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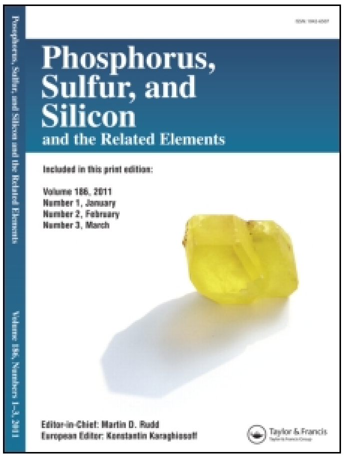

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METAL-OXYGEN-METAL′ RING FORMATION IN METAL ALKOXIDE SYSTEMS

RAM C. MEHROTRA and ANIRUDH SINGH

Department of Chemistry, University of Rajasthan,
Jaipur 302004, India

Salient features of the work carried out during the last few years on the alkoxide ring systems with chelating alcohols such as alkoxyalcohols, aminoalcohols, phosphino alcohols, glycols as well as monofunctional alcohols, are discussed.

Keywords : Metal-oxygen-metal′ rings, siloxides, chelating alcohols, glycoxides, amino- and phosphino-alkoxides..

INTRODUCTION

Metal alkoxides generally tend to oligomerize through alkoxo bridge $M(\mu{-}OR)M'$ formation which allows the central metals to achieve higher coordination state(s). For example an eight-membered ring was suggested by Robinson and Peak[1] as early as in 1935 for tetrameric alkoxides of aluminium with primary alcohols.

As metal alkoxides do not generally yield crystals suitable for X-ray crystallographic structural determinations, their plausible formulae were suggested on the basis of molecular weight determinations and NMR spectroscopy; the latter proved more useful in distinguishing between protons of terminal and bridging alkoxo groups. Almost all these plausible structures suggested earlier have been confirmed recently by X-ray crystallographic studies.

By contrast, due to steric bulk of tertiary butoxo groups aluminium *tert*-butoxide has been shown[2] to be dimeric which has been confirmed[3] by X-ray crystallography. Although trimethylsiloxo (Me_3SiO) group tends to be sterically less demanding, yet the dimeric (Fig.1) nature is retained[4] in aluminum trimethylsiloxide :

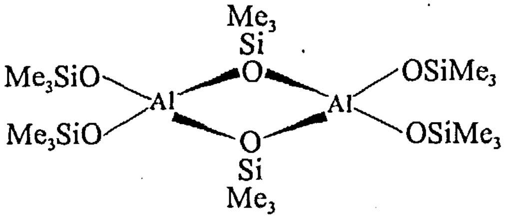


FIGURE 1. Structure of aluminium trimethylsiloxide.

The confusion about the oligomeric nature of aluminium isopropoxide was resolved by Mehrotra[2] who showed that aluminium isopropoxide is dimeric in the vapour state, trimeric as freshly distilled liquid, but the same soon ages into a tetrameric crystalline solid[5,6] (Fig.2):

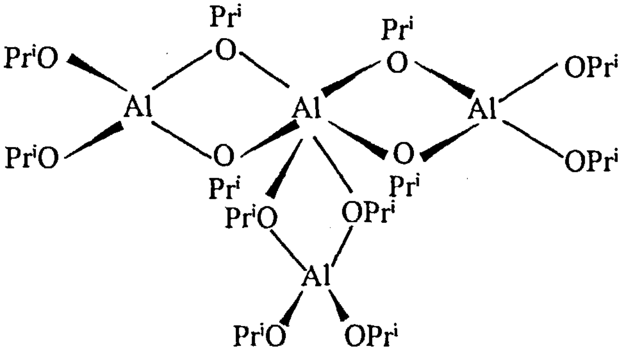


FIGURE 2. Tetrameric aluminium isopropoxide, $[Al(OPr^i)_3]_4$

A similar structure was suggested[7] for the heterobimetallic isopropoxides of lanthanides $[Ln\{\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_3]$, which has been confirmed[8] in 1996. It is noteworthy that the tetraisopropoxoaluminates of lanthanides[9] distil as monomeric species without dissociation.

The basic skeleton of the structure for potassium tetraisopropoxoaluminate isopropylate as suggested by Mehrotra[10] has again been confirmed (Fig.3) by Gilje, et al.[11] in 1993 :

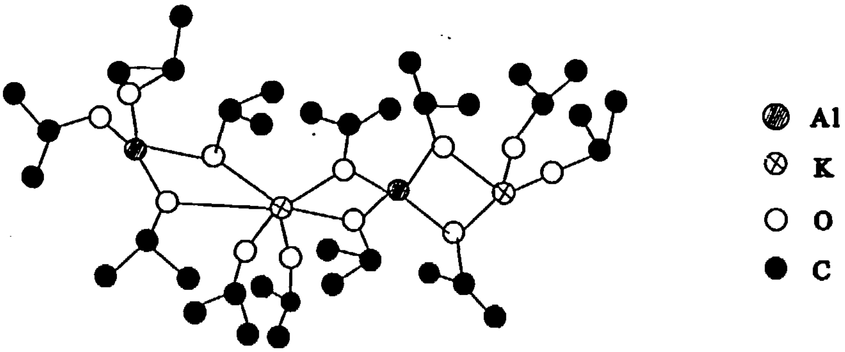


FIGURE 3. Structure of $[(Pr^iOH)_2K(\mu-OPr^i)_2Al(OPr^i)_2]_\infty$

The chloro-derivative $[\{Pr[Al(OPr^i)_4]_2(\mu-Cl)(Pr^iOH)\}_2]$, however, turns out to depict a chloride bridged structure.[12]

It is interesting to record that $[Fe(OMe)_2(O_2CCH_2Cl]_{10}$ adopts an interesting structure termed by Lippard[13] as a molecular ferric wheel, some possible modifications of which have been suggested by Mehrotra and Singh[14]

X-ray structural study of the yttrium methoxyethoxide $[Y(OC_2H_4OMe)_3]_{10}$ shows[15] a centrosymmetric cyclic arrangement of 10 yttrium atoms, each in a seven coordinate environment attaining a pentagonal bipyramidal arrangement. This decameric structure of methoxyethoxide of yttrium does not appear to be in conformity with Bradley's conclusion[16] that metal alkoxides tend to attain the lowest oligomeric form (generally involving four membered ring) consistent with the attainment of the higher coordination state of the central metal.

Again a contrast is presented by the crystal structure of [Cu(OCHMe·CH_2·NMe_2)$_2$] which depicts[17] a *trans* square planar stereochemistry around the copper.

Interestingly, the use of phosphino -alkoxide ligands has not only made accessible metal derivatives with fascinating structural features,[18-20] but also stabilized novel platinum(II) alkoxide complexes[21] (Fig.4) which are in general kinetically unstable with respect to β–hydrogen elimination[21]

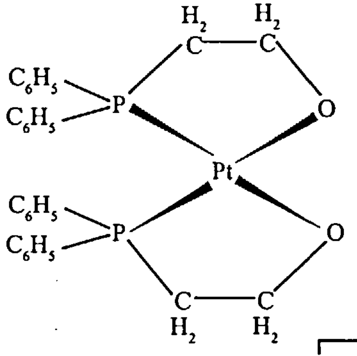


FIGURE 4. Structure of [Pt($Ph_2PCH_2CH_2O$)$_2$]

It is noteworthy that the stability of the chelate alkoxo complexes of the type shown in Figure 4 appears to be due to the conformation of the chelate ring making β-hydrogen elimination unfavourable.

Tetraalkoxoaluminate ligands function generally as bidentate[22-24] (Fig.5a). However, the hexacoordinated nature of nickel[22] in [Ni{Al(OMe)$_4$}$_2$] indicates that {Al(OMe)$_4$}$^-$ functions in a tridentate manner (Fig.5b) :

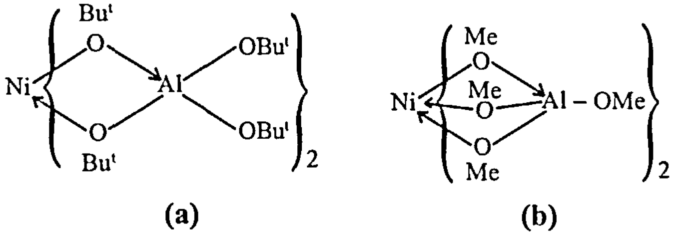


FIGURE 5. Proposed structures of nickel bis-tetraalkoxoaluminates

The versatility of ligated $\{Zr_2(OR)_9\}^-$ groups in responding to the tendency of different metal atoms for achieving their preferred coordination state and geometry with the formation of μ_2- and μ_3- alkoxo bridges has been demonstrated in a number of publications, as summarized in a recent review by the authors.[25]

NEW RESULTS FROM OUR LABORATORIES

Recent unpublished work on homo- and heterometallic glycolates[26] has revealed the formation of novel ring systems (Fig.6) as depicted below :

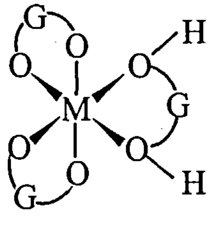


FIGURE 6. Proposed structures of some tris-glycolates of Ti Zr, Hf, Sn (IV) (M).

The above tris-glycolates can be conveniently prepared by reactions of metal tetraisopropoxides with three moles of 2-methylpentane-2,4-diol (generally known as hexylene glycol). The acidic protons of these react readily with alkoxides of different (such as aluminium) metals to give suitable heterobi- and -trimetallic alkoxides, which on further reaction with the glycol yield derivatives of the type (Fig.7) :

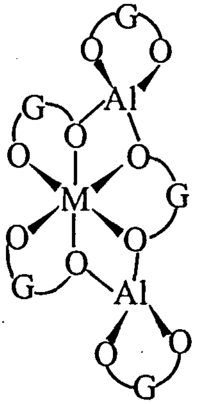


FIGURE 7. Proposed structure for homoleptic heterobimetallic glycolates (M = Ti, Zr, Hf, or Sn(IV))

It is interesting to record that sequential reactions of the tris-glycolates (Figure 6), with different metal isopropoxide (such as $Al(OPr^i)_3$ and $Nb(OPr^i)_5$) afford novel heterotrimetallic glycolate derivatives,[26] plausible structures of which are depicted by the Figure 8 :

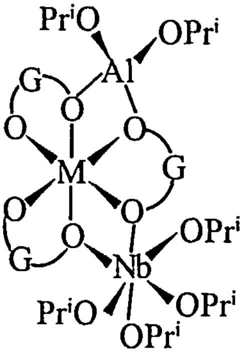
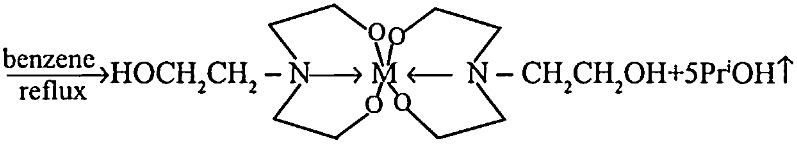


FIGURE 8. Plausible structure for heterotrimetallic glycolate derivatives (M = Ti, Zr, Hf, or Sn(IV))

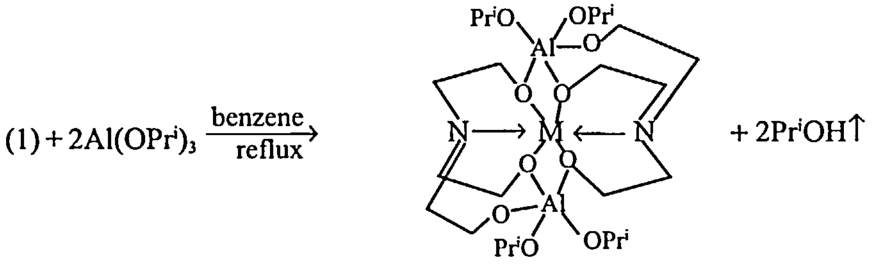
In view of the paucity of heterometallic aminoalkoxide derivatives,[27] we have very recently initiated work on triethanolminate derivatives of some tetravalent metals.[26] These can be synthesized by the following two sequential reactions:

$M(OPr^i)_4.Pr^iOH + 2N(CH_2CH_2OH)_3$



(1)

Insoluble in C_6H_6, PhMe, n–C_6H_{14}
but soluble in CH_2Cl_2



(2)
Soluble in organic solvents

The above structure(2) is consistent with the monomeric nature of the derivatives. The ^1H, ^{27}Al (as well ^{119}Sn)NMR studies depict octahedral and trigonal bipyramidal geometries around metal(M) and aluminium atoms, respectively.

Similar studies have recently been extended on diethanolaminate derivatives of various metals[27] with more exciting results.

Novel tetra- and penta-nuclear alkaline earth metal (M) aluminium isopropoxides of the types $MAl_3(OPr^i)_{11}$ (Fig.9a) and $M_2Al_3(OPr^i)_{13}$ (Fig.9b) have been synthesized[29] for the first time by the reactions in 1:3 and 2:3 molar ratios respectively of alkaline earth and aluminium isopropoxides in isopropyl alcohol under refluxing conditions. Molecular weight determinations, NMR (^1H, ^{13}C, and ^{27}Al) studies, as well as alcoholysis reactions of the above two derivatives with ramified alcohols are in conformity with the structure shown in Figure 9a and 9b.

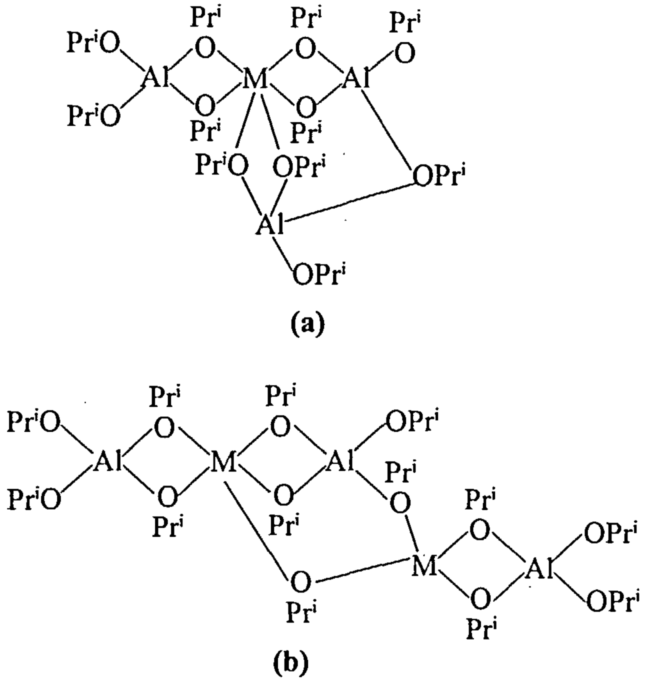
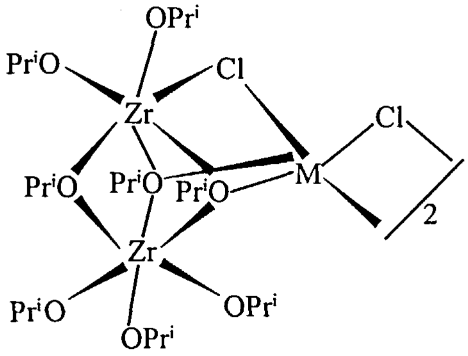


FIGURE 9. Proposed structure of (a) $MAl_3(OPr^i)_{11}$, and (b) $M_2Al_3(OPr^i)_{13}$

As reported[30] in the case of $MgTi_2(OEt)_8Cl_2$, a novel class of heterobimetallic chloride alkoxides : $MZr_2(OPr^i)_8Cl_2$, $MAl_2(OPr^i)_6Cl_2$, and $MNb_2(OPr^i)_{10}Cl_2$ (where M = Be, Mg, Zn, and Sn(II)) have been synthesized[28] by similar reactions of the type illustrated below in the case of $Zr(OPr^i)_4$:

$$2MCl_2 + 4Zr(OPr^i)_4 \xrightarrow{benzene}$$



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