. 160°/0.002 mm) which had a shoulder at 26,300 cm$^{-1}$, which may be due to a "*d–d*" transition (*93*). The infrared spectrum in the region 1000–1150 cm$^{-1}$ (mainly C–O stretching vibrations) was very similar to that of the polymeric ethoxo compounds $Ti_3(OEt)_{12}$, $Nb_2(OEt)_{10}$, and $Ta_2(OEt)_{10}$ (*79*), and together with its low volatility and diamagnetic nature suggests that $Nb(OEt)_4$ is polymeric, but a molecular weight determination was not carried out. The pentaethoxotungsten(V) was obtained by addition of NaOEt to an ethanolic solution of $WCl_5$ (*94*). It was a brown, diamagnetic, liquid which showed only one type of ethoxo group in the $^1$H NMR spectrum down to −80°. This behavior is consistent with a fluxional metal–metal bonded dimer or a very labile ethoxo-bridged polymer, but no molecular weight measurements were made.

*$d^2$ Metal Alkoxides.* Bradley *et al.* (*95*) have recently reported fully on the physico-chemical properties of the interesting volatile, monomeric $Cr(OR^t)_4$ ($R^t$ = *tert*-alkyl) compounds. Previous calorimetric work (*92*) had shown that $Cr(OBu^t)_4$ has considerable thermodynamic stability: $-\Delta H_f^0[Cr(OBu^t)_4, (g)] = -305$ kcal·mole$^{-1}$ and average bond dissociation energy $\bar{D}(Cr–O) = 73$ kcal·mole$^{-1}$; and it is clear that covalent Cr(IV) compounds are quite stable in nonaqueous systems. A parent ion $Cr(OBu^t)_4^+$ was obtained in the mass spectrum, together with several interesting chromium-containing fragment ions and metastable peaks (*95*). The characteristic bright blue color of these compounds is due to absorption in the 15,000 cm$^{-1}$ region, and the complex spectrum was interpreted in terms of the three *d–d* transitions expected for a tetrahedral $d^2$ complex: ${}^3T_2(F) \leftarrow {}^3A_2(F)$ (9100); ${}^3T_1(F) \leftarrow {}^3A_2$ (15,200); ${}^3T_1(P) \leftarrow {}^3A_2$ (25,000 cm$^{-1}$) with $10Dq = 9430$ cm$^{-1}$ and $B = 795$ cm$^{-1}$. However, the lowest energy bands were doublets (8700, 9500 and 13,700, 15,750 cm$^{-1}$) suggesting a lowering in symmetry to $D_{2d}$, which would split the $T$ terms. The magnetic susceptibility data showed practically Curie law behavior with $\mu_{eff} = 2.80 \pm 0.03$ independent of temperature, and ESR signals at 10°K in frozen toluene solution (broad absorption $g \sim 4$, sharp absorption $g = 1.962$) agreed with an orbital singlet ground state (${}^3B_1$ in $D_{2d}$ symmetry) and a distorted tetrahedral configuration with zero-field splitting. Attempts to prepare other Cr(IV) alkoxo compounds showed that only the tertiary alkoxides were stable, since primary and secondary alcohols were oxidized and led to the formation of stable $Cr(III)(OR)_3$ derivatives. During the spectral work on $Cr(OBu^t)_4$, it was noted that dilute solutions (cyclohexane) of the Cr(IV) compound were perceptibly less readily hydrolyzed than the corresponding $d^0$ compound $Ti(OBu^t)_4$, and it was suggested that the presence of *d* electrons in the chromium(IV) compound impeded nucleophilic attack by water molecules (*95*). Wiberg and Foster (*96*) using $^{18}O$-labeled water in a medium of acetic (91%) and perchloric (0.23 *M*) acids showed that in the hydrolysis of $Cr(OBu^t)_4$ the Cr–O bonds underwent cleavage. They also observed that $Cr(OBu^t)_4$ dissolved in styrene was stable for a week showing that butoxo radicals were not produced, thus confirming earlier work of Hagihara and Yamazaki (*97*). The latter authors also showed that polymerization of styrene was initiated by the addition of methanol to $Cr(OBu^t)_4$, which thus produced radicals during the reaction leading to $Cr(OMe)_3$, $Bu^tOH$, and formaldehyde.

The $d^2$ vanadium(III) alkoxides $V(OR)_3$ (R = Me, Et) were obtained as insoluble, nonvolatile, green solids, which were very sensitive to oxidation and presumably are polymeric (*98*). A number of green vanadium(III) chloride methoxide complexes $VCl(OMe)_2$, $VCl(OMe)_2(MeOH)$, $VCl(OMe)_2(Me_2CO)$, and $VCl_2(OMe)(MeOH)_2$ were prepared by Kakos and Winter (*99*), who studied spectral and magnetic properties. The electronic reflectance spectra were interpreted basically in terms of octahedral V(III): $^3T_{2g} \leftarrow {}^3T_{1g}$ (15,500); $^3T_{1g}(P) \leftarrow {}^3T_{1g}$ (25,000); $^3A_{2g} \leftarrow {}^3T_{1g}$ (35,700 $cm^{-1}$) with $10Dq = 17{,}400\ cm^{-1}$ and $B = 745\ cm^{-1}$; but splitting of the bands suggested a lowering of symmetry. The anomalously low magnetic moments were accounted for by spin interactions of neighboring metal atoms in trimeric or tetrameric clusters.

$d^3$ *Metal Alkoxides.* The $d^3$ Cr(III) alkoxides have been known for many years, but only recently have spectral and magnetic studies been carried out (*85*, *100*). The trimethoxide and triethoxide are insoluble, nonvolatile, pale green solids whose reflectance spectra agreed with ligand field predictions for an octahedral $d^3$ ion with $10Dq \sim 17{,}000\ cm^{-1}$. X-Ray powder photographs and infrared and Raman spectra for $Cr(OMe)_3$ were interpreted on the basis of a layer type lattice (hexagonal symmetry) involving edge-sharing methoxo-bridged octahedra (*100*). Magnetic susceptibility measurements gave anomalously low moments owing to antiferromagnetic interactions and extrapolation of the $\chi^{-1}$ vs. $T$ data (Curie–Weiss law) gave very large $\theta$ values (270°–320°), which then gave $\mu_{eff}$ close to the $d^3$ spin-only value of 3.88 (*85*, *100*). Superexchange involving the alkoxo bridges was invoked as a likely mechanism for the antiferromagnetic behavior.

By using bulky alkoxo groups it was shown that chromium can be prevented from achieving octahedral coordination. Thus, chromium tri-*tert*-butoxide is soluble in organic solvents and is extremely easily oxidized to Cr(IV) (*92*, *95*), and it is most probably dimeric with bridging alkoxo groups and distorted tetrahedral Cr(III) (*101*).

The compound $LiCr(OBu^t)_4$ is pink and insoluble with probably an infinite linear structure with alkoxo bridges and alternating lithium and chromium atoms (*102*). The electronic spectrum was assigned on the basis of tetrahedral $d^3$ Cr(III): $^4T_2(F) \leftarrow {}^4T_1(F)$ (10,000); $^4T_1(P) \leftarrow {}^4T_1(F)$ (17,400); $^4A_2 \leftarrow {}^4T_1$ (19,400 $cm^{-1}$) with $10Dq = 11{,}200\ cm^{-1}$ and $B = 560\ cm^{-1}$. The magnetic susceptibility measurements showed that the magnetic moment varied slightly with temperature ($\mu_{eff}^{298} = 3.58$; $\mu_{eff}^{98} = 3.43$) as expected for a system with a $T$ ground state. The ease of oxidation of tetrahedral $d^3$ Cr(III) can be ascribed to the instability resulting from placing one electron in a higher energy $d$ orbital, whereas both electrons in tetrahedral $d^2$ Cr(IV) are in lower energy orbitals.

By contrast molybdenum tri-*tert*-butoxide was found to be a reactive orange solid, which could be sublimed *in vacuo* (100°/$10^{-3}$ mm) (*73*).

The compound was dimeric in benzene and gave a strong parent ion $Mo_2(OBu^t)_6^+$ in the mass spectrum together with many strong fragment ion peaks containing two metal atoms. It was also diamagnetic and the infrared and $^1H$ NMR spectra showed no evidence for bridging alkoxo groups, and it was therefore concluded that the structure entailed a multiple metal–metal bond.

*$d^4$–$d^9$ Metal Alkoxides.* An example of a $d^4$ metal alkoxide is the purple $Cr(OMe)_2$, which is a polymeric, insoluble, nonvolatile solid (*85*). The reflectance spectrum (transitions at 18,200 and 22,200 $cm^{-1}$) showed evidence of a tetragonally distorted octahedral configuration for the metal, and magnetic measurements showed strong antiferromagnetic interaction ($\mu_{eff} = 5.16$; $\theta = 160°$). There are two examples of $d^5$ metal alkoxides $Mn(OMe)_2$ and $Fe(OR)_3$. The manganese dimethoxide is a pale pink, insoluble solid whose magnetic susceptibility conforms to the Curie–Weiss law ($\mu_{eff} = 5.96$; $\theta = 35°$), and the reflectance spectrum (spin-forbidden transitions at: 18,500, 24,400, 27,070, 29,000, and 31,300 $cm^{-1}$) was assigned to octahedral Mn(II). Thus, a polymeric methoxo-bridged octahedral structure is envisaged.

It had been known for several years that ferric alkoxides were trimeric (*103*) and, thus, differed from the tetrameric aluminum alkoxides, but in neither case should there be crystal field effects. Martin and co-workers (*104*) found interesting magnetic susceptibility results for the $Fe_3(OR)_9$ compounds. At room temperature the magnetic moments per iron atom of the normal alkoxides (R = Me, Et, $Bu^n$) were $\mu_{eff} = 4.51$–4.35, compared to 5.9 required for a $d^5$ high-spin system. Moreover, the same value was found in solution independent of concentration, showing that the magnetic anomaly was a property of the trimeric cluster and not due to general lattice interactions. The magnetic moments decreased with temperature ($\mu_{eff}^{90} = 3.4$) and the Curie–Weiss law was obeyed ($\theta \sim 200°K$). The magnetic moment of $Fe_3(OBu_n)_9$ decreased with increasing degree of hydrolysis, but increased with thermal decomposition (>80°). A broad band at 11,000 $cm^{-1}$ was observed in the electronic diffuse reflectance spectrum. Further work (*105*) showed that the magnetic susceptibility data were well represented by a model involving cooperative spin coupling of the $d^5$ ($^6A_1$) metal atoms in an equilateral triangular configuration with an isotropic coupling constant $J = -10\ cm^{-1}$. The 216-fold spin degeneracy of the $Fe_3$ unit is partially split by the spin–spin interactions to give eight spin levels characterized by the spin quantum numbers $S^1 = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots, \frac{15}{2}$; and the magnetic field splits each level into $2S^1 + 1$ sublevels. At temperatures approaching the absolute zero only the lowest level ($S^1 = \frac{1}{2}$) is occupied, and $\mu_{eff}^2 = 1$ $(B.M.)^2$ per $Fe_3$ unit. At higher temperatures the higher levels become populated leading ultimately to $\mu_{\text{eff}}^2 = 105$ (B.M.)$^2$ per $Fe_3$ unit, and it was shown that the Weiss temperature $\theta = 35J/3k$. It was noted that quite a small $J$ value (−15°K) could cause a dramatic temperature variation of the magnetic susceptibility of the trinuclear cluster. It was suggested that a cyclic structure of tetrahedral iron atoms with alkoxo bridges ($D_{3h}$ symmetry) was most probable and that a superexchange mechanism might operate via the bridging ligands.

The only representative of high-spin $d^6$ metal alkoxides is $Fe(OMe)_2$, a dark green compound, which obeys the Curie law ($\mu_{\text{eff}} = 5.14$). Its reflectance spectrum ($^5E_g \leftarrow {}^5T_{2g}$; 10,000 cm$^{-1}$) meets the requirements of an octahedrally coordinating ferrous ion, and it probably has a high polymeric methoxo-bridged edge-sharing octahedral structure (*85*). Cobalt(II) methoxide is an insoluble purple solid, which shows Curie–Weiss law behavior ($\mu_{\text{eff}} = 5.46$; $\theta = 15°$), and its reflectance spectrum [$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (9500); $^2E_g(G) \leftarrow {}^4T_{1g}$ (12,000); $^4A_{2g}(F) \leftarrow {}^4T_{1g}$ (12,000); $^4A_{2g}(F) \leftarrow {}^4T_{1g}$ (17,900); $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ (21,000 cm$^{-1}$)] was assigned in terms of octahedral cobalt(II) ($d^7$ high-spin) (*85*). Nickel(II) methoxide is an insoluble, pale green solid, which showed Curie law behavior ($\mu_{\text{eff}} = 3.38$), and its reflectance spectrum [$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ (8700); $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (14,500); $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (25,000 cm$^{-1}$)] was assigned to octahedral nickel(II) (*85*). Infrared bands (420 and 275 cm$^{-1}$) were assigned to nickel–oxygen stretching vibrations (*86*). Further work by Krüger and Winter (*106*) led to the isolation of a number of methoxohalonickel(II) compounds, e.g., Ni(OMe)Cl; Ni(OMe)Cl(MeOH), $Ni(OMe)Cl(MeOH)_2$, $Ni_3(OMe)_4Cl_2$, $Ni_3(OMe)_5Cl$, etc., and their reflectance spectra were analyzed in terms of octahedral Ni(II). The $10Dq$ values increased steadily as chloride was replaced by methoxide in the above series [i.e., 7900, 8100, 8200, 8200, and 8300, respectively, and for $Ni(OMe)_2$ 8500 and $NiCl_2$ 7200 cm$^{-1}$] as would be expected. These compounds exhibited anomalous magnetic properties with $\mu_{\text{eff}}$ increasing with a decrease in temperature, and the data were ingeniously fitted to a structural model involving "cubane" $Ni_4(OMe)_4$ clusters with the octahedral coordination of each Ni(II) completed by additional ligands in terminal and bridging positions. The magnetic interactions corresponded to ferromagnetic interactions between the four nickel atoms in the cluster ($J$ values +4 to +16 cm$^{-1}$).

Finally we mention work carried out on the $d^9$ Cu(II) alkoxides. Brubaker and Wicholas (*107*) found that at room temperature the magnetic moments for Cu(II) in $Cu(OMe)_2$ and $Cu(OEt)_2$ were abnormally low and they suggested a highly polymeric structure with tetragonally distorted octahedral copper. Martin *et al.* (*85, 108*) measured the magnetic susceptibility of $Cu(OMe)_2$ over the range 80°–350°K; they found a maximum around 260°K and pronounced antiferromagnetic behavior. They favored a linear chain model for polymeric $Cu(OMe)_2$ analogous in structure to $CuCl_2$. The $J$ value for antiferromagnetic spin–spin interactions was calculated to be $-191$ cm$^{-1}$ and is comparable with values found for copper(II) carboxylates. The dimeric methoxo-$\beta$-diketonato compound $Cu_2(OMe)_2(acac)_2$ gave a much larger $J = -725$ cm$^{-1}$, whereas Cu(OMe)Cl showed completely different magnetic behavior (Curie law behavior, $\mu_{\text{eff}} = 2.0$), which was interpreted in terms of pairs of copper atoms interacting to give a triplet ground state.

It is noteworthy that all the dimethoxides $M(OMe)_2$ (M = Cr, Mn, Fe, Co, Ni, Cu) were found to have highly polymeric structures involving octahedral or distorted octahedral metal atoms, and it will be very interesting to obtain complete crystal structures in order to get a better understanding of the mechanism of ferromagnetic and antiferromagnetic interactions of neighboring paramagnetic atoms. Applying Bradley's structural theory (*109*) for the minimum polymer size modified in the light of recent X-ray work to restrict octahedral structures to edge-sharing, an infinite two-dimensional layer lattice ($CdX_2$) would be expected involving each oxygen in bridging to three metals and with the alkyl groups taking up peripheral positions. For the octahedral $Cr(OMe)_3$ a layer lattice is possible with each oxygen bridging only two metals, but a more compact unit would arise if triple bridging occurred. The smaller polymer based on edge-sharing $MO_6$ octahedra would be $M_{14}(OR)_{42}$ with 16 triple-bridging oxygens, 10 double-bridging, and 16 nonbridging.

### E. ALKOXIDES OF LANTHANIDES AND ACTINIDES

Lanthanum trialkoxides were first reported over ten years ago (*110*), but it is only in recent years that lanthanide alkoxide chemistry has received serious attention. Not surprisingly, it has been found that they have similar properties to the metal alkoxides in general.

There are three main preparative routes to the lanthanide alkoxides. For the insoluble methoxides the method of Bradley and Faktor (*110*) can be applied. This involves the addition of lithium methoxide to the methanolic metal chloride solution. The insoluble metal methoxide is filtered off and washed with methanol to remove lithium chloride.

$$3LiOMe + LnCl_3 \rightarrow Ln(OMe)_3\downarrow + 3LiCl \qquad (10)$$

Other alkoxides can be prepared from the methoxide by alcoholysis, but the reaction is very slow and tedious.

$$Ln(OMe)_3 + 3ROH \rightarrow Ln(OR)_3 + 3MeOH \qquad (11)$$

The method of Mehrotra *et al.* (111) is of more general application. This involves preparation of the triisopropoxide by the action of sodium isopropoxide on the lanthanide trichloride isopropanolate and then conversion to other alkoxides by alcoholysis.

$$LnCl_3 + 3NaOPr^i \rightarrow Ln(OPr^i)_3 + 3NaCl \qquad (12)$$

The method has been applied to the preparation of alkoxides of lanthanum, praseodymium and neodymium (*111*), samarium (*112*), gadolinium, erbium, and ytterbium (*113*). Another method of general applicability is due to Mazdiyasni *et al.* (*114*, *115*), who showed that the lanthanide isopropoxides could be obtained from the reaction of the metal and the alcohol catalyzed by mercuric salts.

$$Ln + 3Pr^iOH \rightarrow Ln(OPr^i)_3 + 3/2H_2 \qquad (13)$$

The lanthanide methoxides and ethoxides are insoluble solids, but the higher alkoxides are soluble in typical organic solvents. The lanthanide triisopropoxides sublime at 200°–300°/0.1 mm and it is clear that the lanthanide trialkoxides are polymeric (*110*), but conflicting results have been reported for molecular weight determinations. For example, it was reported that $Ln(OPr^i)_3$ (Ln = La, Pr, Nd) were monomeric in benzene (*111*, *116*), whereas Mazdiyasni *et al.* (*114*) had proposed dimeric structures and samarium isopropoxide was found to be tetrameric (*112*). However, the $^1H$ NMR spectra of ytterium, lanthanum, and lutetium isopropoxides show that polymeric species are present, and preliminary mass spectral studies have indicated fragment ions of dimeric and tetrameric species (*115*). In view of the existence of $LaAl_3(OPr^i)_{12}$ (*117*) and the NMR evidence for polymeric structures, it seems more probable that Sankla and Kapoor (*112*) are correct in finding a tetrameric samarium isopropoxide and it is reasonable to suppose that a tetramer structure similar to that of $Al_4(OPr^i)_{12}$ (Fig. 4) may apply to a number of lanthanide isopropoxides. Brown and Mazdiyasni (*115*) have presented infrared spectral data (350–3000 $cm^{-1}$), visible and ultraviolet spectra, and thermogravimetric data for the series of lanthanide isopropoxides. Typical lanthanide chemistry is also apparent in the oxidation states exhibited by the alkoxides. Thus, although the trialkoxides may be isolated in all cases, it is noteworthy that cerium(IV) gives stable tetraalkoxides (*118*–*120*) and europium(II) is listed as forming a diisopropoxide (*115*).

Rather less is known about actinide alkoxides because, in addition to problems of hydrolysis and oxidation, there is often the special problem of high radioactivity to contend with. Thorium(IV) alkoxides were prepared by Bradley and co-workers (*121*), who studied the effect of steric hindrance of the alkyl group on the degree of polymerization and volatility. The tetraisopropoxide ($\bar{n} = 3.8$) was practically tetrameric and could be sublimed (200°/0.1 mm), whereas the tetra-*tert*-butoxide ($\bar{n} = 3.4$) was nearer to trimeric and more volatile (160°/0.1 mm), while the derivative of triethylcarbinol was monomeric. Uranium alkoxides have received much attention. Earlier synthetic work was carried out by Gilman and co-workers (*122–124*) during a search for volatile uranium compounds suitable for the separation of uranium isotopes. It was found that uranium(IV) tetraalkoxides were extremely susceptible to oxidation and were readily converted to uranium(V) pentaalkoxides.

$$U(OEt)_4 + \tfrac{1}{2}Br_2 + NaOEt \rightarrow U(OEt)_5 + NaBr \qquad (14)$$

With more powerful oxidizing agents (e.g., dibenzoyl peroxide), the uranium(VI) hexaalkoxide was obtained.

$$U(OEt)_5 + NaOEt + \tfrac{1}{2}(C_6H_5CO)_2O_2 \rightarrow U(OR)_6 + C_6H_5CO_2Na \qquad (15)$$

The stability of uranium(V) alkoxides toward disproportionation was demonstrated in two ways. They could be distilled *in vacuo* and they could be prepared by a reproportionation from the uranium(IV) and uranium(VI) alkoxides.

$$U(OR)_4 + U(OR)_6 \rightarrow 2U(OR)_5 \qquad (16)$$

This is yet another example [cf. Cr(IV)] of the stability of an intermediate valence in the covalent state where the aquocation in the same oxidation state is very unstable.

Later work by Bradley and co-workers showed that for the uranium(V) alkoxides the methoxide was trimeric $U_3(OMe)_{15}$, but the other normal alkoxides were dimeric $U_2(OR)_{10}$ (*125, 126*). With very bulky highly branched alkyl groups it was possible to synthesize monomeric uranium(V) alkoxides whereas the penta-*tert*-butoxide gave monomeric 1:1 complexes $U(OBu^t)_5 \cdot L$ ($L = Bu^tOH$, $C_5H_5N$) (*127*). In addition to uranium(VI) hexaalkoxides $U(OR)_6$, it has proved possible to prepare uranyl alkoxides such as the insoluble yellow $UO_2(OMe)_2(MeOH)$ (*128*). With *tert*-butanol the latter compound underwent an unprecedented reaction which produced some of the volatile, deep red crystalline $U(OBu^t)_6$, which was perceptibly resistant toward hydrolysis (*128*). The effect of steric hindrance of the alkyl groups on the degree of polymerization and volatility of uranium(IV) tetraalkoxides was also studied (*129*), and it was shown that uranium tetraalkoxides were significantly more volatile than the corresponding thorium compounds. The extreme ease of oxidation of uranium(IV) alkoxides precluded the isolation of the tetra-*tert*-butoxide.

Recently some spectroscopic studies have been made on $U_2(OEt)_{10}$. Bradley and Westlake (*79*) assigned various bands to C–O and U–O stretching vibrations and deduced from measurements of the intensities of terminal and bridging species that the structure of the dimer was probably the edge-shared octahedral one exhibited by niobium and tantalum alkoxides (Fig. 8). Karraker (*130*) has assigned the electronic absorption spectrum (which shows weak but narrow bands at 5405, 5680, 6622, 6934, 10,200, 11,690, and 14,490 $cm^{-1}$) to *f–f* transitions for a distorted octahedral $f^1$ system with a spin–orbit coupling constant of 1905 $cm^{-1}$. By comparing this spectrum with that of $UCl_5(SOCl_2)$ it was shown that the *f–f* transitions of the U(V) ($f^1$) system are sensitive to ligand field strength and indicated that the *f* orbital extended into the bonding region. Karraker *et al.* (*131*) have confirmed the edge-shared octahedral structure for the dimer by $^1H$ NMR and a low magnetic moment ($\mu_{\text{eff}} = 1.12$) was reported from a susceptibility determination at room temperature, but variable temperature studies are clearly required for any meaningful discussion.

Samulski and Karraker (*132*) have synthesized $Np(OMe)_4$ and $Np(OEt)_4$ from reactions involving $NpCl_4$ and the appropriate lithium alkoxide. The neptunium(IV) tetraalkoxides were nonvolatile, red-brown solids, which doubtless are polymeric. Electronic absorption spectra and infrared spectra were obtained for the tetraethoxide, which was soluble in carbon tetrachloride. Although the green quinquevalent neptunium compound $NpBr(OEt)_4$ was obtained by bromination of $Np(OEt)_4$, attempts to obtain Np(V) or Np(VI) alkoxides were unsuccessful.

Since $PuCl_4$ was unstable, Bradley and co-workers (*133*) used the complex Pu(IV) chloride, $(C_5H_5NH)_2PuCl_6$, as a starting material for preparing plutonium(IV) tetraalkoxides. The tetraisopropoxide was isolated as a soluble green solid, which could be sublimed (220°/0.05 mm) and formed a crystalline solvate $Pu(OPr^i)_4 \cdot Pr^iOH$ analogous to those of Zr, Hf, and Ce(IV). The tetra-*tert*-butoxide $Pu(OBu^t)_4$ was more volatile (sublimes 112°/0.05 mm), and it was pointed out that in contrast to the behavior of uranium(IV) alkoxides those of plutonium(IV) were not readily oxidized by air.

## F. Double Alkoxides

The double alkoxides (derivatives containing two different metals) were first studied systematically by Meerwein and Bersin (*134*) who obtained a wide range of compounds: e.g., $KLi(OPr^i)_2$; $K_2Be(OEt)_4$; $Na_2Mg(OPr^n)_4$; $KZn(OMe)_3$; $LiAl(OR)_4$; $NaFe(OEt)_4$; $MAl_2(OEt)_8$ (M = Ca, Mg, Co, Ni, Cu); $Zn_3Al(OR)_9$; $ZnAl_2(OR)_8$; $NaHSn(OEt)_6$; $KH_3[Ti(OBu^n)_6]_2$; $NaH[Zr(OEt)_6]$; and $NaSb(OEt)_6$. They considered these compounds to be alkoxo salts derived from a basic alkoxide and an acidic alkoxide, and they showed that in several cases the "acidic" alkoxide could be titrated to a sharp end point with sodium alkoxides. However, it is now evident that double alkoxides will be formed generally from polymeric metal alkoxides, although the stability of the double alkoxides may vary considerably depending on the nature of the two metals and the alkoxo group. In fact, it would not be surprising to find multiple alkoxides, e.g., $M_1M_2M_3M_4(OR)_x$, and a triple alkoxide $K_2Sn^{II}Sn_2^{IV}(OEt)_{12}$ was listed by Meerwein and Bersin (*134*). They also drew attention to the fact that the double alkoxides $MgAl_2(OR)_8$ and $CaAl_2(OR)_8$ ($R = Et, Pr^i$) could be distilled *in vacuo*, whereas the calcium and magnesium alkoxides individually were infusible and nonvolatile. Later work by Wardlaw and co-workers (*135*) on the reactions of zirconium tetrachloride with sodium alkoxides and on titrations of $Zr(OR)_4$ with NaOR failed to confirm the existence of $NaH[Zr(OR)_6)$ (*134*), but showed that stable compounds of the type $NaZr_2(OR)_9$ could be obtained. The alkali metal–zirconium alkoxides $MZr_2(OR)_9$ ($M = Li, Na, K$) were soluble in organic solvent and could be distilled *in vacuo*, and they are clearly substantially covalent in nature. Similarly, tin(IV) gave the double alkoxide $NaSn_2(POr^i)_9$ (*136*). An interesting volatile uranium(IV) aluminum alkoxide $UAl_4$ $(OPr^i)_{16}$ was reported by Albers *et al.* (*137*), and Gilman *et al.* (*138*) have obtained double alkoxides of uranium(V): $NaU(OEt)_6$; $CaU_2(OEt)_{12}$; and $U_3Al(OEt)_{18}$. Recently Mehrotra and Agarwal (*117*) have reported the preparation of volatile double alkoxides of aluminum and lanthanides $MAl_3(OPr^i)_{12}$ ($M = La, Pr$), and they suggested a structure analogous to that of the tetrameric $Al_4(OPr^i)_{12}$ (Fig. 4) with the central octahedral aluminum replaced by the lanthanide. The $^1H$ NMR spectrum of $LaAl_3(OPr^i)_{12}$ showed only one type of isopropoxo group down to $-60°$, indicating a rapid intramolecular exchange of bridging and terminal ligands (*54*), and the mass spectrum gave the parent ion $LaAl_3(OPr^i)_{12}^+$ and several fragment ions and metastables including a very intense peak for $LaAl_3(OPr^i)_{11}^+$. Using a pH titration method involving lithium methoxide and metal chlorides in anhydrous methanol, Gut (*139*) obtained evidence for the presence of several anionic species: $B(OMe)_4^-$, $Al(OMe)_4^-$, $Ti_2(OMe)_9^-$, $Nb(OMe)_6^-$, and $Ta(OMe)_6^-$. Mehrotra and Agrawal (*140*) have confirmed the existence of $MZr_2(OR)_9$ ($M = Li, Na, K$) and showed that other double alkoxides such as $Li_2Zr_3(OEt)_{14}$, $Na_2Zr_3(OPr^i)_{14}$, and $MZr(OBu^t)_5$ ($M = Li, Na, K$) could also be isolated. They were all soluble in organic solvents and could be sublimed *in vacuo*. It is apparent from this short review that the field of multiple metal alkoxides offers scope for further interesting research.

## G. METAL TRIALKYLSILYLOXIDES

The metal trialkylsilyloxides $M(OSiR_3)_x$ are a special case of the general class of compounds containing the heterosiloxane group Si–O–M. They are of interest in revealing the effect on physicochemical properties of replacing the carbinol carbon of the tertiary alkoxo group $OCR_3$ by silicon. The larger silicon atom should reduce the steric effect of the alkyl groups, since they are placed further away from the central atom, although the silicon atom will exert more shielding than the carbon atom. Electronic effects are twofold and mutually opposed. Thus, silicon is less electronegative than carbon, and this should lead to the $^{-}OSiR_3$ ion being a better electron donor than $^{-}OCR_3$, but this is opposed by the fact that silicon has vacant *d* orbitals which may withdraw electron density from the oxygen by $p\pi$–$d\pi$ bonding. The field has received much attention during the past decade mainly by Andrianov and co-workers, Bradley and co-workers, and Schmidt and Schmidbaur and their co-workers, and derivatives of a wide range of metals are known. Since recent comprehensive reviews are available (*7*, *141*, *142*), we shall deal here only with the highlights and very recent publications.

The metal trialkylsilyloxides generally have good thermal stability and are perceptibly less readily hydrolyzed than the alkoxides. The least stable are $Cr^{VI}O_2(OSiMe_3)_2$ (dangerously explosive), $Hg(OSiMe_3)_2$, and $[Au^{III}(OSiMe_3)_3]_2$ (decomposes at room temperature) (*142*). A novel method of thermal decomposition was exhibited by bistrimethylsilyoxymercury(II) involving intramolecular transmethylation (*142*).

$$[Hg(OSiMe_3)_2]_n \rightarrow n MeHg(OSiMe_3) + (Me_2SiO)_n \qquad (17)$$

A similar behavior was shown by the zinc compounds, but not by cadmium. The methyltrimethylsilyloxymetal(II) compounds $[MeM(OSiMe_3)_4]$ (M = Zn, Cd, Hg) are all tetrameric in the crystalline state and have the interesting cubane structure (Fig. 3) analogous to that of $(MeZnOMe)_4$ (*142*). The same structure is exhibited by $[MeBe(OSiMe_3)]_4$ (*143*). Zeitler and Brown (*144*) showed that $Ti[OSi(C_6H_5)_3]_4$ had exceptionally high thermal and hydrolytic stability, while Chamberland *et al.* found that $VO[OSi(C_6H_5)_3]_3$ could be purified by washing with water (*145*).

Such $p_\pi$–$d_\pi$ bonding between silicon and oxygen as is present in $R_3SiO$ groups does not inhibit the oxygen from acting as a bridging group. Thus, the compounds $[MeM(OSiMe_3)]_4$ contain trimethylsilyloxy groups in triple-bridging configurations, and in the alkali metal compounds $[MOSiMe_3]_4$ (M = K, Rb, Cs) (*146*) the cubane structure is present analogous to that (Fig. 1) exhibited by the *tert*-butoxides (*15*). Mass spectra showed the presence of tetrameric fragment ions $M_4(OSiMe_3)_3(OSiMe_2)^+$ (M = K, Rb, Cs), whereas the lithium and sodium derivatives gave hexameric fragment ions $M_6(OSiMe_3)_5(OSiMe_2)^+$ (M = Li, Na) (*146*). Earlier work by Bradley and Thomas (*147*) had shown that crystalline tetrakistrimethylsilyloxyzirconium (m.p. 152°; sublimes at 135°/0.1 mm) was dimeric $[Zr(OSiMe_3)_4]_2$, presumably with five-coordinated zirconium, in marked contrast to the very volatile, monomeric liquid $Zr(OCMe_3)_4$. It was also noted that the pentakistrialkylsilyloxyuranium(V) compounds $[U(OSiR_3)_5]_n$ were more polymeric than the corresponding tertiary alkoxides, but the hexakis derivatives $U(OSiR_3)_6$ were all monomeric (*148*). Schmidbaur and Schmidt (*149–151*) have shown that tristrimethylsilyloxymetal(III) compounds $[M(OSiMe_3)_3]_2$ (M = Al, Ga, Fe) are dimeric and yield saltlike double compounds, e.g., $M[Fe(OSiMe_3)_4]$ (M = Li, Na, K, $SbMe_4$), containing tetrahedrally coordinated metals (*142*). A novel complex $Fe(OSiMe_3)_3(Me_3NO)$ (yellow crystals; m.p. 86°–90°; (b.p. 145°–148°/1 mm.) was obtained by treating the dimeric $[Fe(OSiMe_3)_3]_2$ with trimethylamine oxide (*142*). Recently, Shiotani and Schmidbaur (*152*) have succeeded in isolating gold (I) trimethylsilyl oxide stabilized by phosphine- or arsine-donor ligands.

$$\mathrm{AuCl\cdot L + NaOSiMe_3 \rightarrow Au(OSiMe_3)L + NaCl} \qquad (18)$$
$$(\mathrm{L = Me_3P,\ \phi_3P,\ \phi_3As})$$

The trimethylphosphine complex $Au(OSiMe_3)(PMe_3)$ was a soluble, colorless crystalline compound which was monomeric and could be sublimed *in vacuo*. It gave a parent molecular ion in the mass spectrum, and at temperatures above 190° it dissociated to a gold mirror, hexamethyldisiloxane, trimethylphosphine oxide, and trimethylphosphine. The trimethylarsine adduct was less stable. These interesting new compounds are examples of univalent gold exhibiting the coordination number of two.

The first examples of lanthanide trimethylsilyloxides were recently reported by Batwara and Mehrotra (*153*).

$$\mathrm{Ln(OPr^i)_3 + \mathit{n}Me_3SiO_2CMe \rightarrow Ln(OPr^i)_{(3-\mathit{n})}(OSiMe_3)_\mathit{n} + \mathit{n}Pr^iO_2CMe} \qquad (19)$$
$$(\mathrm{Ln = Gd, Er};\ n = 1, 2, 3)$$

These tristrimethylsilyloxy derivatives of gadolinium and erbium had an average degree of polymerization *ca.* 3.5 and were thus more polymerized than the corresponding *tert*-butoxides which were closer to trimeric.

Several investigators have pointed out that the metal trialkylsilyl oxides are less susceptible to hydrolysis than the corresponding alkoxides.

Bradley and Prevedorou-Demas have studied the controlled hydrolysis of trialkylsilyloxy derivatives of titanium, zirconium, and tantalum (*7*) in dioxane solution and the thermal stability and degree of polymerization of the hydrolysis products. The titanium compound $Ti(OSiMe_3)_4$ was notably resistant toward hydrolysis, but the initial products of hydrolysis were unstable owing to disproportionation to the parent compound and more highly condensed products (*154*).

$$2Ti(OSiMe_3)_4 + H_2O \rightarrow Ti_2O(OSiMe_3)_6 + 2Me_3SiOH \qquad (20)$$

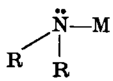
$$3Ti_2O(OSiMe_3)_6 \rightarrow 4Ti(OSiMe_3)_4 + \tfrac{1}{4}[Ti_8O_{12}(OSiMe_3)_8] \qquad (21)$$

The solid polymer $Ti_8O_{12}(OSiMe_3)_8$ was soluble in cyclohexane and a cubic cage was proposed for the $Ti_8O_{12}$ unit with the tetrahedral coordination of each titanium being completed by a pendant trimethylsilyloxy group. The more highly polymeric products obtained at higher degrees of hydrolysis were formulated in terms of Ti–O–Ti cross-linking of octamer units. The initial products of hydrolysis of $[Zr(OSiMe_3)_4]_2$ conformed to a polymer system reminiscent of the zirconium oxide alkoxides (*7*) based on octahedrally coordinated zirconium (*155*). This is understandable since the steric constraint on coordination expansion exerted by the bulky $Me_3SiO$ groups is relieved by the removal of these groups by hydrolysis. However, the degrees of polymerization of the residual more highly condensed polymers remaining after thermal disproportionation appeared to require the presence of octameric units analogous to those of titanium (*155*). The hydrolysis products from $Ta(OSiMe_3)_5$ could all be related to structures involving five-coordinated tantalum (*156*), whereas the behavior of $Ti(OSiEt_3)_4$ (*157*, *158*) was significantly different from $Ti(OSiMe_3)_4$. In the hydrolysis of $[Al(OSiMe_3)_3]_2$ it was noted that a small proportion of OH groups was present, but the polymers formed were interpreted on the basis of Al–O–Al cross-linking of dimeric units (*159*). A preliminary account has recently appeared (*160*) on the preparation and properties of dialkylsilanediol derivatives of transition metals. Thermolysis of the gummy polymer $[TiO_2(OSiEt_2)_2]_n$ gave an insoluble nonvolatile residue $[(TiO_2)_x(OSiEt_2)_y]$, and a titanium-containing distillate corresponding to $TiO_2(OSiEt_2)_{10}$ was obtained. The distillate may be a mixture of $(Et_2SiO)_3$, $(Et_2SiO)_4$, and $TiO_2(OSiEt_2)_x$ ($x = 2$–$4$), since it appeared to disproportionate readily to the volatile cyclic diethyldisiloxanes leaving a polymeric residue $[TiO_2(OSiEt_2)_4]_n$. However, fragment ions corresponding to species of the general formula $TiO_2(OSiEt_2)_x$ ($x = 4$–$10$) were clearly observed in mass spectrometric studies (*160*). A recent account of the comprehensive studies by Andrianov and co-workers on the elementoorganosiloxanes has appeared in review form (*161*).

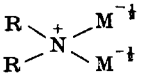
## III. Metal Dialkylamides

Although metal dialkylamides $M(NR_2)_x$ ($M$ = a metal of valency $x$; $R$ = an alkyl group) have been known for many years, the subject experienced a rather slow development until recently. In a review covering amino derivatives of metals and metalloids in 1965 by Jones and Lappert (*162*), twenty-eight elements were listed as known to form dialkylamido derivatives, and it was noteworthy that only a few transition metals were featured. Since that time the list has been extended, the reactivity of metal–nitrogen bonds has been explored, and some crystal structures have been elucidated, but much still remains to be investigated in this fascinating field.

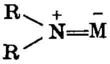
Considering covalently bonded dialkylamido groups, there are three distinct possibilities:



(V)



(VI)



(VII)

In structure (V) is depicted a metal–nitrogen $\sigma$ bond with a pyramidal nitrogen containing a basic lone pair of electrons. If steric factors allow, this lone pair may be involved in donation to another metal giving rise to the dialkylamido bridge (VI). If bridging is precluded by steric factors, the nitrogen lone pair may engage in $\pi$ bonding giving rise to a trigonal-planar nitrogen as shown in structure (VII).

### A. The Preparation of Metal Dialkylamides

There are three main preparative procedures for synthesizing metal dialkylamides. Some derivatives can be obtained by treating the metal hydride with the secondary amine.

$$MH_x + xR_2NH \rightarrow M(NR_2)_x + xH_2 \qquad (22)$$

Derivatives of aluminum hydride were used by Ruff (*163*) to prepare aluminum dialkylamides.

$$LiAlH_4 + 4Me_2NH \rightarrow LiAl(NMe_2)_4 + 4H_2 \qquad (23)$$

$$3LiAl(MNe_2)_4 + AlCl_3 \rightarrow 2Al_2(NMe_2)_6 + 3LiCl \qquad (24)$$

$$AlH_3(NMe_3) + 3Pr_2^iNH \rightarrow Al(NPr_2^i)_3 + Me_3N + 3H_2 \qquad (25)$$

The second method involves the reaction between the secondary amine and a metal alkyl.

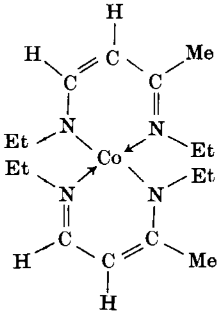
$$MR_x + xR_2NH \rightarrow M(NR_2)_x + xRH \qquad (26)$$

This method was used by Coates and Glockling (*164*) to prepare the trimeric beryllium bisdimethylamide $Be_3(NMe_2)_6$. It is also the most convenient method for obtaining lithium dialkylamides since *n*-butyllithium is commercially available.

The third method involves the reaction of a metal halide (usually the chloride) with an alkali metal (usually Li or Na) dialkylamide, e.g.,

$$MCl_x + xLiNR_2 \rightarrow M(NR_2)_x + xLiCl \qquad (27)$$

The first transition metal derivative synthesized was $Ti[N(C_6H_5)_2]_4$, which was prepared from $TiCl_4$ and potassium diphenylamide (*165*). The only uranium derivative prepared to date is $U(NEt_2)_4$, which was obtained from $UCl_4$ and lithium diethylamide (*122*). In recent years tetradialkylamides of titanium (*166*), vanadium (*167*), chromium (*168, 169*), zirconium (*166*), niobium (*170*), hafnium (*171*), thorium (*171*), and tin (*167*), pentadialkylamides of niobium (*170*) and tantalum (*172*), and the hexadimethylamide of tungsten (*173*) have all been obtained by means of metal chloride/lithium dialkylamide reactions. However, the reaction of metal chloride and lithium dialkylamide does not always proceed according to the requirements of Eq. (27) (*3*). For example, in the case of $NbCl_5$, the bulkier dialkylamides give rise to tetradialkylamidoniobium(IV) compounds (*170*), whereas the same ligands with $TaCl_5$ gave the monoalkylimidotrisdialkylamidotantalum(V) compounds $RN{=}Ta(NR_2)_3$ (*172*). This behavior was ascribed to steric factors which led to the instability of $M(NR_2)_5$ derivatives, but the different modes of breakdown obviously reflect differences in electronic factors (redox properties) between niobium and tantalum. Further complications occurred when chlorides of Mn(II), Fe(III), Co(II), and Ni(II) were treated with $LiNEt_2$ and no diethylamido derivatives were isolated. Instead the interesting unsymmetrical nitrogen chelate (VIII) was obtained from a reaction which is summarized by Eq. (28) (*174, 175*).



(VIII)

$$7CoCl_2 + 14LiNEt_2 \rightarrow CoN_4C_{16}H_{30} + 6Co + 14LiCl + 10Et_2NH \qquad (28)$$

In some reactions reduction of the metal to a lower oxidation state occurs even with the less bulky groups such as $NMe_2$. Thus, the major product from the $MoCl_5/LiNMe_2$ reaction was a polymeric Mo(III) dimethylamide $[Mo(NMe_2)_3]_x$, which afforded the volatile $Mo(NMe_2)_4$ by disproportionation (*176*). Similarly the $WCl_6/LiNMe_2$ reaction gave as the major product polymeric W(III) dimethylamide $[W(NMe_2)_3]_x$ with only a small yield of $W(NMe_2)_6$ (*173*). Mass spectral studies suggested that some $W_2(NMe_2)_{10}$ was formed in the disproportionation of $[W(NMe_2)_3]_x$ (*177*). Disproportionation was also a characteristic feature of the trisdialkylamido derivatives of titanium (*178*), vanadium (*178*), and chromium (*168, 169*).

$$MCl_3 + 3LiNEt_2 \rightarrow M(NEt)_2)_3 + 3LiCl \tag{29}$$

$$2M(NEt_2)_3 \rightarrow M(NEt_2)_4 + M(NEt_2)_2 \tag{30}$$
$$(M = Ti, V, Cr)$$

However, by using the very bulky ligand $NPr^i_2$ it was possible to stabilize trisdiisopropylamidochromium(III) as a volatile, monomeric derivative containing three-coordinated chromium (*168*, *179*). Bürger and Wannagat have prepared a number of interesting bistrimethylsilylamido derivatives $M[N(SiMe_3)_2]_x$ using the reaction of the sodium derivative $NaN(SiMe_3)_2$ with a metal halide. Thus, the tris derivatives of Cr(III) (*180*) and Fe(III) (*181*), the bis derivatives of Mn(II) (*180*), Co(II) (*181*), nickel(II) (*180*), and the zinc subgroup (*182*), and the mono derivative of Cu(I) (*180*), were isolated by the general method:

$$MX_x + xNaN(SiMe_3)_2 \rightarrow M[N(SiMe_3)_2]_x + xNaCl \tag{31}$$

Recently the tris derivatives of Ti(III) and V(III) $M[N(SiMe_3)_2]_3$ ($M = Ti, V$) were obtained by Bradley and Copperthwaite (*183*), using the reaction of $LiN(SiMe_3)_2$ with the five-coordinated metal trichloride complexes $MCl_3(Me_3N)_2$. Also, the first lanthanide(III) tris derivatives have been obtained using the lithium derivatives of diisopropylamine and bistrimethylsilylamine (*184*).

In some cases {e.g., $Cr[N(SiMe_3)_2]_2$ $(T.H.F.)_2$ (*185*), $Mn[N(SiMe_3)_2]_2$ (T.H.F.) (*186*)} solvent molecules (T.H.F. = tetrahydrofuran) remained coordinated to the metal silylamide and in other reactions involving phosphine complexes of metal chlorides the phosphine remained coordinated {e.g., $Me_3P \cdot AuN(SiMe_3)_2$ (*152*), $(C_6H_5)_3P \cdot Co[N(SiMe_3)_2]_2$ and $[(C_6H_5)_3P]_2NiN(SiMe_3)_2$ (*187*)}.

In addition to the three main preparative methods dealt with above, there is a novel method recently reported by Ashby and Kovar (*188*) for the synthesis of aluminum trisdiethylamide and the diethylaminoalanes.

$$Al + 3/2H_2 + nEt_2NH \rightarrow H_{(3-n)}Al(NEt_2)_n + nH_2 \tag{32}$$
$$(n = 1, 2, 3)$$

The reaction was carried out at moderate temperatures and pressures in benzene solution and careful control of the conditions led to the formation of $H_2AlNEt_2$, $HAl(NEt_2)_2$, or $Al(NEt_2)_3$. A 91% yield of $Al(NEt_2)_3$ was obtained using diethylamine as solvent at 150° under 3000 psig of hydrogen for 4 hr. This direct synthesis of aluminum diethylamide from the metal may well have commercial applications.

Another procedure of limited application is the aminolysis or transamination reaction (*166*, *170*, *172*).

$$M(NR_2)_x + yHNR_2' \rightarrow M(NR_2')_y(NR_2)_{(x-y)} + yHNR_2 \qquad (33)$$

The extent of this reaction is often limited by steric hindrance.

An unusual reaction which was reported to produce the dimethylamide of Na, K, Cu(II), Cd, Hg(II), and Al involved prolonged heating of the metal cyanide (Na, K) or acetate (Na, K, Cu, Cd, Hg, Al) with anhydrous dimethylformamide (*189*).

In this review we are primarily concerned with the fully substituted metal dialkylamides $M(NR_2)_x$, but reference to the synthesis of "mixed ligand compounds" $TiX_n(NR_2)_{(4-n)}$ ($n = 1, 2, 3$; X = alkyl, aryl, cyclopentadienyl, halide, alkoxide, etc.) may be found in the comprehensive account by Bürger and Neese (*5*). Most of the reactions described for Ti(IV) will be applicable to other polyvalent metals.

## B. Chemical Properties of Metal Dialkylamides

Most of the metal dialkylamides are very readily hydrolyzed to the amine and metal oxide or hydroxide. This is a special case of the more general reactivity of the metal dialkylamides with molecules HL containing active hydrogen.

$$M(NR_2)_x + yHL \rightarrow MLy(NR_2)_{(x-y)} + yHNR_2 \qquad (34)$$
$$(L = \text{halogen, OH, OR, etc.})$$

Some interesting tetrakis-Schiff base complexes $TiL_4$ (*190*) and $ZrL_4$ (*191*) were thus obtained. The scope of this reaction has been very systematically explored by Lappert and co-workers with special reference to the reactivity of the Sn–$NR_2$ bonds, but some reactions of $M(NMe_2)_4$ (M = Ti, Zr, Hf) and $Ti(NR_2)_3$ have been included (*162*, *192–196*). Streitwieser and co-workers (*197*) have utilized the reactivity of lithium and cesium cyclohexylamides to determine the acidity of hydrocarbons.

Another type of reaction is ligand exchange or metathetical reaction.

$$\begin{aligned} M(NR_2)_4 + M'X_4 &\rightarrow MX(NR_2)_3 + M'X_3(NR_2) && (35)\\ &\rightarrow MX_2(NR_2)_2 + M'X_2(NR_2)_2 && (36)\\ &\rightarrow MX_3(NR_2) + M'X(NR_2)_3 && (37)\\ &\rightarrow MX_4 + M'(NR_2)_4 && (38) \end{aligned}$$

The equilibria involved for $M = M' = Ti$ and $X$ = halogen or OR, have been studied by Weingarten and Van Wazer (*66*), and this type of reaction has been well documented for titanium derivatives by Bürger and Neese (*5*) and for organotin dialkylamides by George and Lappert (*198*).

The third type of reaction involves insertion of an unsaturated group between the metal–nitrogen bond. The *N*,*N*-dialkyl dithiocarbamates of the early transition metals were first prepared by insertion of carbon disulfide into metal dialkylamides (*199*).

$$M(NR_2)_x + xCS_2 \rightarrow M(S_2CNR_2)_x \qquad (39)$$

The generalized insertion reaction [Eq. (40)] has been thoroughly and systematically explored by Lappert and co-workers (*162*, *200*), who

$$L_xM(NR_2)_y + yA{=}BC \rightarrow L_xM[AB(NR_2)C]_y \qquad (40)$$

demonstrated the great synthetic value of this reaction. Nitriles undergo a variety of reactions including polymerization (*200–202*).

Dialkylamides of transition metals in lower valencies [e.g., Ti(III), V(III), V(IV), Cr(III), Nb(IV), and Mo(IV)] and some of the bistrimethylsilylamides are extraordinarily sensitive to oxygen and demand exceptional precautions in handling these compounds for spectroscopic and other physical measurements. It is possible that peroxo or superoxo compounds are initially formed by addition of molecular oxygen, but the instability of such derivatives poses problems and hazards in characterizing them. Thus, under certain conditions the highly reactive chromium(III) trisdiisopropylamide $Cr(NPr^i_2)_3$ formed a 1 : 1 compound $Cr(O_2)(NPr^i_2)_3$, which may be a peroxochromium(V) derivative (*203*), but at a low temperature the uptake of oxygen corresponds to the formation of $CrO_3(NPr^i_2)_3$, a dangerously explosive compound (*204*). However, with nitric oxide the reaction with $Cr(NPr^i_2)_3$ gave rise to the diamagnetic $Cr(NO)(NPr^i_2)_3$, which is a rare example of four-coordinated chromium(II) (*205*). The stability of the Cr–NO system was evident from reactions with *tert*-butanol, which gave derivatives such as $Cr(NO)(OBu^t)(NPr^i_2)_2$ and $Cr(NO)(OBu^t)_3$ without loss of nitric oxide.

It has been found that metal dialkylamides $M(NR_2)_4$ (M = Ti, Zr, Hf) undergo "addition reactions" with metal carbonyls $M'(CO)_x$ (M′ = Cr, Fe, Ni) to form intractable compounds which were formulated as $\{M(NR_2)_4[M'(CO)_x]_2\}$ (*206*).

## C. Physical Properties of Metal Dialkylamides

The metal dialkylamides are reasonably volatile compounds which may be sublimed or distilled *in vacuo*, and they are usually soluble in nonreactive organic solvents. This has enabled molecular weights, absorption spectra, and NMR and ESR spectra to be determined in solution. Some of these compounds are crystalline and a few X-ray crystal analyses have been carried out.

The dialkylamido group may act as a bridging ligand as shown in structure (VI), and oligomeric species are found for the alkali metals, beryllium and aluminum. In the case of quadrivalent, quinquevalent, and sexivalent metals the dialkylamides are usually monomeric owing to steric hindrance which prevents coordination polymerization. The zirconium (hafnium) tetradimethylamide is a borderline case since it showed some polymerization in solution (number average degree of polymerization = 1.22) (*166*), which was confirmed by variable temperature NMR studies (*171*) and low-temperature infrared spectra (*207*).

### *1. The Nature of the Metal–Nitrogen Bond*

It is sometimes assumed that the high chemical reactivity of metal dialkylamides must be due to weak metal–nitrogen bonds with a tendency to ionic character $\overset{+}{M}\overset{-}{N}R_2$. This does not necessarily follow, and it is well established that some metal complexes containing strongly covalently bonded ligands are also reactive or labile owing to the availability of vacant low-energy orbitals in the metal which can facilitate interactions with a nucleophilic reagent. The observation of strong infrared- and Raman-active metal–nitrogen bands is indicative of substantial covalent character in the polyvalent metal dialkylamides. The ESR spectra of vanadium(IV) and niobium(IV) dialkylamides may also be interpreted as suggesting the presence of covalent metal–nitrogen bonds. In the few X-ray structures which have been completed, it is noteworthy that the nonbridging dialkylamido groups invariably have trigonal-planar nitrogens implying $\pi$-donor characteristics in the dialkylamido group as shown in structure (VII). In addition, the electronic absorption spectra of transition metal dialkylamides show a substantial ligand-field splitting energy for dialkylamido groups. Altogether these physical data give a picture of the metal–nitrogen bond as being substantially covalent and directional in character.

Thermochemical studies by Bradley and Hillyer (*84*) on $Ti(NEt_2)_4$ led to a value of the standard heat of formation $\Delta H_f^0[Ti(NEt_2)_4, (liq.)] = -116 \pm 2.0$ kcal/mole with an estimated $\Delta H_f^0[Ti(NEt_2)_4, (g)] = -100 \pm 2.3$ kcal/mole. Uncertainty in the value of $\Delta H_f^0[Et_2N, (g)]$ precluded an accurate estimate of the average bond dissociation energy, but the value $\bar{D}(Ti–N) \sim 73$ kcal/mole was derived. This shows that the metal–nitrogen bonds are moderately strong in $Ti(NEt_2)_4$. However, a preliminary report on $Me_3Sn{-}NMe_2$ gave the Sn–N bond energy as ~40 kcal/mole (*162*).

Mass spectral studies gave independent evidence of the considerable thermodynamic stability of transition metal dialkylamides. Thus, parent ion peaks were observed for $Ti(NMe_2)_4^+$, $V(NMe_2)_4^+$, $Zr(NMe_2)_4^+$, $Hf(NMe_2)_4^+$, $Nb(NMe_2)_5^+$, and $Ta(NMe_2)_5^+$ (*207*), $Cr(NEt_2)_4^+$ (*169*), $Nb(NEt_2)_4^+$ (*208*), $Mo(NMe_2)_4^+$ (*176*), $W(NMe_2)_6^+$ (*173*), $Al_2(NMe_2)_6^+$ and $Al(NPr_2^i)_3^+$ (*209*), in addition to many metal-containing fragment ions, metastable peaks, and doubly charged metal-containing species. Parent ion peaks were also obtained in the mass spectra of $M[N(SiMe_3)_2]_3$ (M = Ti, V, Cr, Fe) (*183*).

### 2. *Infrared and Raman Spectra of Metal Dialkylamides*

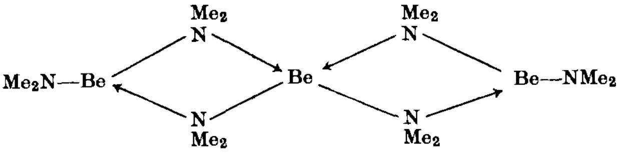
The infrared and Raman spectra for $Ti(NMe_2)_4$ were first reported by Bürger *et al.* (*210*). The spectra were interpreted on the basis of a tetrahedral ($T_d$) $TiN_4$ skeleton with a strong infrared band at 590 $cm^{-1}$ assigned to the stretching mode $\nu_{as}TiN_4(F_2)$ and a polarized Raman band at 532 $cm^{-1}$ assigned to $\nu_sTiN_4(A_1)$. Other characteristic strong infrared absorptions were assigned to ligand vibrations: $\delta CH_3$ (1249 $cm^{-1}$), $\nu_sNC_2$ (945 $cm^{-1}$). Bürger and Sawodny (*211*) also reported infrared and Raman spectra for the series $M(NMe_2)_4$ (M = Si, Ge, Sn) and calculated the $MN_4$ and $NC_2$ force constants. It is noteworthy that the force constants for $Sn(NMe_2)_4$ (Sn–N = 3.110; C–N = 4.351 mdyne/Å) and $Ti(NMe_2)_4$ (Ti–N = 3.111; C–N = 4.355 mdyne/Å) were virtually identical, although the frequencies differed significantly. An interesting compilation of data on Ti–N frequencies for compounds of the type $Ti(NR_2)_xX_{(4-x)}$ [where R = Me, Et; X = Cl, Br, I, Me, Et; and $x = 4, 3, 2, 1$], is available in the review by Bürger and Neese (*5*). Bradley and Gitlitz (*212*) obtained infrared spectra on a range of dialkylamides of Ti(IV), V(IV), Zr(IV), Nb(V), Nb(IV), Hf(IV), Ta(V), Th(IV), and $Ta{=}NR(NR_2)_3$. The data were interpreted in terms of the dialkylamido groups acting as $\pi$ donors with significant contributions of the type $\overset{+}{M}{=}\overset{-}{N}R_2$ to the metal–nitrogen bonds. Although the tetrahedral molecules $M(NR_2)_4$ should give only one infrared-active M–N stretching frequency the five-coordinated species $M(NMe_2)_5$ (M = Nb, Ta) should exhibit either two ($A_2''$, $E'$ in $D_{3h}$) for a trigonal bipyramid or three ($2A$, $E$ in $C_{4v}$) for a tetragonal pyramid. Both niobium and tantalum pentadimethylamides gave only one band in the M–N stretching region in cyclohexane solutions, and it was concluded that the other bands were too close in frequency to be resolved. Similarly, only one Zr–N band was observed for $Zr(NMe_2)_4$, although it was known to contain some polymeric species.

Further work using mulled samples of the metal dimethylamides has revealed more spectral details (*176*, *207*). Thus, the infrared spectrum $Ti(NMe_2)_4$ gave a single symmetrical Ti–N band, but $V(NMe_2)_4$ and $Mo(NMe_2)_4$ gave M–N bands exhibiting shoulders on the high-frequency side indicative of a lowering of symmetry to $D_{2d}$. The pentadimethylamides of Nb and Ta each showed two partially resolved M–N bands and, taken in conjunction with their Raman spectra, suggested a trigonal-bipyramidal configuration. At low temperatures (~100°K) most of the M–N bands shifted (5–10 $cm^{-1}$) to lower frequencies, but for $Ti(NMe_2)_4$, $V(NMe_2)_4$, $Mo(NMe_2)_4$, $Nb(NMe_2)_5$, $Ta(NMe_2)_5$, and $W(NMe_2)_6$ there were no major changes. With $Zr(NMe_2)_4$ and $Hf(NMe_2)_4$ some important changes occurred on lowering the temperature, which could be explained on the assumption that the degree of polymerization increased markedly at lower temperatures. The infrared and Raman spectra of $W(NMe_2)_6$ (W–N stretching bands at 555 $cm^{-1}$ Raman and 545 $cm^{-1}$ infrared) were consistent with the known octahedral structure of this compound (*173*).

Infrared and Raman spectra have also been obtained for some of the bistrimethylsilylamido derivatives $M[N(SiMe_3)_2]_x$. Bürger *et al.* (*213*) assigned the spectra of $Be[N(SiMe_3)_2]_2$ in terms of a linear two-coordinated beryllium compound with the $D_{2d}$ configuration for the $Si_2NBeNSi_2$ framework. Force constant calculations gave Be–N, 2.957 and Si–N, 3.395 mdyne/Å. Similarly the infrared and Raman spectra of $M[N(SiMe_3)_2]_2$ (M = Zn, Cd, Hg) were also assigned on the basis of linear monomeric molecules (*182*). The monomeric $Co[N(SiMe_3)_2]_2$ gave a very similar infrared spectrum to those of the zinc, cadmium, and mercury derivatives (*214*).

### 3. *NMR Spectra of Metal Dialkylamides*

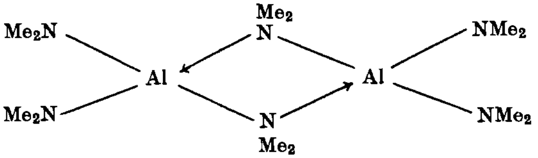
On the basis of its proton NMR spectrum (*215*), one form of $Be(NMe_2)_2$ was given the linear trimeric structure (IX). The NMR spectra have also



(IX)

been reported for some dialkylaminoberyllium alkyls by Coates *et al.* (*216*, *217*).

The proton NMR spectrum of $Al_2(NMe_2)_6$ also showed distinct peaks corresponding to terminal and bridging $NMe_2$ groups in accordance with structure (X). These peaks showed no tendency to coalesce even up to 150°C, indicating a relatively strong nitrogen bridge (*209*). The monomeric derivative $Al(NPr^i_2)_3$ showed only a single type of dialkylamide group.



(X)

Moedritzer (*218*) obtained the chemical shifts for $NMe_2$ protons in $Si(NMe_2)_4$, $Ge(NMe_2)_4$, $P(NMe_2)_3$, $As(NMe_2)_3$, $Sb(NMe_2)_3$, and $Ti(NMe_2)_4$ on the neat liquids. Bradley and Gitlitz (*219*) reported chemical shift data for a number of transition metal dialkylamides in cyclohexane solution, but could find no correlation with other properties of the metals. However, in the case of $Zr(NMe_2)_4$, they found evidence for polymerization at low temperatures. Proton NMR data are also given by Bürger and Neese (*5*) for a range of derivatives $Ti(NR_2)_xX_{(4-x)}$ ($x = 3, 2, 1$; X = R, Cl, Br, SEt). Single NMR peaks were also found for the diamagnetic, monomeric species $Mo(NMe_2)_4$ (*176*) and $W(NMe_2)_6$ (*173*).

The proton NMR spectra of $Be[N(SiMe_3)_2]_2$ (*213*) and $M[N(SiMe_3)_2]_2$ (M = Zn, Cd, Hg) (*182*) all gave single peaks only a few hertz downfield (2–6 Hz) from T.M.S., but satellites due to proton coupling to $^{29}Si$ and $^{13}C$ enabled $J_{\mathrm{H-Si}}$ (6–7 Hz) and $J_{\mathrm{H-C}}$ (116–119 Hz) to be determined.

### 4. *Paramagnetic Metal Dialkylamides (d–d Bands, Magnetism, and ESR Spectra)*

Some of the transition metal dialkylamides are paramagnetic owing to the presence of unpaired *d* electrons, and these give rise to measurable ligand-field and magnetic effects.

*a. Four-Coordinated Derivatives.* The compounds $V(NR_2)_4(d^1)$, $Nb(NR_2)_4(d^1)$, $Cr(NEt_2)_4(d^2)$, and $Mo(NMe_2)_4(d^2)$ are all monomeric and all except $Mo(NMe_2)_4$ are paramagnetic. Electron spin resonance studies (*89*, *220*) on $V(NMe_2)_4$ and $V(NEt_2)_4$ showed conclusively that these molecules have a distorted ($D_{2d}$) tetrahedral $VN_4$ structure. Thus, a regular tetrahedral $d^1$ species would have a degenerate ground state ($^2E$) and an ESR signal would not be expected at room temperature. However, both $V(NMe_2)_4$ (*89*) and $V(NEt_2)_4$ (*220*) gave strong signals at room temperature suggestive of an orbitally nondegenerate ground state and in frozen solution at −150°C the anisotropic $g$ values ($g_{\parallel} < g_{\perp}$) corresponded to axial symmetry ($D_{2d}$) with the electron occupying the $d_{x^2-y^2}$ orbital (see Fig. 15). The two partially resolved *d–d* bands at ~17,500 and ~13,300 cm$^{-1}$ may be assigned to the transitions $^2E \leftarrow {}^2B_1$ and $^2B_2 \leftarrow {}^2B_1$ (see Fig. 15), respectively (*89*). The $3d^1$ electron thus benefits from a significant amount of ligand-field stabilization energy. At low temperature (77°K) the higher frequency band in $V(NEt_2)_4$ was split into a doublet ($\lambda\lambda_{max}$ 18,700 and 16,600 cm$^{-1}$). This may be due to the Jahn–Teller effect on the $^2E$ excited state. The magnetic susceptibility of $V(NEt_2)_4$ obeyed the Curie–Weiss law (small $\theta$ value) and gave the magnetic moment $\mu_{eff} = 1.70 \pm 0.02$ independent of temperature as expected for the $^2B_1$ ground state (*89*). This agreed well with the value (1.71) calculated from the $g$-values. Holloway *et al.* (*220*), following and refining the methods used by Kokoszka *et al.* (*90*) for $V(OBu^t)_4$, calculated the molecular orbital parameters for $V(NEt_2)_4$ from the values of $g_{\parallel}$, $A_{\parallel}$, $g_{\perp}$, and $A_{\perp}$ determined by electron spin resonance (the $V^{51}$ nucleus with spin $I = 7/2$ gives an eight-line spectrum owing to electron-nuclear hyperfine coupling). According to these calculations the $d_{xy}(B_2)$ orbital appeared to be most affected by covalency, but from the energy level diagram (Fig. 15) the $d_{xz}$ and $d_{yz}$ orbitals are most involved. Apart from this discrepancy the electronic spectra and the ESR spectra both suggest that a considerable amount of covalency is involved in these molecules.

Bradley and Chisholm (*208*) have studied the $Nb(NR_2)_4$ compounds since these involve $4d^1$ systems. Each compound had a "*d–d*" band around 18,000–21,000 cm$^{-1}$, which was assigned to the $^2E \leftarrow {}^2B_1$ transition and at low temperature (77°K) this band split into two partially resolved bands (20,400 and 18,200 cm$^{-1}$). This behavior was similar to that observed with $V(NR_2)_4$ compounds. However, the $Nb(NR_2)_4$ spectra showed no bands due to the $^2B_2 \leftarrow {}^2B_1$ transition, presumably because the separation in energy of $^2E$ and $^2B_2$ states was much greater for niobium(IV) than vanadium(IV) and, thus, the $^2B_2 \leftarrow {}^2B_1$ symmetry-forbidden transition was too weak to be observed. The ESR spectra of $Nb(NR_2)_4$ compounds showed well-resolved ten-line spectra ($Nb^{93}$; $I = \frac{9}{2}$) at room temperature, whereas frozen solutions (toluene; 123°K) gave clear evidence for a $D_{2d}$ distortion with $d_{x^2-y^2}(b_1)$ ground state ($g_{\parallel} < g_{\perp}$). Nevertheless, the magnetic susceptibilities all gave anomalously low values ($\mu_{eff} \sim 0.8$), although the Curie–Weiss law was obeyed.

Interesting results were obtained with the $3d^2$ and $4d^2$ systems $Cr(NR_2)_4$ and $Mo(NR_2)_4$. The chromium(IV) compounds gave an intense ($\epsilon_m = 1200$) *d–d* transition at 13,700 cm$^{-1}$, which was provisionally assigned to $^3A_2 \leftarrow {}^3B_1$ in $D_{2d}$ symmetry. Magnetic susceptibilities conformed to the Curie–Weiss law with small $\theta$ values and gave $\mu_{eff} \sim 2.80$

independent of temperature (*169*). The molybdenum(IV) compounds $Mo(NR_2)_4$ (R = Me, Et) were diamagnetic and gave strong "*d–d*" bands [$Mo(NMe_2)_4$, broad doublet 21,740 and 19,600 $cm^{-1}$; $Mo(NEt_2)_4$, broad band at 18,500 $cm^{-1}$] assigned to $^1E \leftarrow {}^1A_1$ (in $D_{2d}$) transitions which are symmetry-allowed. $Mo(NMe_2)_4$ gave weaker shoulders at 14,300 and 10,500 $cm^{-1}$ assigned to $^1A_2 \leftarrow {}^1A_1$ and $^1B_1 \leftarrow {}^1A_1$ transitions, but all bands gave further splitting into unresolved doublets at low temperature (*176*). Referring to the single-electron energy level diagram in $D_{2d}$ (Fig. 15), it appears that in $Mo(NR_2)_4$ the separation between the $d_{x^2-y^2}$ and higher energy orbitals is sufficient to cause spin pairing. It was pointed out (*176*) that in $D_{2d}$ symmetry the $M(NR_2)_4$ molecule with the conformation giving minimum interligand steric hindrance would allow all *d* orbitals except $d_{x^2-y^2}$ to be involved in both $\sigma$ and $\pi$ bonding. Thus, the spin pairing in $Mo(NR_2)_4$ may be considered as a consequence of strong covalent bonding.

*b. Three-Coordinated Derivatives.* Some preliminary reports have appeared on the spectra and magnetic properties of the trigonally coordinated transition metals in compounds such as $M[N(SiMe_3)_2]_3$ (M = Ti, V, Cr, Fe) and $Cr(NPr^i_2)_3$. The $d^1$ compound $Ti[N(SiMe_3)_2]_3$ gave an ESR signal at room temperature indicative of a $^2A_1'$ ground state, and frozen solutions (135°K) exhibited *g*-anisotropy which confirmed axial symmetry ($D_{3h}$) for the $TiN_3$ framework (*183*). Magnetic susceptibility data and electronic spectra have also been obtained (*186*). The vanadium compound ($d^2$) did not give an ESR signal, although it is paramagnetic and this behavior is also consistent with the trigonal coordination of the metal (*183*). The $d^3$ compounds $Cr(NPr^i_2)_3$ and $Cr[N(SiMe_3)_2]_3$ both gave magnetic susceptibilities corresponding to spin-only magnetic moments ($\mu_{eff} = 3.80$) independent of temperature (*179*). Neither compound in solution at room temperature gave an ESR signal, but in frozen solutions at 130°K a spectrum was obtained with $g_\parallel = 2.0$ and $g_\perp = 4.0$ corresponding to an axially symmetric ($D_{3h}$) system with a large zero-field splitting (*221*, *222*). The iron(III) compound $Fe[N(SiMe_3)_2]_3$ obeyed the Curie–Weiss law (small $\theta$) and gave a temperature-independent magnetic moment ($\mu_{eff} = 5.91$) corresponding to a high-spin $d^5$ species. The ESR spectra on a powder and on oriented single crystals ($g_\parallel = 2.007$; $g_\perp = 6.021$) showed that a large zero-field splitting was present in this axially symmetric compound (*222*, *223*). An interesting Mössbauer spectrum was also obtained (*223*). At 77°K a typical two-line spectrum was obtained ($\delta = 0.43$ mm $sec^{-1}$) with a large quadrupole splitting ($\Delta E = 5.12$ mm·$sec^{-1}$). At 4.2°K a five-line spectrum appeared which on application of a weak magnetic field gave a fully resolved six-line spectrum. It was deduced that the principal component of the electric field gradient tensor was positive. The electronic absorption spectrum of $Fe[N(SiMe_3)_2]_3$ gave bands which were rather strong for spin-forbidden transitions associated with the $^6A_1'$ ground state, but the two *d–d* transitions at 16,100 and 20,000 $cm^{-1}$ were assigned to $(^4A_1'', {}^4A_2'') \leftarrow {}^6A_1'$ and $^4E' \leftarrow {}^6A_1'$, respectively. Assignments of the electronic spectra of the $d^1$, $d^2$, and $d^3$ trigonal compounds have also been made on a crystal field model for $D_{3h}$ symmetry (*224*).

*c. Two-Coordinated Derivatives.* The cobalt(II) derivative $Co[N(SiMe_3)_2]_2$ (*181*) was shown by Bradley and Fisher (*214*) to be monomeric in solution, and it gave the same electronic absorption spectrum in solution, liquid, or crystalline states. The spectrum was therefore assigned by analogy with gaseous $CoCl_2$ for a linear two-coordinated ($D_{\infty h}$) species. Its magnetic susceptibility obeyed the Curie law with $\mu_{eff} = 4.83$ independent of temperature.

### 5. *Structures of Metal Dialkylamides Determined by X-Ray or Electron Diffraction*

Structures of various metal dialkylamides have recently been determined and important data on M–N bond lengths and the bond angles in these molecules are being collected.

The single crystal X-ray analysis of $W(NMe_2)_6$ showed (Fig. 16) the expected octahedral $WN_6$ framework (W–N = 2.032 ± 0.025 Å) (*173*). A feature of special interest was the shape and conformation of the

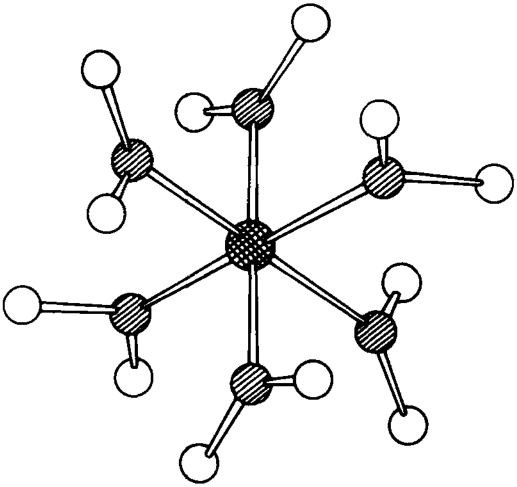


FIG. 16. The structure of $[W(NMe_2)_6]$. Cross-hatched, W; hatched, N; plain, Me.

dimethylamide ligands. The symmetry point group of the heavy atom framework $W(NC_2)_6$ was $T_h$ due to extensive planarity (e.g., $C_2NWNC_2$ units are all coplanar). Thus, the nitrogen atoms are trigonal planar rather than pyramidal, and this is consistent with delocalized nitrogen-to-tungsten $\pi$ bonding involving molecular orbitals of $T_{2g}$ symmetry. An 18-electron valency group can thus be accorded to the $d^0$ tungsten(VI) atom, but lack of comparable data on W(VI)–N bond lengths renders uncertain an assessment of $\pi$ character from the observed W–N bond length. Another point of interest was the small $C\hat{N}C$ (104.92°) angle of the ligand and the unexpectedly long C–N (1.516 Å) bonds. It thus appears that the W–N bond has more *s*-character (approx. *sp* hybridization) than the N–C bonds (approx. $sp^3$ hybridization). If the W–N and N–C bonds all involved $sp^2$-hybrid nitrogen $\sigma$ orbitals the N–C bond length should be close to 1.485 ± 0.002 Å (*225*) and the $C\hat{N}C$ angle 120°, whereas the observed $C\hat{N}C$ is close to the tetrahedral angle and the N–C bond length is close to the $N(sp^3)$–$C(sp^3)$ value of 1.51 Å. The structure also shows that the central atom is well shielded by the symmetrical array of twelve $CH_3$ groups and this, in conjunction with the 18-electron valency group for tungsten, explains the relatively inert character of this compound to attack by nucleophilic reagents.

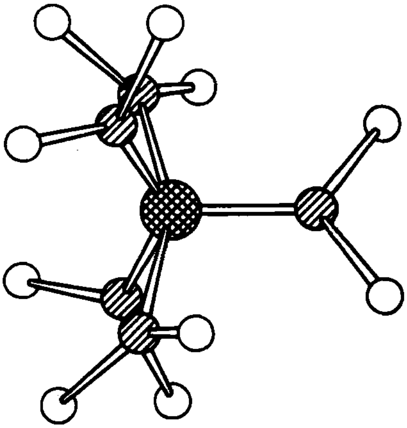


FIG. 17. The structure of $[Nb(NMe_2)_5]$. Cross-hatched, Nb; hatched, N; plain, Me.

Heath and Hursthouse (*226*) have published a preliminary account of the structures of the five-coordinated metal dialkylamides $Nb(NMe_2)_5$ and $Nb(piperidide)_5$. In both compounds the structure of the partial framework $Nb(NC_2)_5$ is the same and approximates to a distorted tetragonal pyramid (Fig. 17). The Nb–N(1) bond occupies the axial position (it is a 2-fold axis), and it is significantly shorter (1.977 ± 0.017 Å) than the basal Nb–N bonds (average 2.042 ± 0.015 Å). The nitrogens are again trigonal planar implying that the nitrogen is acting as a $\pi$ donor to the niobium(V) $d^0$ atom. However, it was pointed out that the shape of the ligand could be due to intramolecular congestion. It is interesting that both $Nb(NMe_2)_5$ and $Nb(piperidide)_5$ adopt this structure with one Nb–N bond shorter than the other four. It may be that the short bond Nb–N(1) is due to the presence of a localized $\pi$ bond involving one vacant metal $d$ orbital and the nitrogen $p_\pi$ orbital, while the longer bonds are due to delocalized partial $\pi$ bonds involving only two $d$ orbitals with the remaining four nitrogens.

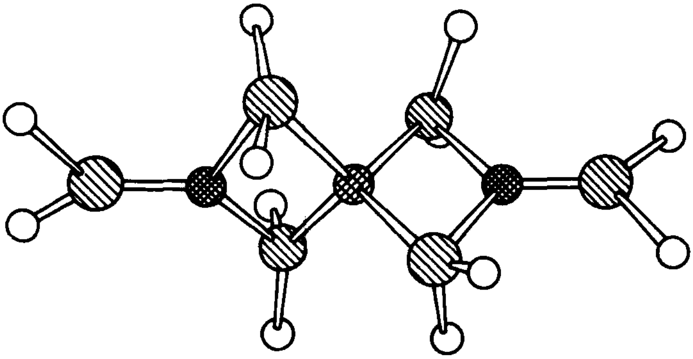


FIG. 18. The structure of $[Be(NMe_2)_2]_3$. Fine cross-hatched, Be (tetrahedral); cross-hatched, Be (trigonal); hatched, N; plain, Me.

Vilkov *et al.* (*227*) have determined the structure of $Sn(NMe_2)_4$ in the vapor state by electron diffraction. The $SnN_4$ framework was tetrahedral (Sn–N = 2.045 ± 0.060 Å; $N\hat{Sn}N = 109.5°$) and the nitrogen atoms were close to trigonal planar ($C\hat{N}C = 119 \pm 3$; $SnNC = 117.5 \pm 1.5°$). The calculations were based on a $C_{2v}$ point group for the molecules and gave C–N = 1.450 ± 0.045 Å and C–H = 1.10 ± 0.10 Å.

The structure of the trimer $Be_3(NMe_2)_6$ was determined by X-ray diffraction analysis by Atwood and Stucky (*228*). The molecule (Fig. 18) has a linear configuration of three berylliums with the central one being four-coordinated by bridging dimethylamide groups and the outer ones three-coordinated giving a symmetry point group of $D_{2d}$. A number of interesting features are apparent in this structure. For example, the terminal dimethylamide groups contain trigonal-planar nitrogens with $C\hat{N}C = 103.6°$ and a short Be–N bond length (1.560 Å). This is consistent with a localized beryllium–nitrogen $\pi$ bond involving the three-coordinated beryllium atom and the terminal nitrogen atom. The bridging dimethylamides are unequally bonded to the two types of beryllium. Thus, $N_{\text{bridge}}\text{–}Be_{\text{terminal}} = 1.61$ Å and $N_{\text{bridge}}\hat{Be}N_{\text{bridge}} = 102.9°$, whereas $N_{\text{bridge}}\text{–}Be_{\text{central}} = 1.76$ Å and $N_{\text{bridge}}\hat{Be}_{\text{central}}N_{\text{bridge}} = 92.3°$. The distorted tetrahedral central beryllium atom has slightly longer bonds to nitrogen than the trigonal terminal berylliums as would be expected. The bridging dimethylamides have $C\hat{N}C = 108.2°$, which is much closer to the tetrahedral angle than in the terminal ligands, but the C–N distances (terminal = 1.52; bridging = 1.53 Å) are practically the same. Presumably interligand intramolecular steric interactions prevent the development of an infinite linear polymer with all-tetrahedral beryllium.

Although methylamino metal derivatives $MeNH\text{–}ML_x$ are not strictly dialkylamido metal compounds, it seems relevant to note the very interesting example of stereoisomerism reported for the trimeric compounds $(Me_2AlNHMe)_3$ (*229*). Both forms were obtained from the reaction of $Al_2Me_6$ with methylamine and were separated by fractional sublimation. The stable less volatile form (I) (m.p. 110°) was rhombohedral and had the $Al_3N_3$ ring in the chair conformation with all *N*-methyl groups in equatorial positions. The metastable form (II) gave monoclinic crystals with the $Al_3N_3$ ring in a skew-boat conformation with two *N*-methyl groups equatorial and the third one axial. Interestingly, the trimer $[Me_2AlN(CH_2)_2]_3$ also adopted the skew-boat conformation (*230*). A preliminary report on the crystal structure of the tetramer $(C_6H_5AlNC_6H_5)_4$ showed the presence of a cubane configuration of the $Al_4N_4$ framework reminiscent of the metal–oxygen cubanes $(RMOR)_4$ (Figs. 1 and 3).

Some structures have recently been determined for bistrimethylsilylamido metal compounds. The lithium derivative behaves as a dimer in solution, but it was found to be trimeric in the crystalline state (*143*). X-Ray crystal analysis gave the ring structure for $Li_3N_3$ (Fig. 19) with Li–N = 2.00, Si–N = 1.72, and Si–C = 1.89 Å; $N\hat{Li}N = 148°$, $Li\hat{N}Li = 92°$, and SiNSi = 118°. For the parent amine $(Me_3Si)_2NH$ it was shown by electron diffraction (*231*) that Si–N = 1.735 Å and $Si\hat{N}Si = 125.5°$.

The beryllium compound was shown by Bürger *et al.* (*213*) to be monomeric in solution and thus contained two-coordinated beryllium. The structure of this compound in the vapor state was determined by Clark and Haaland (*232*) by electron diffraction. As shown in Fig. 20, the $Si_2NBeNSi_2$ framework has $D_{2d}$ symmetry consistent with the presence of $p_\pi\text{–}p_\pi$ bonding involving vacant acceptor *p* orbitals on the beryllium. Although this $\pi$ bonding (ligand-to-metal) is in competition with donation of the nitrogen lone pair into vacant *d* orbitals on the silicons, the Si–N bond length (1.726 Å) is very similar to that in

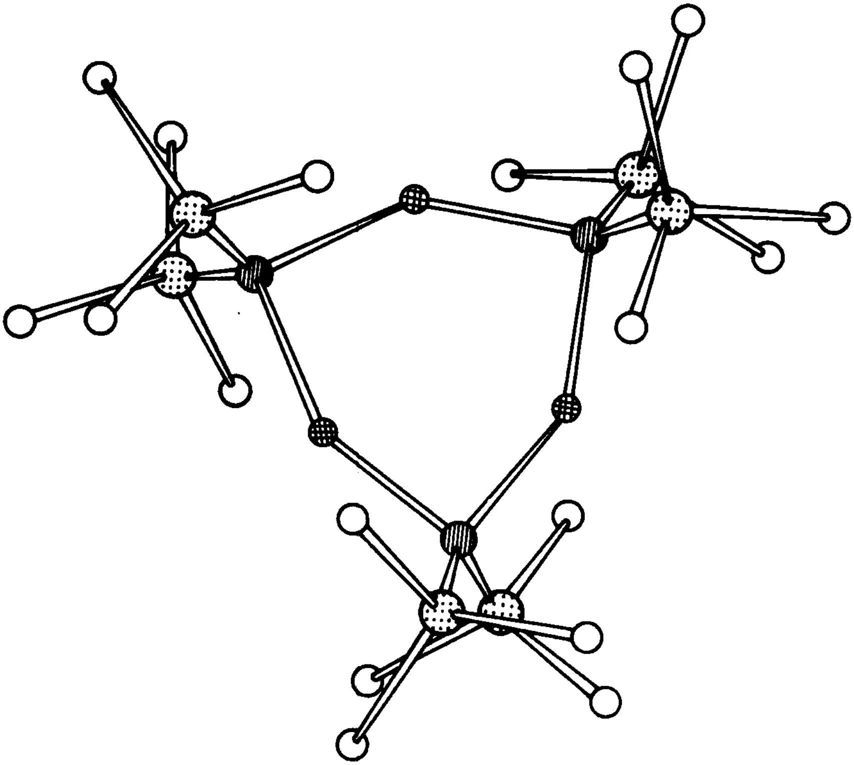


FIG. 19. The structure of $[LiN(SiMe_3)_2]_3$. Cross-hatched, Li; hatched, N; stippled, Si; plain, Me.

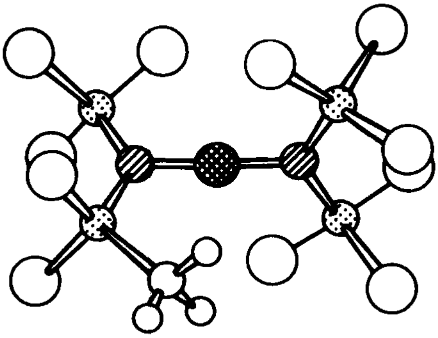


FIG. 20. The structure of $\{Be[N(SiMe_3)_2]_2\}$. Cross-hatched, Be; hatched, N; stippled, Si; plain, Me.

$(Me_3Si)_2NH$. However, the Be–N bond length (1.566 Å) is very close to that found (1.56 Å) in the terminally bonded Be–$NMe_2$ group in $Be_3(NMe_2)_6$, and this suggests that significant beryllium–nitrogen $\pi$ bonding is present. The $Si\hat{N}Si$ (129.3°) is wider than in $(Me_3Si)_2NH$ or $[LiN(SiMe_3)_2]_3$. Owing to intramolecular congestion involving methyl groups, there was rotation of $SiMe_3$ groups about the Si–N bonds resulting in a conformation corresponding to $D_2$ symmetry, although the $D_{2d}$ symmetry of the $Si_2NBeNSi_2$ unit was preserved.

The first three-coordinated metal silylamide structure was reported by Bradley *et al.* (*233*), who determined the structure of $Fe[N(SiMe_3)_2]_3$ by single crystal X-ray analysis. As expected the $FeN_3$ unit was trigonal planar (Fig. 21) with Fe–N = 1.918 ± 0.004 Å and the nitrogens were also trigonally planar, but each $FeNSi_2$ plane made a dihedral angle of 49° with the $FeN_3$ plane. Thus, the $Fe(NSi_2)_3$ framework had the symmetry point group $D_3$. The ligand geometry, Si–N = 1.731 ± 0.003 Å and $Si\hat{N}Si$ = 121.24°, was rather similar to that found in the free amine and in the lithium and beryllium derivatives. The chromium derivative $Cr[N(SiMe_3)_2]_3$ had the same structure as, indeed, have all the transition metal trissilylamides (*234*).

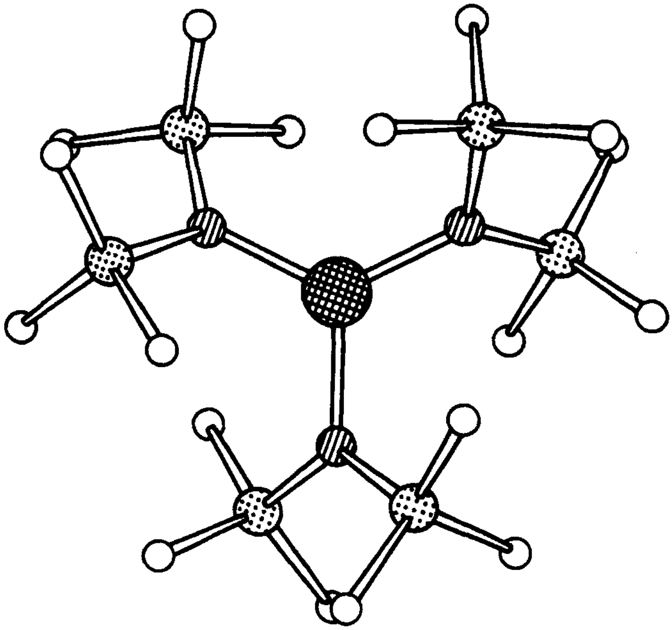


FIG. 21. The structure of $\{Fe[N(SiMe_3)_2]_3\}$. Cross-hatched, Fe; hatched, N; stippled, Si; plain, Me.

The only nontransition metal trissilylamide structure so far reported is that of the aluminum compound $Al[N(SiMe_3)_2]_3$ (*235*). This compound is isostructural with the transition metal derivatives and, although it has shorter metal–nitrogen bonds (Al–N = 1.78 ± 0.02 Å), it has practically the same dihedral angle (50°) between $MNSi_2$ and $MN_3$ planes. Also the ligand geometry (Si–N = 1.75 ± 0.01 Å; $Si\hat{N}Si = 118 \pm 1°$) appears to be the same within a wider uncertainty than that found in the other silylamides. It is very difficult to assess the degree of $\pi$ bonding in the metal–nitrogen bonds in the silylamides, because no authentic single $\sigma$-bond distances are known for these metals with such low coordination numbers. The planarity of the $MNSi_2$ groups does not necessarily prove that nitrogen is donating $\pi$ electrons to the metal because nitrogen-to-silicon $\pi$ donation would have the same effect (viz., in the free amine). Further light has been shed on this fascinating problem by the determination of the structure of chromium trisdiisopropylamide, which was also known to be monomeric in solution (*179*). Single-crystal X-ray analysis (*221*) showed that the structure (Fig. 22) was trigonal with the $Cr(NC_2)_3$ approximating to $D_3$ symmetry as in the metal trissilylamides. The $CrNC_2$ units were planar suggesting nitrogen-to-metal $\pi$-electron donation and the ligand planes made dihedral angles of ~70° with the $CrN_3$ plane. The short Cr–N bond distance (1.87 Å) also suggested that some metal–nitrogen $\pi$ bonding was involved. Further X-ray structural analyses of crystalline metal dialkylamides may be expected in the near future.

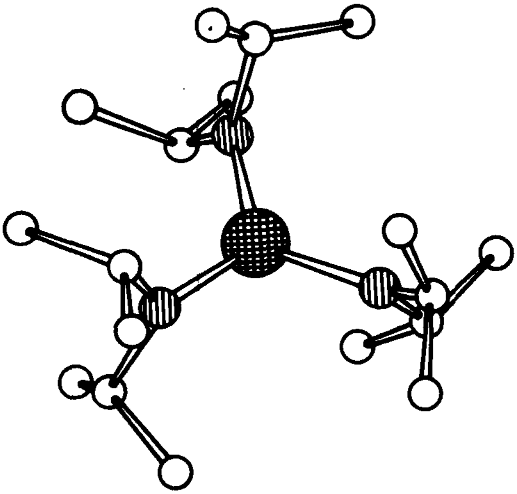


FIG. 22. The structure of $[Cr(NPr^i_2)_3]$. Cross-hatched, Cr; hatched, N; plain, C.

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