

DOUBLE METAL ALKOXIDES/ HETEROMETALLIC ALKOXIDES

By Ramesh Kapoor
University of Dehli
Department of Chemistry
Dehli, 110007 India

Heterometallic alkoxides [$M_xM_yM_z(OR)_n$] are those alkoxides having two or more different metals linked via μ or μ_3 — bridging alkoxy groups, via oxo-groups or sometimes metal-metal bonding (1-8). The large majority of heterometallic alkoxides corresponds to derivatives in which one of the metals is either an alkali or alkaline earth metal (viz. Li, Na, Mg). The chemistry of the heterometallic alkoxides involving scandium, yttrium and the lanthanides has progressed rapidly during the last decade.

Physical Properties

Heterometallic alkoxides exhibit great differences in physical properties depending upon the metals and alkyl group used for their preparation. The solubility of these compounds in common organic solvents is as expected similar to the metal alkoxides. The presence of Lewis acids (metals) and Lewis bases (alkoxo oxygens capable of donating electron lone pairs), causes these compounds to exist as polymeric species,¹ although the degree of association depends upon many factors such as solvent, steric bulk of the alkoxide group, and the nature of the metal including its coordination number.² The stabilities of heterometallic alkoxides are generally judged by their spontaneous dissociation in solution or upon volatilization. Many of these compounds can be crystallized from solution but it has been found that the temperature at which crystallization occurs plays an important role in the stability of the heterometallic alkoxides. For example, sometimes at higher temperature they dissociate to homometallic alkoxides. Many heterometallic alkoxides are distillable and are stable over a wide range of temperature.

Heterometallic alkoxides are precursors of ultrapure multicomponent oxides finding a wide range of applications in the field of catalysis and materials science. Preparation of oxides from heterometallic alkoxides has advantages over those obtained by traditional routes such as those using metal carbonates, oxides, oxalates etc. which require heating to higher temperatures. These advantages include low temperature of formation low crystallization temperatures, better compositional uniformity at the molecular level and high purity conformal coverage in the case of thin films. Techniques for the formation of such materials from heterometallic alkoxides include sol-gel methods and MOCVD (Metal-organic chemical vapor deposition).

PLEASE INQUIRE ABOUT BULK QUANTITIES

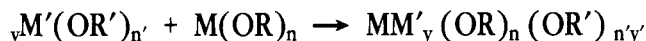
Preparation of Heterometallic Alkoxides

1. LEWIS ACID – BASE REACTIONS:

Reaction between a halide and excess of alkali-metal (mostly lithium) alkoxide leads to heterometallic alkoxides.



A particular example ($X = OR'$) can also be used to prepare these alkoxides by simple mixing at room temperature.



The most studied classes are $M[Al(OR_4)]_n$ and $MM'(OR)_6$ where $M = Li, Na, K$ and $M' = Nb, Ta$.

Using bulky 'R' groups, chloroheterometallic alkoxides can be prepared by the above method. Heterometallic alkoxides involving three different metals such as $(iPrO)_x M(\mu-OiPr)_2 Be(\mu-OiPr)_2 Al(OiPr)_2$ (where $M = Ti(IV), Zr(IV)$ or $Hf(IV)$ for $x = 3$ or $M = Nb(V)$ or $Ta(V)$ for $x = 4$) have been isolated by simple mixing of the homometallic species.

2. CONDENSATION REACTIONS:

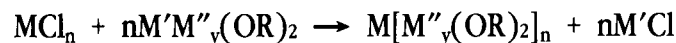
Heterometallic oxoalkoxides can be obtained according to following equation:



where Z usually = CH_3CO- group and $R'OZ$ is a volatile by product.

Using the above method a number of bimetallic- μ – oxoalkoxides of the type $(RO)_n M-O-M^{II}-O-M(OR)_n$ (where $M = Al(III)(n = 2), Ti(IV)(n = 3)$; $M^{II} = Zn, Co, Fe, Mn, Mo, Cr, Mg, Pb$) have been prepared by thermal condensation of metal (II) acetate with metal alkoxides in 1:2 ratio. In certain cases alkaline earth metals or alkali metals can be treated directly with different homometallic alkoxides to give heterometallic alkoxides.

3. SALT ELIMINATION REACTIONS:



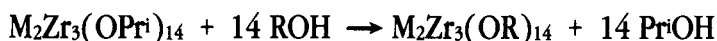
M' generally alkali metal, $M''_y(OR)_2$ unit is usually $[Al(OR)_4]^-$, $[M(OR)_6]^-$ where $M = Nb, Ta$ or $M_2(OR)_9$ where $M = Zr, Hf$. A large number of halides (MCl_n) can be employed they are: (i) divalent and trivalent transition metals such as Fe, Cr, Mn, Co, Ni, Cu etc. (ii) lanthanides and actinides (iii) Pb(II), Sb(III).

Reactivity

1. Reactivity of the alkoxide bond

Alcoholysis, reactions with diketones, hydrolysis and transmetalation reactions are the reactions which have been

most studied in the case of heterometallic alkoxides. Substitution reactions lead to new molecular precursors displaying different volatilities, thermal stabilities and behavior with respect to hydrolysis and condensation.



M = Li, Na and R = Me, Et

2. Reactivity with other functional groups

In chloroheterometallic alkoxides the chloro group can be substituted with another group so as to form a new compound:



3. Redox reaction

Methanolic solutions of $[Mg(MeOH)_6]$, and $[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4](MeOH)_6$ are reduced electrochemically to an undefined Mo(II) complex that is an "effective catalyst for N_2 reduction" in mild conditions.

4. Catalytical activity and organic synthesis

Bimetallic- μ -oxoalkoxides $[\mu-O]_2Al_2(OR)_4]_m$ (where M = Co, Zn, Mn, Fe) are highly active catalysts for the polymerization of oxiranes, thiiranes and lactones. The activity of the well defined compound $[Ti_2(OEt)_8Cl]_2^- Mg_2(\mu-Cl)_2$ has been estimated for the polymerization of polyethylene or 1,3-butadiene in the presence of $AlEt_3$, and similarly many other bimetallic alkoxides have been found to act as catalysts in polymerization and organic synthesis reactions.

References

1. Caulton, K.G. and Hubert-Pfalzgraf. *Chem. Rev.* **1990**, 90, 969.
2. Veith, Michael. *Chem. Rev.* **1990**, 90, 3.
3. Ouhadi, T., Bioul, J.P., Stevens, C., Warin L. Hocks, and Teyssie, P.H. *Inorganica Chimica Acta*, **1976**, 19, 203.
4. Mehrotra, R.C., Singh, Anirudh, and Tripathi, Upendra M. *Chem. Rev.*, **1991**, 91, 1287.
5. *Metal Alkoxides*; Bradley, D.C., Mehrotra, R.C., and Gaur, D.P., Eds.; Academic Press: New York, NY, 1978.
6. Chandler, Clive D., Roger, Christophe, and Hampden-Smith, Mark, J. *Chem. Rev.*, **1993**, 93, 1205.
7. Mehrotra, R.C. *Adv. Inorg. Chem. Radiochem.*, **1983**, 26, 269.
8. Bradley, D.C. *Chem. Rev.*, **1989**, 89, 1317.

TABLE: HETEROMETALLIC ALKOXIDES

$MM'(OR)_6$; $M[M'(OR)_6]_2$; M = Li, K, Na M = Mg, Ca, Sr, Ba M' = Nb, Ta, ; R = Et, Pr ⁱ	$Ln[Al(OPr^i)_4]_3$; Ln = Pr, Ce, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu, Y, Sc
	$MO_2(OAc)_2[Al(OPr^i)_4]_2$
$Zn[Nb(OEt)_6]_2$ $M[M'(OR)_6]_2$; M = Cu, Ni, Co, ; M' = Nb, Ta, ; R = Me, Et, Pr ⁱ , Bu ⁿ	$(OPr^i)_{4-x}M[Al(OPr^i)_4]_x$ M = Hf, Zr ; x = 1, 2
	$M[Al(OPr^i)_4]_4$; M = U
$Cr[M'(OR)_6]_3$; M' = Ta ; R = Me, Et, pr ⁱ	$(OPr^i)_{5-x}M[M'(OPr^i)_4]_x$; M = Nb, Ta ; x = 1, 2 ; M' = Al, Ga
$NaU(OEt)_6$ $M[U(OEt)_6]_n$; M = Ca ; n = 2 M = Al ; n = 3	$(Ln[Zr(OPr^i)_3]_3)$; Ln = La, Sm
	$(Ln[Zr_2(OPr^i)_9]_xCl_{3-x})$; Ln = La, Pr, Nd, Sm ; x = 1, 2, 3
$M[M'_2(OPr^i)_9]$; M' = Zr ; M = Li, Na, K ; M' = Ti ; M = Li	$M_2Hf_3(OPr^i)_4$; M = Li, K
$M[Zr_2(OR)_9]_2$ M = Cu, Co, Ni ; R = Me, Et, Pr ⁿ , Pr ⁱ , Bu ⁿ , Bu ^s M = Fe, R = Pr ⁱ	$NaSn_2(OPr^i)_9$
	$MSn(OR)_3$; M = Na, K ; R = Me, Et, Pr ⁿ , Pr ⁱ , Bu ⁿ , Bu ^s , Am ⁱ
$M[Zr_2(OPr^i)_9(OR)]$; M = Cu, Co ; R = Me, Bu ^s , Bu ^t M = Co ; R = Pr ⁱ , Bu ^t	$Sr[Sn(OBu)_3]_2$
$Fe[Zr_2(OPr^i)_9]_3$	$Sb[Sn(OR)_3]_3$
$M[Zr_2(OPr^i)_9]_2$; M = Ca, Ba	$Pb[Sb(OR)_4]_2$; R = Me, Pr ⁿ , Pr ⁱ , Bu ^t , Am ⁱ
$Na_2Zr_3(OPr^i)_4$;	$M[Fe(OEt)_4]_n$; M = Li, Na, K ; n = 1 M = Ba ; n = 2
$MHf_2(OPr^i)_9$; M = Li, K	$Ba_3Fe_2(OEt)_{12}$
$M[Al(OR)_4]_2$; M = Be; R = Me, Et, Pr ⁿ , Pr ⁱ , Bu ⁿ , Bu ^s , Am ⁱ M = Mg, Ca, Sr, Ba ; R = Et, Bu ⁿ M = Zn ; R = Me, Et, Pr ⁿ , Pr ⁱ , Bu ⁿ , Bu ^s , Am ⁱ M = Cd, Hg ; R = Pr ⁱ M = Co, Ni, Cu ; R = Me, Et, Pr ⁿ , Pr ⁱ , Bu ⁿ	$YZr_3(OPr^i)_{15}L_3$; L = THF, Pr ⁱ OH
	$YFe_2(OPr^i)_9$
	$YFe_3(OPr^i)_{12}$
$ClCo[Al(OPr^i)_4]$	$Li_4Zn(OMe)_6$
$M[M'(OPr^i)_4]_3$; M = Al, Ga, In ; M' = Al, Ga	$Li_2Zn(OEt)_6$
$M[Al(OR)_4]_3$; M = Co ; R = Pr ⁱ M = Cr, Mn, Fe ; R = Me, Et, Pr ⁱ , Bu ⁿ , Bu ^t , CEt ₂ Me ₂ , CH ₂ CF ₃	$LiZn_2(OEt)_4X$; X = OEt, Cl