Russian Chemical Reviews **73** (11) 1041 – 1064 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n11ABEH000855

Metal oxoalkoxides. Synthesis, properties and structures

N Ya Turova

Contents

I.	Introduction	1041
II.	Pathways of formation of oxoalkoxides from alkoxides	1043
III.	Properties of oxoalkoxides	1057
IV.	Structural types of oxoalkoxides	1057
V.	Oxoalkoxides as true precursors of oxide phases	1060

Abstract. The review surveys the pathways of formation of crystalline oligomeric oxoalkoxides $M_mO_n(OR)_p$, which are products of partially controlled (or uncontrolled) hydrolysis, oxidation, thermal decomposition of mono- and bimetallic alkoxides of the ortho series $M(OR)_n$ and $M_mM'_n(OR)_p$ or elimination of ethers from these compounds. The physicochemical properties of oxoalkoxides (solubility, the behaviour in solutions, volatility, *etc*.) differ considerably from the properties of the corresponding alkoxides. Hence, oxoalkoxides can be considered as immediate precursors of oxide materials produced by sol – gel technology. The $M_mO_n(OR)_p$ compounds are classified according to the sizes of associates. The crystal chemistry of alkoxides is discussed. The bibliography includes 249 references.

I. Introduction

Polymeric metal oxoalkoxides (OA) of the general formula $M_mO_n(OR)_p$, which are amorphous products of partial hydrolysis or thermolysis of alkoxides, have been used for years as heat-resistant insulating coatings, elastomers, resins for the production of plastics, lacquers, paints, enamels, *etc*. Andrianov,[1] who has made a considerable contribution to this area of chemistry, considered OA as 'polymers with inorganic main chains enclosed by OR groups',

$$-M(OR)_2-O-M(OR)_2-O-M(OR)_2-O-.$$

In the late 1950s, Bradley[2] studied hydrolysis of titanium alkoxides (and, in part, of zirconium alkoxides) primarily by ebullioscopy. He assigned structures to hydrolysis intermediates (which either occur in solution or exist in the amorphous state) based on his 'structural theory', according to which a metal atom has the maximum coordination number in the case of the lowest degree of association of $[MO_n(OR)_p]_x$. However, Bradley always emphasised that it is necessary to establish the structures by direct methods for solving this problem.

The present review is devoted to oligomeric crystalline oxoalkoxides belonging to a new class of oxo-bridged molecular compounds. These compounds have attracted considerable interest because they are immediate precursors in the 'sol – gel technology' of oxide materials, which is based on hydrolysis of alkoxides in organic solvents.[3]

$$M(OR)_n \xrightarrow{H_2O} MO_x(OR)_{n-2x} \xrightarrow{H_2O} M_2O_n\cdot y\,H_2O \xrightarrow[-H_2O]{} M_2O_n$$

The sol – gel method has assumed great importance, as evidenced by regular international conferences devoted to this problem. Beginning in 1981, information presented at these conferences was published in *J. Non-Cryst. Solids* and *J. Sol-Gel Sci. Technol*. The physicochemical fundamentals of various processes of sol – gel technology were discussed in the comprehensive monograph by Brinker and Scherer.[4] Applied aspects of this technology were covered in two collections of articles.[5, 6]

A substantial advantage of the alkoxide-based sol – gel technology is the possibility of deep purification of the starting compounds. Besides, mono- and bimetallic oxides are prepared as amorphous substances consisting of highly reactive nanosized particles. This allows one to perform ceramic sintering at lower temperatures compared to those used in alternative technologies. In the synthesis of complex oxides, the use of alkoxide solutions makes it possible to overcome the main difficulty of alternative methods, *viz*., the necessity of homogenising various metals at the molecular level. Subsequent hydrolysis and thermal treatment of such samples afford submicron particles. In particular, this method enables one to prepare particular composites inaccessible by direct reactions of oxides. Data on the compositions and structures of real particles involved in these processes are required to elucidate the mechanisms of formation of simple and complex oxide phases and to optimise the synthesis of materials based on these phases.

The class of oligomeric crystalline oxoalkoxides was discovered by the X-ray diffraction method. In the late 1960s, this method was used for establishing the structures of the partial hydrolysis products of titanium, niobium and zirconium alkoxides, *viz*., $Ti_7O_4(OEt)_{20}$,[7] $Nb_8O_{10}(OEt)_{20}$,[8] and $Zr_{13}O_8(OMe)_{36}$ (see Ref. 9) (Fig. 1 *a* – *c*). It was found that all oxo ligands in these molecules serve as bridges (even the Nb complex contains no terminal 'yl' oxygen atoms, which are typical of compounds with this metal). Oxo bridges were considered as units that formed upon condensation of two hydroxy groups resulting from the replacement of an OR group in the first step of hydrolysis.

X-Ray diffraction studies of OA revealed new molecules of various sizes and with different structures, which have greatly extended our knowledge of the crystal chemistry of metal alkoxo

N Ya Turova Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation.
Fax (7-095) 932 88 46. Tel. (7-095) 939 33 39.
E-mail: natalie@inorg.chem.msu.ru

Received 16 June 2003
Uspekhi Khimii **73** (11) 1131 – 1154 (2004); translated by T N Safonova

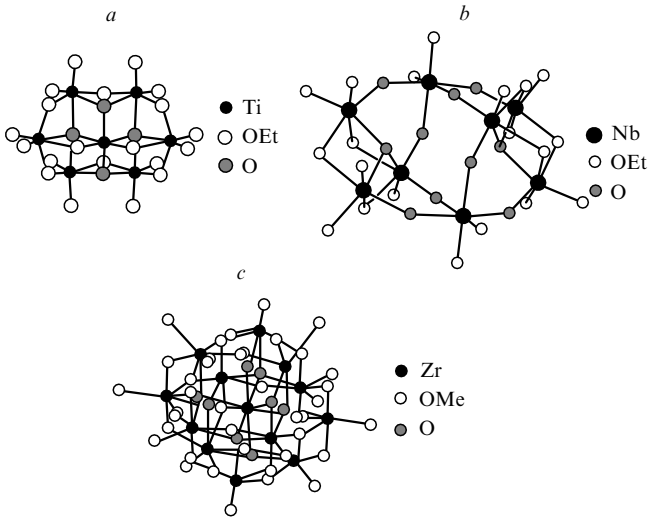


Figure 1. Metal–oxygen cores in the structures of $Ti_7O_4(OEt)_{20}$ (*a*),[7] $Nb_8O_{10}(OEt)_{20}$ (*b*)[8] and $Zr_{13}O_8(OMe)_{36}$ (*c*).[9]

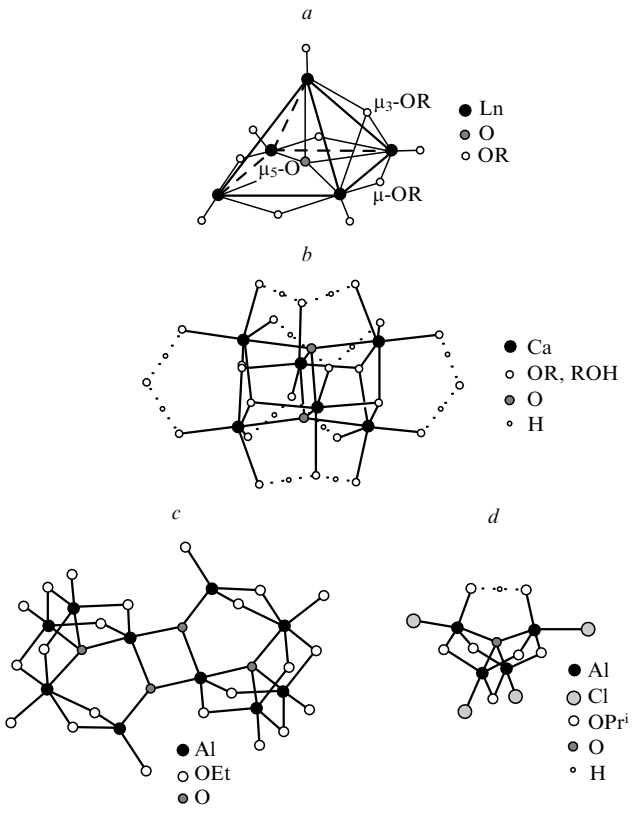


Figure 2. Metal–oxygen cores in the structures of $[M_5(\mu_5\text{-}O)(OR)_{13}]$ (M = Sc, Y, Ln, In, Al, Fe) (only one of four μ_3-OR groups is shown) (*a*),[10–15] $[Ca_6(\mu_4\text{-}O)_2(OEt)_8(EtOH)_{14}]$ (*b*),[16] $[Al_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(OEt)_{22}]$ (*c*)[17] and $[Al_4(\mu_4\text{-}O)(OPr^i)_6(Pr^iOH)Cl_4]$ (*d*).[18]

complexes. It appeared that many crystalline compounds, which were initially considered as alkoxides of the ortho series $M(OR)_n$, contain, in reality, oxo ligands generally with high dentate numbers. Examples of such compounds are 'isopropoxides' of rare-earth elements[10–14] and In,[14] 'iron(III) ethoxide'[15] (these compounds, in reality, contain the pentadentate oxo group $[M_5(\mu_5\text{-}O)(OR)_{13}]$) (Fig. 2 *a*), 'calcium ethoxide disolvate' $[Ca_6(\mu_4\text{-}O)_2(OEt)_8(EtOH)_{14}]$ (Fig. 2 *b*),[16] and 'crystalline aluminium ethoxide' $[Al_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(OEt)_{22}]$ (Fig. 2 *c*).[17] The '$AlCl(OPr^i)_2$' compound, which is a well-known catalyst and reducing agent used in organic chemistry, consists of the tetrahedral $[Al_4(\mu_4\text{-}O)(OPr^i)_6(Pr^iOH)Cl_4]$ molecules[18] (Fig. 2 *d*). Due to inclusions of organic solvents in the intercrystallite space and the formation of numerous solvates of OA with alcohols or hydrocarbons, the results of chemical analysis for OA are no different from those for $M(OR)_n$. For this reason, the present review deals only with compounds whose compositions were confirmed by the data on their structures. These compounds are listed in Tables 1–10 in order of increasing nuclearity. Unfortunately, space does not permit a discussion of abundant information on heteroleptic complexes, such as oxo alkoxo carboxides, oxo alkoxo β-diketonates, *etc*.

Table 1. Dinuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
$[(OsO)O(OCMe_2CH_2NHBu^t)]_2$	two tetrahedra sharing a $(\mu\text{-}O)_2$ edge	$OsO_3(NBu^t) + Me_2C{=}CH_2$	19
$[Nd_2O(OCH_2Bu^t)_4]$	two tetrahedra sharing a $[(\mu\text{-}O)(\mu\text{-}OR)_2]$ face	–	20
$[Ti(\mu\text{-}O)(OC_6H_3Pr^i_2\text{-}2,6)_2 \cdot (NC_5H_4\text{-}4\text{-}NC_4H_8)]_2$ (see [a])	two trigonal bipyramids sharing a $(\mu\text{-}O)_2$ edge	$Ti(OC_6H_3Pr^i_2\text{-}2,6)_2[Bu^tNCBn_2]Py + H_2O$	21
$[Nb(\mu\text{-}O)(OC_6H_3Pr^i_2\text{-}2,6)_3]_2$	the same	$[Nb(OC_6H_3Pr^i_2\text{-}2,6)_3(CH_2C_6H_4Me\text{-}4)]_2 + H_2O$	22
$[Me_2NH_2]^+_2[(Mo^{V}O)(\mu\text{-}O)(OC_6F_5)_2]^-_2$	anion — two square pyramids sharing a $(\mu\text{-}O)_2$ edge	$Mo_2(NMe_2)_6 + C_6F_5OH$	23
$[(OsO)O(\eta^2\text{-}1,2\text{-}O_2C_2Me_4)]_2$	two square pyramids sharing a $(\mu\text{-}O)_2$ edge	$OsO_4 + Me_2C{=}CMe_2$	24
$[W_2O(OBu^t)(OSiMe_2Bu^t)_5Py_2]$	five-vertex polyhedron and an octahedron sharing a $[(\mu\text{-}O)(\mu\text{-}OR)]$ edge	$W_2(OSiMe_2Bu^t)_6 + Bu^tOH + NO + Py$	25
$[Li(THF)_3Nb(\mu\text{-}O)(OC_6H_3Me_2\text{-}2,6)_4]$	tetrahedron $[LiO(THF)_3]$ and the $[NbO(OR)_4]$ square pyramid sharing a $(\mu\text{-}O)$ vertex	$NbCl_3 + LiOC_6H_3Me_2\text{-}2,6$	26
$[Mo^{III}_2O(OCH_2Bu^t)_4(PMe_3)_4]$	five-vertex polyhedron and an octahedron sharing a $[(\mu\text{-}O)(\mu\text{-}OR)]$ edge	$Mo_2(OCH_2Bu^t)_6 + PMe_3 + H_2O$	27
$(MoO)_2O[O(CMe_2)_2O]_2[O(CMe_2)_2OH]_2$	$[(MoO)_2O(\eta^2\text{-}RO_2)_2(\eta^2\text{-}OROH)_2]$, two octahedra sharing a $(\mu\text{-}O)$ vertex	$MoO_3 + HO(CMe_2)_2OH$	28, 29

Table 1 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
$[(WO)O(RO_2)(OROH)]_2$, R = C_2Me_4, cyclo-C_7H_{12}, cyclo-C_8H_{14}	two octahedra sharing a $(\mu\text{-O})_2$ edge	$W(O_2R)_3 + H_2O$	30
$K_4[TiO(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2]_2 \cdot 9\,H_2O$	the same	$K_2Ti(C_6H_4O_2\text{-}1,2)_3 + H_2O$	31
$[(W^{VI}O)O(OSiMe_2Bu^t)_2Py]_2$	"	$W_2(OSiMe_2Bu^t)_6 + NO$	25
$[(Os^{VI}O)O(O_2C_6H_{10}\text{-cyclo})(C_7H_{13}N)]_2$	"	$OsO_4 + C_6H_{10} + C_7H_{13}N$	32
$[Ta_2O(OPr^i)_8(Pr^iOH)]$	two octahedra sharing a $[(\mu\text{-O})(\mu\text{-OR})]$ edge	electrochemical synthesis (Ta + Pr^iOH)	33, 34
$[Ta_2OCl_3(OC_6H_3Pr^i_2\text{-}2,6)_5]$	two octahedra sharing a $[(\mu\text{-O})(\mu\text{-Cl})_2]$ face	$TaCl_2(OC_6H_3Pr^i_2\text{-}2,6)_3$ + traces H_2O	35
$W^V_2O(OCH_2Bu^t)_8$	two octahedra sharing a $[(\mu\text{-O})(\mu\text{-OR})_2]$ face, W = W bond	$W_2(OCH_2Bu^t)_8$ + pyridine oxide	36
$M_2[(MoO_2)_2O(C_6H_4O_2\text{-}1,2)_2] \cdot n\,H_2O$, M = NH_4 (n = 2), Ba/2 (n = 5)	$[(MoO_2)_2O(\mu_3,\eta^2\text{-}RO_2)_2]^{2-}$, two octahedra sharing a $[\mu\text{-O}]_3$ face (from two RO_2 groups)	$M_2MoO_4 + C_6H_4(OH)_2\text{-}1,2$	37
$[Me_3NBn]_2[(WO_2)_2O(OMe)_4]$	two octahedra sharing a $[(\mu\text{-O})(\mu\text{-OR})_2]$ face	$[Me_3NBn]_2WO_4 + WO(OMe)_4$	38
$[(Re^{VI}O)_2O(OMe)_6]$	the same	$ReOCl_4 + MeOH + Et_3N$	39

[a] 4-NC_4H_8 is 4-pyrrolidino-.

Table 2. Trinuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
Triangles $[M_3(\mu_3\text{-O})]$			
$[Sn_3O(OBu^i)_{10}(Bu^iOH)_2]$	three octahedra sharing a $[(\mu_3\text{-O})(\mu\text{-OR})]$ edge	$Sn(OBu^i)_4 + H_2O$	40
$[BiTi_2O(OPr^i)_8]$	two $[TiO_6]$ octahedra sharing a $[(\mu_3\text{-O})(\mu\text{-OR})_2]$ face and $[(\mu_3\text{-O})(\mu\text{-OR})]$ edges, Ψ-five-vertex polyhedron [:BiO_4]	$Ti(OPr^i)_4 + Bi(OPr^i)_3 + H_2O$	41
Triangles $[M_3(\mu_3\text{-O})(\mu_3\text{-X})]$, three $[M(\mu_3\text{-O})(\mu_3\text{-X})(\mu\text{-OR})_2(OR)_2]$ octahedra sharing $[(\mu_3\text{-O})(\mu_3\text{-X})(\mu\text{-OR})]$ faces			
$[Ti_3O(OMe)(OPr^i)_9]$	X = OMe	$Ti(OPr^i)_4 + H_2O + MeOH$ (h = 0.07)	42–44
$[Ti_3OCl(OCH_2Bu^t)_9]$	X = Cl	$TiCl_4 + NaOCH_2Bu^t$	42–44
$[Zr_3OCl(OCH_2Bu^t)_9]$	X = Cl	$ZrCl_4 + KOCH_2Bu^t$	42–44
$[Zr_3O(OH)(OBu^t)_9]$	X = OH	$ZrCl_4 + LiOBu^t$	44
$[Zr_3O(OBu^t)_{10}]$	X = OBu^t	prolonged storage of electrolyte	45
$[M^{IV}_3O(OR)_{10}]$ (M = Mo, W; R = Pr^i, CH_2Bu^t)	X = OR [a]	$M_2(OR)_6 + O_2$	46, 47
$[U_3O(OBu^t)_{10}]$	X = OBu^t (see [b])	$U_2(OBu^t)_8 + H_2O$	48
Triangles $[M_3(\mu_3\text{-O})(\mu_3\text{-X})]$, three $[M(\mu_3\text{-O})(\mu_3\text{-X})(\mu\text{-OR})_2(OR)_2]$ octahedra sharing $[(\mu_3\text{-O})(\mu_3\text{-X})(\mu\text{-OR})]$ faces			
$[Ba(Mo_2O_5)(OC_2H_4OMe)_4(MeOC_2H_4OH)]$	$[Ba(Mo_2O_5)_2(\mu_3,\eta^2\text{-OR})_2(\mu,\eta^2\text{-OR})_2(\eta^2\text{-ROH})]$, two Mo octahedra sharing a $[(\mu\text{-O})(\mu_3\text{-OR})_2]$ face, CN of Ba is 10	$Ba(OC_2H_4OMe)_2$ + + $MoO_2(OC_2H_4OMe)_2$	49
Ring			
$[W^{IV}_3O_2(OBu^t)_8]$	$[-W-(\mu\text{-O})-W=W-(\mu\text{-O})-]$, two W–W bonds, one W = W bond, CN of W are 3, 4, 5	$W_2(OBu^t)_6 + O_2$	50
Linear chain			
$[UO_2][U(\mu\text{-O})(OBu^t)_5]_2$	three octahedra sharing a $[(\mu\text{-O})(\mu\text{-OR})]$ edge	$UO_2Cl_2 + KOBu^t$	51
Angular molecule			
$Nb_3O_2[(CMe_2)_2O_2]_5[(CMe_2)_2O_2H]$	three $[Nb_3(\mu\text{-O})_2(\mu,\eta^2\text{-}O_2R)_2]_2[\eta^2\text{-}RO_2]_4H$ octahedra	$Nb(OEt)_5 + (CMe_2)_2(OH)_2$	52

Note. Accepted abbreviations: h = [H_2O] : [alkoxide], Ψ is an incomplete polyhedron with a localised electron pair, CN is the coordination number.
[a] The bond length M = M 2.53 Å; [b] the U···U distance is 3.57 Å.

II. Pathways of formation of oxoalkoxides from alkoxides

There are several main pathways of formation of oxo ligands in alkoxide molecules. Among them are hydrolysis and oxidation, thermolysis, desolvation of solvates $M(OR)_n \cdot m\,L$ and decomposition accompanied by elimination of ethers. Only the first two above-mentioned processes can be controlled. Although some authors persist in considering OA only as products of uncontrolled hydrolysis (and often do not discuss the origin of oxo

Table 3. Tetranuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
Tetrahedra $[M_4(\mu_4\text{-}O)]$			
$[Al_4O(OPr^i)_6Cl_4(Pr^iOH)]$	$[Al_4(\mu_4\text{-}O)(\mu\text{-}OR)_5][H(\mu\text{-}OR)_2]Cl_4$, $[AlO_4Cl]$ trigonal bipyramids sharing $[O(\mu\text{-}OR)]$ edges	$Al(OPr^i)_3 + AlCl_3 + Pr^iOH$	18
$[Al_4O(OBu^i)_{10}(Bu^iOH)]$	pairs of $[AlO_5]$ trigonal bipyramids sharing $[(\mu_4\text{-}O)(\mu\text{-}OR)]$ edges	$Al(OBu^i)_3 + H_2O$	53, 54
$[Al_4O(OCH_2CF_3)_{10}(CF_3CH_2OH)]$	the same	$Al(OCH_2CF_3)_3 + H_2O$; $AlMe_3 + CF_3CH_2OH$	55
$[Y_4OCl_3(OBu^t)_7(THF)_3]$	$[Y(THF)_3(\mu\text{-}Cl)_3Y_3(\mu_4\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_3]$; base of a tetrahedron consists of three $[YO_6]$ octahedra centred with μ_3-OR, CN of Y_{ax} is 7	$Y_3Cl_2(OBu^t)_7 \cdot 2\,THF + LiAlMe_4$	56
$[Ce_4^{IV}O(OPr^i)_{14}]$	two octahedra and two seven-vertex polyhedra sharing $[(\mu_4\text{-}O)(\mu\text{-}OR)_2]$ faces	$Ce(OPr^i)_4 \cdot Pr^iOH$ (70 °C, 10^{-3} mm Hg)	57
$[Lu_4O(OH)(OCMe_2CH_2OMe)_9]$	$[Lu_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\eta^2,\mu_3\text{-}OR)(\eta^2,\mu\text{-}OR)_3(\eta^1,\mu\text{-}OR)(\eta^1\text{-}OR)_4]$, two octahedra and two seven-vertex polyhedra	$Lu[N(SiMe_3)_2] +$ $+ MeOCH_2CMe_2OH$	58
$[Pb_4O(OSiPh_3)_6] \cdot PhH$	six $(\mu\text{-}OR)$ bonds along tetrahedron edges; $[:PbO_4]$ is a Ψ-trigonal bipyramid	$PbCp_2 + Ph_3SiOH + PhH$, Δ	59
$[Pb_2Ti_2O(OPr^i)_{10}]$	two $[:PbO_5]$ Ψ-octahedra and two $[TiO_6]$ octahedra	$Pb(OPr^i)_2 + Ti(OPr^i)_4$	60
$[Ce_4^{3.75+}O(OPr^i)_{13}(Pr^iOH)]$	'butterfly wings' — $[OCe_4]$; two octahedra are linked only *via* μ_4-O, two Ce seven-vertex polyhedra sharing $[O(\mu\text{-}OR)_2]$ faces	$[Ce(OPr^i)_4 \cdot Pr^iOH]$, UV irradiation	61
$[Pb_3ZrO(OBu^t)_8]$	'butterfly wings', a Zr octahedron and a Pb Ψ-tetrahedron are linked *via* μ_4-O, two Pb square pyramids sharing a $[(\mu\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)]$ face	$PbZr(OBu^t)_6 + Pb(OBu^t)_2$, Δ	62
$[Th_4O\{O(C_2H_4O)_4\}_3Cl_8] \cdot 3\,MeCN$	$[Th_4O(\eta^5,\mu\text{-}ORO)_3Cl_8]$, each $[O(C_2H_4O)_4]$ fragment is bound to one Th atom	$ThCl_4 + MeCN +$ $+ HO(C_2H_4O)_3C_2H_4OH$	63
$[NaBi_3O(OC_6F_5)_8THF]$	–	$BiCl_3 + NaOC_6F_5 + THF$	64
$[Li_2(NbO)_2O(OCMe_2CH_2OMe)_6]$	$[Li_2(NbO)_2(\mu_4\text{-}O)(\eta^2,\mu\text{-}OR)_4(\eta^2\text{-}OR)_2]$; two Nb octahedra; CN of Li is 5	–	65
Uncentred $[M_4]$ tetrahedron			
$[W_4^{III}O(OPr^i)_9Cl] \cdot 0.5\,Et_2O$	$[W_4(\mu\text{-}O)(\mu\text{-}OR)_2(OR)_7Cl]$; three W = W bonds, three W – W bonds, $[WO_4]$ square	$W_2(OPr^i)_6 + NaOPr^i + [Bu^n_2NH_2]Cl +$ $+ H_2O$ (traces) $+ Et_2O$	66
Cube $[M_4(\mu_3\text{-}O)_4]$			
$[(MoO)O(OSiMe_3)(Me_2NH)]_4$	cube $[M_4(\mu_3\text{-}O)_4]$	–	67
'Butterfly' — cluster of two $[M_3]$ triangles sharing a $[M_2]$ side			
$[Mo_4^{III}O(OCH_2Bu^t)_{10}Py]$	$[Mo_4(\mu_3\text{-}O)(\mu\text{-}OR)_4(OR)_6Py]$, one triangle is centred with μ_3-O; five Mo = Mo bonds, two OR groups at the end of one 'wing'; two OR and Py groups at the end of another 'wing'; one terminal OR group at each of the central atoms	$Mo_2(OCH_2Bu^t)_6 + O_2$	68
$[K(18^z\text{-}6)_2]^+[Mo_4O(OCH_2Bu^t)_{11}]^-$	one terminal OR group at each central Mo atom, two OR groups at one 'wing', three OR groups at another 'wing'	$Mo_2(OCH_2Bu^t)_6 + AsH_3 +$ $+ KOH + 18\text{-}C\text{-}6$ (see [a])	69
Rings of two dimers (two pairs of octahedra are linked to a ring *via* two μ-O groups)			
$[Nb_2Cl_4(OEt)_2(THF)_2]_2O_2$	$[Nb_2(\mu\text{-}Cl)(\mu\text{-}OR)Cl_3(OR)(THF)_2]_2(\mu\text{-}O)_2$	$NbCl_3 + EtOH + THF$	70
$[Re_2^V(OMe)_8]_2O_2$	$[Re_2(\mu\text{-}OR)_2(OR)_6]_2(\mu\text{-}O)_2$	electrochemical synthesis (Re + MeOH)	71
$[Re_2^{VI}O_3(OMe)_6]_2$	$[(ReO)_2(\mu\text{-}OR)_2(OR)_4]_2(\mu\text{-}O)_2$	the same	72
Planar $[M_4]$ rhombuses with two μ_3-L and four μ-L ['$Ti_4(OMe)_{16}$ type']			
$[Bi_4O_2(OBu^t)_8]$	Bi^1 five-vertex polyhedron, a Bi^2 tetrahedron	$Bi[N(SiMe_2)_2]_3 + Bu^tOH$	73
$[(V^VO)_4O_4(OMe)_4(bipy)_2]$	two $[V^1O(\mu_3\text{-}OR)_2(\mu\text{-}O)_2(OMe)]$ octahedra and two $[V^2O(\mu_3\text{-}OR)(\mu\text{-}O)_2bipy]$ octahedra	$V^{IV}O(sal\text{-}glu) \cdot H_2O$ [b] + bipy	74
$[Nb_4O_4\{O(Me_2C)_2O\}_2(OPr^i)_8]$	two $[Nb^1(\mu_3\text{-}O)_2(\mu\text{-}O)(OPr^i)(\eta^2,\mu\text{-}RO_2)]$ octahedra and two $[Nb^2(\mu_3\text{-}O)(\mu\text{-}O)(OPr^i)_3(\eta^2,\mu\text{-}RO)]$ octahedra	$Nb(OPr^i)_5 + (Me_2C)_2(OH)_2$	52
$[Ce_2Ti_2O_2(RO_2)_4(OPr^i)_4(Pr^iOH)_2]$, $R = (Me_2C)_2$	two $[Ti^1(\mu_3\text{-}O)_2(\eta^2,\mu\text{-}RO_2)_2]$ octahedra and two $[Ce^2(\mu_3\text{-}O)(\eta^2,\mu\text{-}RO)_2(OPr^i)_2(Pr^iOH)]$ octahedra	$Ce_2O[(Me_2C)_2O_2]_2[(Me_2C)_2O_2H]_2 +$ $+ Ti(OPr^i)_4$	75
$[Ce_2Nb_2O_2\{O(Me_2C)_2O\}_4(OPr^i)_6]$	two $[Nb^1(\mu_3\text{-}O)_2(\eta^2,\mu\text{-}RO_2)_2]$ octahedra and two $[Ce^2(\mu_3\text{-}O)(\eta^2,\mu\text{-}RO)_2(OPr^i)_3]$ octahedra	$Ce(OPr^i)_4(Pr^iOH) + [Nb_2O.$ $.\{(Me_2C)_2O_2\}_4\{(Me_2C)_2O_2H\}_2(OPr^i)]$	75

Table 3 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Planar $[M_4]$ rhombuses with two μ_3-L and four μ-L ['$Ti_4(OMe)_{16}$ type']			
$[MgNbO(OMe)_5(MeOH)_2]_2$	two $[Mg^1(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(ROH)_2]$ octahedra and two $[(Mo^2O_2)(\mu_3\text{-}OR)(\mu\text{-}OR)(\mu\text{-}O)(OR)]$ octahedra	$Mg(OMe)_2$ + MeOH + + $Nb(OMe)_5$, Δ	76
$[(MoO_2)_4O_2(OMe)_4(Me_2CNOH)]$	two $[(Mo^1O_2)(\mu_3\text{-}OR)_2(\mu\text{-}OR)(\mu\text{-}O)]$ octahedra and two $[(Mo^2O_2)(\mu_3\text{-}OR)(\mu\text{-}OR)(\mu\text{-}O)(OR)]$ octahedra	$[Bu^n_4N]_4Mo_8O_{26}$ + MeOH + + Me_2CNOH	77
$[Bu^n_4N]^+_2[(MoO_2)_4O_2(OMe)_6]^{2-}$	the same	$[Bu^n_4N]_4Mo_8O_{26}$ + MeOH	78
$[Bu^n_4N]^+_2[(MoO_2)_2(MoO)_2O_4(OMe)_2.$ $.(C_6H_4O_2\text{-}1,2)_2]^-$	two $[(Mo^1O_2)(\mu_3\text{-}OR)_2(\mu\text{-}O)_2]$ octahedra and two $[(Mo^2O)(\mu_3\text{-}OR)(\mu\text{-}O)_2(\eta^2\text{-}ArO_2)]$ octahedra	$[Bu^n_4N]_4Mo_8O_{26}$ + + $C_6H_4(OH)_2$-1,2 + MeOH	78, 79
$[(Mo^VO)_4O_4(OPr^i)_4Py_4]$	two $[(Mo^1O)(\mu_3\text{-}O)_2(\mu\text{-}O)(\mu\text{-}OR)Py]$ octahedra and $[(Mo^2O)(\mu_3\text{-}O)(\mu\text{-}O)(\mu\text{-}OR)(OR)Py]$ octahedra, Mo = Mo bonds	$Mo_2(OPr^i)_6 + O_2$ + Py	80
$[(Mo^VO)_2OCl_2(OEt)_2L]_2$, L = EtOH, PMe_3	two $[(Mo^IO)(\mu_3\text{-}O)_2(\mu\text{-}OR)_2Cl]$ octahedra and two $[(Mo^2O)(\mu_3\text{-}O)(\mu\text{-}OR)_2ClL]$ octahedra, Mo — Mo bonds	$[(MoO)_2Cl_4(OEt)_2$ + EtOH] + + PMe_3 + SbF_3 + $Me_3SiC_3H_5$	81
$[(Mo^{V,VI}O)_4O_2Cl_4(OPr^n)_6]$	two $[(Mo^1O)O_2(\mu\text{-}OR)_2Cl]$ octahedra and two $[(Mo^2O)O(\mu\text{-}OR)_2(OR)Cl]$ octahedra, Mo — Mo bonds	$MeMoCl_2(OPr^n)_2 + Pr^nOH$	82
$[UO_2]_2[U_2O_2(OPh)_{10}(THF)_4]$	two $[(U^{VI(1)}O_2)(\mu_3\text{-}O)_2(\mu\text{-}OR)_2THF]$ pentagonal bipyramids and two $[U^{V(2)}(\mu_3\text{-}O)(\mu\text{-}OR)_2(OR)_3THF]$ pentagonal bipyramids	UCl_3 + NaOPh + THF	83
$[Re^{V,VI}_4O_6(OPr^i)_{10}]$	four $[Re_4(\mu_3\text{-}O)_2(\mu\text{-}O)_4(OR)_{10}]$ octahedra, five Re — Re bonds	electrochemical synthesis (Re + Pr^iOH)	84
$[LiNbO(OEt)_4(EtOH)]_2$	tetrahedron $[Li^2(\mu_3\text{-}OR)(\mu\text{-}OR)_2(ROH)]$ and the $[Nb^1(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(OR)O]$ octahedron	$LiNb(OEt)_5$ (decomposition in solution)	85
Linear chain of tetrahedra and octahedra			
$[(V^VO)(V^{IV}O)O(OEt)_3Phen]_2$ (see [c])	$[(V^VO)(OR)_2(\mu\text{-}O)(V^{IV}O)(\mu\text{-}OR)Phen]_2$	VCl_3 + NaSPh + EtOH + Phen	86
Zigzag molecule			
$[(Re^{VII}O_3)NbO(OMe)_4]_2$	$[(ReO_3)(\mu\text{-}O)Nb(OR)_3(\mu\text{-}OR)]_2$; Re — O — Nb angle $\approx 180^\circ$	$Re_2O_7 + Nb(OR)_5$	87
Octahedron is linked to a vertex of the $[M_3]$ triangle *via* a common $(\mu\text{-}OR)_3$ face			
$[W^{IV}_4O_2(OPr^i)_{12}]$	$[W_4(\mu\text{-}O)_2(\mu\text{-}OR)_3(OR)_9]$, along two ($\mu$-O) sides, W ≡ W bonds	$W_2(OPr^i)_6 + Me_2CO$	88

Note. Accepted abbreviations: ax is axial.
[a] 18-C-6 is 18-crown-6; [b] sal-glu is *N*-salicylideneglycinate; [c] Phen is phenathroline.

Table 4. Pentanuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
Square pyramids $[M_5(\mu_5\text{-}O)]$ and $[M_5(\mu_5\text{-}OH)]$			
$[Ba_5O(OPh)_8(PhOH)(THF)_8]$	$[Ba_5H(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_9(THF)_8]$, four μ_3-OR groups above lateral faces, four μ-OR groups along the base, CN of Ba_{ax} is 6, CN of Ba_{eq} is 7	Ba + PhOH + THF	89
$[Ba_5(THF)_4(H_2O)(OH)\{OCH(CF_3)_2\}_9]\cdot THF$	$[(BaTHF)_4Ba(H_2O)(\mu_5\text{-}OH)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)]\cdot THF$, four μ_3-OR groups above lateral faces, four μ-OR groups along the base	Ba + $(CF_3)_2CHOH$ + THF	90
$[(Ba_5(OH)(OC_6H_3Bu^t_2\text{-}3,5)_9(THF)_5]$	$[(BaTHF)_5(\mu_5\text{-}OH)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)]$; four μ_3-OR groups above lateral faces, four μ-OR groups along the base, OR group at Ba_{ax}, CN of Ba are 7, 8	Ba + 3,5-$Bu^t_2C_6H_3OH$ + + THF	91
$[M_5O(OPr^i)_{13}]$, M = In, Sc,Y, [Y4Pr], Pr, Er, Yb, Gd	$[M_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_5]$; four μ_3-OR groups above lateral faces, four μ-OR groups along the base, CN of M is 6	electrochemical synthesis; M + Pr^iOH; MCl_3 + $NaOPr^i$; $Pr(OPr^i)_3\cdot Pr^iOH$ + Pr^iOH	10–14, 92, 93
$[Al_5O(OBu^i)_{13}]$	$[Al_5(\mu_5\text{-}O)(\mu\text{-}OR)_8(OR)_5]$; Al_{ax} — an octahedron, four Al_{eq} atoms — trigonal bipyramids, 8 μ-OR groups along all edges	$Al_4O(OBu^i)_{10}\cdot Bu^iOH$ + + DBU [b]	53
$[Fe_5O(OEt)_{13}]$	Fe_{ax} — an octahedron, four Fe_{eq} atoms — trigonal bipyramids, eight μ-OR groups along all edges	$FeCl_3$ + NaOEt	15

Table 4 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Square pyramids $[M_5(\mu_4\text{-O})]$ with a centred base			
$[IBa(LiTHF)_4(OH)(OBu^t)_4]$	$[IBa(LiTHF)_4(\mu_4\text{-OH})(\mu_3\text{-OR})_4]$	$BaI_2 + LiOBu^t + H_2O + THF$	94
$[Sr_5O(OCH_2Bu^t)_8(Bu^tCH_2OH)(THF)_4]$	$[Sr_5(\mu_4\text{-O})(\mu_3\text{-OR})_4(\mu\text{-OR})_4(ROH)(THF)_4]$	$Sr + Bu^tCH_2OH + THF$	95
$[Eu^{III}Eu^{II}_4O_5(OAr)(ArOH)_5(MeCN)_8]$, Ar = $C_6H_3Pr^i_2$-2,6	$[Eu_5(\mu_4\text{-O})(\mu_3\text{-O})_4(\mu\text{-OAr})(\mu\text{-ArOH})(ArOH)_4(MeCN)_8]$, Eu^{III}_{ax} — an octahedron, CN of Eu^{II}_{eq} is 7	$Eu(OPr^i)_2 +$ + 2,6-$Pr^i_2C_6H_3OH$	96
$[Ti_3(OMe)_2(OPr^i)_9]^+[Fe^{II}_2Fe^{III}_2TiOCl_4(OPr^i)_9]^-$	$[(FeCl)_4Ti(\mu_3\text{-O})(\mu\text{-OR})_8(OR)]^-$ (see [a])	$FeCl_2 + KOPr^i +$ + $Ti(OPr^i)_4$ + MeOH	97
Trigonal bipyramids $[M_5(\mu_5\text{-O})]$			
$[Li(MgTHF)_4O(\mu\text{-}OC_6H_4Me\text{-}2)_7]$	two Mg_{ax} atoms; Mg — a trigonal bipyramid, Li — T-like coordination	$LiBu^n + MgBu^n_2 +$ + 2-$MeOC_6H_3OH$	98
$[Nd_5O(OPr^i)_{13}(Pr^iOH)_2]$	$[Nd_5(\mu_5\text{-O})(\mu_3\text{-OR})_2(\mu\text{-OR})_6(OR)_5(ROH)_2]$, two μ_3-OR groups above faces of two different pyramids, six *mer*-μ-OR groups, Nd — an octahedron	$Nd + Pr^iOH$ ($HgCl_2$)	10, 13, 99
$[Sm_4TiO(OPr^i)_{14}]$, $[(Tb_{0.9}Eu_{0.1})_4TiO(OPr^i)_{14}]$	two μ_3-OR groups above faces of two different pyramids, six *mer*-μ-OR groups, Ti — a trigonal bipyramid, Ln — an octahedron	$LnI_2 + NaTi(OPr^i)_5$, Ln = Sm, Tb, Eu	100, 101
Two $[MM'_2]$ triangles sharing an M vertex			
$Sr(Pr^iOH)_2[Ti_2O(OPr^i)_7]_2$	$Sr(ROH)_2[Ti_2(\mu_3\text{-O})(\mu\text{-OR})_2(OR)_5]_2$; $[Ti_2O(OR)_7]$ — two trigonal bipyramids sharing a $[(\mu_3\text{-O})(\mu\text{-OR})]$ edge	$Sr(OPr^i)_2 + Ti(OPr^i)_4 +$ + Pr^iOH	102
$[Ta_5O_7(OBu^t)_{11}]$	$[Ta_5(\mu_3\text{-O})_4(\mu\text{-O})_3(\mu\text{-OR})(OR)_{10}]$, $[Ta_5]$ is a trigonal pyramid	$Ta(OBu^t)_5 + H_2O$ (h = 1)	103
$[NaBi_4O_2(OC_6F_5)_9(THF)_2]$	$[NaBi_4(\mu_3\text{-O})_2(\mu\text{-OR})_7(OR)_2]$, $[NaBi_2(\mu\text{-OR})_3]$ ring in the centre	$BiCl_3 + NaOC_6F_5$	64
Rings containing five M atoms			
$[Mo^V_2Mo^{VI}Ta_2O_8(OPr^i)_{10}]$	Two $[Ta(\mu\text{-O})(\mu\text{-OR})_2(OR)_3]$ octahedra, one $[(Mo^VO)_2(\mu\text{-O})_2(\mu\text{-OR})_4]$ group (CN 5) and the $[(Mo^{VI}O_2)(\mu\text{-O})_2]$ tetrahedron	$Mo^V_4Ta_2O_8(OPr^i)_{14} +$ + O_2 traces	104

Note. Hereinafter, eq is equatorial.
[a] The authors considered the oxo ligand as tridentate taking into account the presence of three short bonds, *viz*., two $Fe_{eq}-O$ bonds and one $Ti_{ax}-O$ bond. [b] DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

Table 5. Hexanuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
Octahedra $[M_6(\mu_6\text{-O})]$			
$[Ba_6O(OC_2H_4OMe)_{10}(MeOC_2H_4OH)_4]$	$[Ba_6(\mu_6\text{-O})(\mu_3,\eta^2\text{-OR})_8(\eta^2\text{-ROH})_4(\mu\text{-OR})_2]$, a $[M_6]$ octahedron, μ_3-OR groups on eight faces, CN of Ba_{ax} is 8, CN of Ba_{eq} is 9	$Ba + MeOC_2H_4OH$	105
trans-$[Na_2Gd_4O(OBu^t)_{12}]$	$[Na_2\{Gd(OR)\}_4(\mu_6\text{-O})(\mu_3\text{-OR})_8]$, the $[NaO(\mu_3\text{-OR})_4]$ square pyramid in the axial position, the $[GdO(\mu_3\text{-OR})_4.$ $.(OR)]$ octahedron in the equatorial position	$GdCp_3 + NaOBu^t$	106
trans-$[K_4Zr_2O(OPr^i)_{10}]$	$[K_4Zr_2(\mu_6\text{-O})(\mu_3\text{-OR})_8(OR)_2]$, the $[ZrO(\mu_3\text{-OR})_4(OR)]$ octahedron in the axial position, the $[KO(\mu_3\text{-OR})_4]$ square pyramid in the equatorial position	$KH +$ '$Zr(OPr^i)_4$' $+ H_2O$	107
trans-$[K_4Zr_2O(OAr)_8(OEt)_4]$, Ar = C_6H_3OMe-2-All-4	$[K_4Zr_2(\mu_6\text{-O})(\mu_3\text{-OAr})_8(\mu\text{-OR})_2]$, K atoms are coordinated by eight OMe groups of eugenol	'$Zr(OEt)_4$' + + KOC_6H_3OMe-2-All-4	108
trans-$[M^I_4M^{III}_2O(OBu^t)_8]\cdot n$ THF, M^I = Na, K; M^{III} = Sb, Bi; n = 0, 1, 4	$[M_6(\mu_6\text{-O})(\mu_3\text{-OR})_8]$, M^I and M^{III} are disordered	$M(OBu^t)_3 + NaOBu^t + THF$ $(-Bu^t_2O)$	109
trans-$[Na_4Sb_2O(OSiMe_3)_8]$	$[M_6(\mu_6\text{-O})(\mu_3\text{-OR})_8]$, Na and Sb are disordered	$Sb(OSiMe_3)_3 + NaOSiMe_3$	110

Table 5 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Octahedra [$M_6(\mu_6\text{-}O)$]			
cis-[$Na_4Bi_2O(OC_6F_5)_8(THF)_4$]	[$(NaTHF)_4Bi_2(\mu_6\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_6$]	$2\,NaOC_6F_5 + Bi(OC_6F_5)_3 +$ + THF	111
[$V_6^{IV,V}O_7(OEt)_{12}$]	[$(VO)_6(\mu_6\text{-}O)(\mu\text{-}OR)_{12}$]	$VO(OEt)_3 + H_2O$ (traces)	112
$M_2[V_6^{IV,V}O_7(OH)_n\{MeC(CH_2O)_3\}_{(12-n)/3}]$, $n = 0, 3$; $M_2[(V^{IV,V}O)_6O_{7-n}(OH)_n\{RC(CH_2O)_3\}_2]$, R = NO_2, CH_2OH, Me, Et, Bn; $n = 0, 2, 4, 6$; $[M][(V^VO)_6O_6(OMe)_7]$, M = R_4N, Na	[$M_6(\mu_6\text{-}O)(\mu\text{-}O)_{12}O_6$], structural analogue of the [M_6O_{19}] 'large octahedron', μ-O groups along twelve edges of the octahedron	$V_2O_5 + V_2O_3 + NaVO_3 +$ + NH_4Cl + $MeC(CH_2OH)_3$ + + H_2O (Δ, high pressure)	113–117
[$Bu^n_4N]_{n-1}[M(WO)_5O_{13}(OMe)]$, M = Ti, Zr, Nb, Ta	analogue of the 'large octahedron', one terminal O atom is replaced by OMe	$M(OMe)_n + WO_4^{2-} +$ + MeOH + $(Bu^n_4N)Cl$	118
[$Bu^n_4N]_3[Nb_2W_4O_{18}(OR)$], R = Me, Et, Pr^i, Bu^t, $SiMe_3$	analogue of the 'large octahedron', $[Nb_2(WO)_2(WO_2)_2(\mu\text{-}O)_{12}(OR)]^{3-}$	$[HNb_2W_6O_{19}]^{3-}$ + ROH + + $(Bu^n_4N)Cl$	119
$[Me_4N]_2[Fe_6O\{MeC(CH_2O)_3\}_6]\cdot 4\,MeOH$ $[Me_4N]_2[Fe_6O\{MeC(CH_2O)_3\}(OMe)_6Cl_6]\cdot 2\,H_2O$	analogue of the 'large octahedron', one of three O atoms of the RO_3 ligand is μ-coordinated, two other O atoms are terminal	$FeCl_3 + [Me_4N]OMe +$ + $MeC(CH_2OH)_3$ + MeOH + H_2O	120, 121
$Tl_4Ti_2O(OR)_5(OEt)_5$, R = Et, Pr^i	[$Tl_4Ti_2(\mu_6\text{-}O)(\mu_3\text{-}OR)_8(OEt)_2$], Ti_{ax} atoms — distorted octahedron, Tl_{eq} atoms — Ψ-octahedra [a]	TlOEt + $Ti(OR)_4$, R = Et, Pr^i	122
Trigonal antiprism			
$[Mo_6^{3,3+}O(\mu\text{-}OEt)_{12}(OEt)_6]\cdot 4.8\,H_2O$	[$Mo_6(\mu_6\text{-}O)$]; μ-OR groups along nine edges and three μ-OR groups along diagonals of lateral faces	$Mo(OEt)_3 + H_2O$ (h = 15)	123
Uncentred [M_6] octahedra			
[$Sn_6O_4(OR)_4$], R = Me, Pr^i	[$Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$], μ_3-O and μ_3-OR groups alternate on eight octahedron faces	$Sn(OR)_2 + H_2O$, R = Me, Pr^i	124–126
[$Pb_6O_4(OR)_4$], R = Pr^i, Bu^t	[$Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$], μ_3-O and μ_3-OR groups alternate on eight octahedron faces	electrochemical synthesis ($Pb + Pr^iOH$); $Pb(OBu^t)_2 + H_2O$	127
[$Bi_6O_3(OC_6F_5)_{12}(THF)_2$]	[$Bi_6(\mu_4\text{-}O)(\mu_3\text{-}O)_2(\mu\text{-}OR)_{12}(THF)_2$]	$BiCl_3 + NaOC_6F_5 + THF$	64
[$La_2(MoO)_4(\mu_4\text{-}O)_4(\mu\text{-}OPr^i)_8(OPr^i)_6$]	[$La_2(MoO)_4(\mu_4\text{-}O)_4(\mu\text{-}OR)_8(OR)_6$], Mo atoms — octahedra, CN of La is 9	$La_5O(OPr^i)_{13}$ + + $MoO(OPr^i)_4$ ($-R_2O$)	128
Two [M_4] tetrahedra sharing an [M_2] edge			
$[Fe_6O_2(OMe)_{12}\{N(C_2H_4NH_2)_3\}_2]^{2+}\cdot$ $\cdot[CF_3SO_3]_2^-\cdot 2\,MeOH$	[$Fe_6(\mu_4\text{-}O)_2(\mu\text{-}OR)_8(OR)_4L_2]^{2+}$	$[Fe_3O_2(OH)N(C_2H_4NH_2)_3]^{4+}$ + + MeOH + CF_3SO_3H	129
Two cubes sharing an [$M_2(\mu_4\text{-}O)_2$] face			
$[Ca_6O_2(OEt)_8]\cdot 14\,EtOH$	[$Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OR)_4(OR)_4$]; three terminal OR groups at the terminal Ca atom, two terminal OR groups at the central Ca atom	$Ca(OEt)_2 + EtOH +$ + $O_2 + H_2O$ (traces), Δ	16
Two [$M_3(\mu_n\text{-}O)$] triangles			
[$Gd_6O(MeOC_2H_4O)_{16}$]	[$Gd_6(\mu_4\text{-}O)(\eta^2,\mu_3\text{-}OR)_4(\eta^2,\mu\text{-}OR)_6(\eta^1,\mu\text{-}OR)_2(OR)_4$], two triangles in perpendicular planes sharing a μ_4-O vertex, CN of Gd are 7, 8	$Gd + MeOC_2H_4OH$	130
$[Ba_2Ti_4O(OMe)_{18}(MeOH)_7]\cdot MeOH$	[$Ba_2Ti_4(\mu_3\text{-}O)(\mu_3\text{-}OR)_6(\mu\text{-}OR)_2(OR)_{10}(ROH)_7]\cdot ROH$, [$BaTi_2(\mu_3\text{-}O)$] triangles sharing a [$Ba_2$] edge, CN of Ba is 9	$Ba + MeOH + Ti(OMe)_4$	131
[$Bi_6O_3(OC_6H_3Cl_2\text{-}2,6)_{12}$]	two [$Bi_3(\mu_3\text{-}O)(\mu\text{-}OR)_2(OR)_2$] triangles are linked *via* two μ_3-O groups and three μ-OR groups	$BiPh_3 + 2,6\text{-}Cl_2C_6H_3OH$	132
$[Hf_3O(OEt)_{10}(EtOH)]_2$	two [$Hf_3(\mu_3\text{-}O)(\mu\text{-}OR)_2(OR)_5$)] triangles are linked to each other to form a ring *via* two pairs of μ-OR groups	electrochemical synthesis ($Hf + EtOH$)	45

Table 5 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Rings of two $[M_3(\mu_3\text{-O})]$ triangles linked *via* two linear μ-O groups			
$[MoTa_2O_4(OMe)_8]_2$	$[(MoO_2)Ta_2(\mu_3\text{-O})(\mu\text{-OR})_3(\mu\text{-O})(OR)_5]_2$	$MoO(OMe)_4 + 2\,Ta(OMe)_5 + H_2O$	133
$[IZnTa_2O_2(OPr^i)_7]_2$	$[IZnTa_2(\mu_3\text{-O})(\mu\text{-OR})_3(\mu\text{-O})(OR)_4]_2$	$ZnI_2 + KTa(OPr^i)_6$	134
$[Mo_3^{V}O_4Cl_4(OEt)_3]_2$	$[(MoOCl)_3(\mu_3\text{-O})(\mu\text{-OR})_3(\mu\text{-Cl})]_2$	$Mo_2Cl_4O_2(OEt)_2\cdot EtOH + Me_3SiC_3H_5\,(-C_3H_6)$	135
$[LiMo_2O_4(OC_2H_4OMe)(OPr^i)_4]_2$	$[Li(MoO_2)(MoO)(\eta^2,\mu_3\text{-}OC_2H_4OMe)(\mu_3\text{-OR})(\mu\text{-O}).(\mu\text{-OR})_2(OR)]_2$	$Li_2Mo_2O_4(OEt)_5\cdot EtOH + Pr^iOH + MeOC_2H_4OH$	136
$[NaMo_2O_4(OPr^i)_5(Pr^iOH)]_2$	$[Na(ROH)(MoO_2)(MoO)(\mu_3\text{-OR})_2(\mu\text{-OR})_2.(\mu\text{-O})(OR)]_2$	$MoO(OPr^i)_4 + NaOPr^i\,(-Pr^i_2O)$	137, 138
$[Ta_2(Re^{VI}O_4)O(OMe)_7]_2$	$[(ReO_3)(\mu\text{-O})Ta(\mu\text{-OR})_2Ta(OR)_3(\mu\text{-O})]_2$	$Re_2O_7 + Ta(OMe)_5$	139
Derivatives of $Ti_4(OMe)_{16}$ structural type			
$[Er_2Ti_4O_2(OEt)_{18}(EtOH)_2]$	$[Er_2Ti_4(\mu_4\text{-O})_2(\mu_3\text{-OR})_2(\mu\text{-OR})_8(OR)_8(ROH)_2]$, two $[Ti(\mu_3\text{-OR})(\mu\text{-OR})_2(OR)_2]$ fragments are bound to μ_3-O groups	$ErCl_3 + KOEt + Ti(OEt)_4 + H_2O$	140
$[NaBi_2O(OC_6F_5)_5THF]_2$	$[\{Na(THF)_2\}Bi_4(\mu_4\text{-O})_2(\mu\text{-OR})_{10}]$, two $\{Na(THF)\}$ fragments are bound to μ_3-O groups	$NaOC_6F_5 + Bi(OC_6F_5)_3 + THF$	64
$[Li_4(WO)_2O_2(OR)_6(ROH)]^{2+}[W_6O_{19}]^{2-}$, R = C_2H_4OMe	$[Li_4(WO)_2(\mu\text{-O})_2(\eta^2,\mu_3\text{-OR})_2(\eta^2,\mu\text{-OR})_4(\eta^2\text{-ROH})]^{2+}$, two $[Li(\mu\text{-O})(\eta^2\text{-ROH})]$ fragments are bound to terminal [WO] groups	$WO(OC_2H_4OMe)_4 + LiCl + O_2$	136
$[H_3Ba_6O(OBu^t)_{11}(R'O_2)(THF)_3]$, $R'O_2$ = $OCEt_2CH_2O$	$[Ba_5(\mu_5\text{-O})(\mu_3\text{-OR})_4(\mu\text{-OR})_3(OR)(THF)_3](\mu_3\text{-OR}).(\mu\text{-OR})_2Ba(\eta^2\text{-}R'O_2)]$, two Ba atoms are bound to three Ba atoms, $Ti_4(OMe)_{16}$ structural type with μ_5-O and μ-OR groups	$Ba + Bu^tOH + THF + HOCEt_2CH_2OH$	89
Zigzag chains			
$[Mo_3^{5.3+}O_5(OPr^i)_6]_2$ (A)	$[(Mo^{VI}O)(OR)_3(\mu\text{-OR})_2(Mo^{V}O)(\mu\text{-O})_2(Mo^{V}O)(\mu\text{-OR})_2]$, all Mo atoms are in a single plane; Mo = Mo bonds	$Mo_2(OPr^i)_6 + O_2$; $MoO(OPr^i)_4 \rightarrow A + Pr^i_2O + Pr^iOH + Me_2CO$	46, 141
$[Mo_2^{V}TaO_4(OPr^i)_7]_2$	$[(RO)_3Ta(\mu\text{-OR})_3(MoO)(\mu\text{-O})_2(MoO)(\mu\text{-OR})]_2$, Mo = Mo bonds	$MoO(OPr^i)_4 + Ta(OPr^i)_5$	104

[a] The authors considered this molecule as an octahedron centred only along the $Ti_{ax}-(\mu\text{-O})-Ti_{ax}$ direction taking into account a substantial difference in the Ti—O and Tl—O bond lengths.

Table 6. Heptanuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
$[Ti_7O_4(OEt)_{20}]$	$[Ti_7(\mu_4\text{-O})_2(\mu_3\text{-O})_2(\mu\text{-OEt})_8(OEt)_{12}]$, six edge-sharing octahedra about the central $[TiO_4(\mu\text{-OEt})_2]$ octahedron	$Ti(OEt)_4 + H_2O$ (h = 0.5–0.7)	7, 142, 143
$[Ta_7O_9(OPr^i)_{17}]$	$[Ta_7(\mu_3\text{-O})_3(\mu\text{-O})_6(\mu\text{-OR})_4(OR)_{13}]$, two vertex-sharing $[Ta_4]$ tetrahedra are linked *via* one μ_3-O and two μ-OR groups	electrolyte (Ta + Pr^iOH), $Ta(OPr^i)_5 + H_2O$ (h = 0.5–1)	33, 34 103
$[Pb_7O_2(OPr^i)_{10}]$	fragment $[Pb_4(\mu_4\text{-O})(OR)_6]$ is linked to the $[Pb_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu\text{-OR})_2]$ chain *via* one μ_3-OR group and two μ-OR groups	$Pb(OPr^i)_2 + H_2O$	144
$[Pb_7O_2(OSiMe_3)_{10}]$	fragment $[Pb_4(\mu_4\text{-O})(OR)_6]$ is linked to the $[Pb_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu\text{-OR})_2]$ chain *via* one μ_3-OR group and two μ-OR groups	$Pb[N(SiMe_3)_2]_2 + Me_3SiOH\,[-(Me_3Si)_2O]$	145
$[Fe_7O(OH)(RO_3)_4Cl_6(MeCN)_2]$, R = $(CH_2)_3CCH_2OH$	$[Fe(OH)(MeCN)_2][Fe_6(\mu_6\text{-O})Cl_6(RO_3)_4]$, the $[Fe_6(\mu_6\text{-O})]$ octahedron is linked to the $[Fe(\mu_3\text{-O})_3(MeCN)_2(OH)]$ octahedron	$FeCl_2\cdot 4\,H_2O + V_2O_5 + C(CH_2OH)_4 + MeCN$,	146

Table 7. Octanuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
Centred $[M_n(\mu_n\text{-O})]$ polyhedra			
$[Al_8O_2(OH)_2(OBu^i)_{18}]$	$[Al_4(\mu_4\text{-O})(\mu\text{-OH})(\mu\text{-OR})_5(OR)_4]_2$, two $[Al_4(\mu_4\text{-O})]$ tetrahedra sharing a $(\mu\text{-OR})_2$ edge	distillation of $Al_4O(OBu^i)_{10}$	53
$[K_2Sb_2O(OPr^i)_6]_2$	two $[K_2Sb_2(\mu_4\text{-O})(\mu_3\text{-OR})_6]$ tetrahedra are linked *via* the $[K_4(\mu_3\text{-OR})_8]$ group	$KSb(OPr^i)_4$, Δ	109
$[Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4]$	$[Ni_5Sb_3(\mu_4\text{-O})_2(\mu_3\text{-OR})_4(\mu\text{-OR})_8(OR)_3(ROH)_4]$, $[Ni_4(\mu_3\text{-OR})_2(\mu_4\text{-O})_2]$ cube in the centre is surrounded by $[{:}SbO_4]$ groups of Ψ-octahedra and three Ni octahedra	$Sb(OEt)_3 + NiCl_2 + NaOEt$	147
$[Na_4Cr^{III}_4O_3(OPh)_{10}(TMEDA)_4]$ [a]	$[(Na_4(TMEDA)_4Cr_4(\mu_3\text{-O})_3(\mu_3\text{-OR})_4(\mu\text{-OR})_6]$; two $[NaCr_2(\mu_3\text{-O})]$ triangles, one $[Cr_3(\mu_3\text{-O})]$ and a $[Na(\mu\text{-OR})_3Cr]$ group; CN of Na and Cr is 5	$Na_4Cr^{II}_2(OPh)_8 +$ + TMEDA + O_2	148
$[Na_2Fe_6O(OMe)_{18}(MeOH)_6]$	$[Na(ROH)_3]_2[Fe_6(\mu_6\text{-O})(\mu_3\text{-OR})_6(\mu\text{-OR})_6(OR)_6]$; Na_{ax}	$FeCl_3 + NaOMe$	149
$[Pr_4O_2(OC_2H_4OMe)_8(OPMe_3)]_2$	spherical $[Pr_4(\mu_4\text{-O})_2(\eta^2,\mu_3\text{-OR})_2(\eta^2,\mu\text{-OR})_4(\eta^1,\mu\text{-OR})(OR).$ $.(OPMe_3)]_2$ molecule; CN of Pr are 7 and 8	$Pr[N(SiMe_3)_2]_3 +$ + $MeOC_2H_4OH$	150
Isopolyanion-type structures			
$[Ti_8O_6(OBn)_{20}]\cdot Et_2O$	$[Ti_8(\mu_3\text{-O})_4(\mu\text{-O})_2(\mu\text{-OR})_8(OR)_{12}]$	$Ti(OBn)_4 + H_2O$, $h = 1$	143
$[M_8O_{10}(OEt)_{20}]$, M = Nb, Ta	$[M_8(\mu_3\text{-O})_2(\mu\text{-O})_8(\mu\text{-OR})_6(OR)_{14}]$, two octahedra fragments $[M(\mu\text{-O})_4(OR)_2]$ are linked to each other to form a ring *via* two triads of $[M_3(\mu_3\text{-O})(\mu\text{-OR})_3(OR)_6]$ octahedra	$M(OEt)_5 + H_2O$ ($h = 1-1.25$) $NbO(EtO)_3$ ($-Et_2O$)	8, 103, 151, 152
$Na_4[Mo_8O_{24}(OMe)_4]\cdot 8\,MeOH$	$Na_4[(MoO_2)_6(MoO)_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu\text{-O})_4(\mu\text{-OR})_2(OR)_2]$, structure is similar to $[Mo_8O_{26}]$ (metamolybdate)	$H_2MoO_4 + MeOH +$ + Na zeolite	153
$[Bu_4N]^+_2[Mo_8O_{20}(OMe)_4(RO_3)_2]^{2-}$, R = $MeC(CH_2)_3$	$[\{(MoO_2)_6(MoO)_2(\mu\text{-O})_6(\mu_3\text{-OMe})_2(\eta^3,\mu_3,\mu\text{-}(RO_3)\}_2(OMe)_2]^{2-}$, quadruples of octahedra sharing μ-O vertices	$[Bu_4N]_2Mo_2O_7 +$ + $MeC(CH_2OH)_3$	154
$[Bu_4N]^+_4[Mo^{V,VI}_8O_{24}(OMe)_2]^{4-}\cdot MeOH$	$[(Mo^{VI}O_3)_2(Mo^{VI}O_2)_2(Mo^{V}O)_4(\mu_3\text{-O})_2(\mu\text{-O})_8(\mu\text{-OR})_2]^{4-}$, $[Mo^{V}O_6]$ octahedron and $[Mo^{VI}O_4]$ tetrahedra, two Mo^V-Mo^V bonds	$[Bu_4N]_2Mo^{VI}_2O_7 + MeOH +$ + $Me_2C{=}NNH_2$	155
$[LiMo_4Ta_3O_{14}(OPr^i)_9(OC_2H_4OMe)_3]$	$[Li(MoO)_4Ta_3(\mu\text{-O})_{10}(\mu,\eta^3\text{-OR}')(OR)_9]$, $[LiMo_3O_4]$ cube is linked to three $[Ta(\mu\text{-O})_3(OR)_3]$ groups and one $[MoO(\mu\text{-O})_3]$ group	$LiMo_2O_4(OPr^i)_4(OC_2H_4OMe) +$ + $MoO(OPr^i)_4$	133
Rings			
$[Cu_4Zr_4O(OPr^i)_{18}]$	$[Cu_2Zr_2(\mu\text{-OR})_5(OR)_4]_2(\mu_4\text{-O})$, two eight-membered $[OCu_2(\mu\text{-OR})_2Zr_2(\mu\text{-OR})_3(OR)_4]$ rings sharing a μ_4-O vertex	$Cu_2Zr_2(OPr^i)_{10} + H_2O$	156
$[(Mo^VO)_4Cl_3O_2(OH)_3(OEt)_2(EtOH)_2]_2$	$[(MoO)_8Cl_6(\mu_3\text{-O})_4(\mu\text{-OH})_4(OH)_2(\mu\text{-OR})_4(ROH)_4]$; two rings consisting of four $[Mo_2(\mu_3\text{-O})]$ triangles sharing (μ-OH) vertices, Mo^V-Mo^V bonds	$(Mo^VO)_2Cl_4(OEt)_2 + SbF_3$	81, 157
Cuboidal-type structures			
$[LiTiO(OPr^i)_3]_4$	$[Li_4Ti_4(\mu_5\text{-O})_2(\mu_3\text{-O})_2(OPr^i)_4]$	$LiTi(OPr^i)_5 + H_2O$	158
$[Ba_4Ti_4O_4(OPr^i)_{16}(Pr^iOH)_4]$	$[Ba_4Ti_4(\mu_4\text{-O})_4(\mu_3\text{-OR})_2(\mu\text{-OR})_8(\mu\text{-OR})_6(ROH)_4]$	$BaTi_4(OPr^i)_{18}$ ($-Pr^i_2O$)	159
$[Mg_4Ta_4O_4(OBu^n)_{20}(Bu^nOH)_4]$	$[Mg_4Ta_4(\mu_4\text{-O})_4(\mu\text{-OR})_8(OR)_{12}(ROH)_4]$	$MgTa_2(OBu^n)_{12}$ ($-Bu^n_2O$)	160
$[Sr_4Ta_4O_4(OMe)_{20}(MeOH)_{10}]$	$[Sr_4Ta_4(\mu_4\text{-O})_4(\mu\text{-OR})_8(OR)_{12}(\mu\text{-ROH})_2(ROH)_8]$	$SrTa_2(OMe)_{12}$ ($-Me_2O$)	160
$[Ba_4M_4O_4(OEt)_{20}(EtOH)_6]$, M = Nb, Ta	$[Ba_4M_4(\mu_4\text{-O})_4(\mu_3\text{-OR})_4(\mu\text{-OR})_6(OR)_{10}(ROH)_6]$	$BaM_2(OEt)_{12}$ ($-Et_2O$)	85, 160
$[Mo_4Ta_4O_{16}(OPr^i)_{12}]$	vertices of the $[Mo_4Ta_4]$ cube are occupied by vertex-sharing $[(MoO)(\mu\text{-O})_3]$ tetrahedra and $[Ta(OR)_3(\mu\text{-O})_3]$ octahedra	$MoO(OPr^i)_4 + Ta(OPr^i)_5$	133
$H_x[Eu^{II}_8O_6(OC_6H_3Me_2\text{-}2,6)_{12}(OPr^i)_8]$	$H_x[Eu_8(\mu_4\text{-O})_6(\mu\text{-OAr})_{12}(OPr^i)_8]$, μ_4-O groups in the centres of faces, μ-OR are located along edges	$Eu + Pr^iOH + 2,6\text{-}Me_2C_6H_3OH$, Δ	96
$H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}.$ $.(OPr^i)_2THF]$	$H_{10}[Eu^{II}_6Eu^{III}_2(\mu_4\text{-O})_6(\mu\text{-O})_2(\mu\text{-OAr})_{10}(OPr^i)_2THF]$	$[Eu(OAr)_2(THF)_2] + Pr^iOH$	96

Table 7 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Ribbon			
$[Cu_4^{II}Zr_4O_3(OPr^i)_{18}]$	$[Cu_4Zr_4(\mu_4\text{-}O)_3(\mu\text{-}OR)_{10}(OR)_8]$; $[Cu_4(\mu_4\text{-}O)(\mu\text{-}OR)_2]$ group in the centre of the molecule, two $[Cu_2Zr_2(\mu_4\text{-}O)(\mu\text{-}OR)_4(OR)_4]$ tetrahedra on opposite sides	$CuCl_2 + H_2O + K_4Zr_2O(OPr^i)_{10}$, $Cu_2^{I}Zr_2(OPr^i)_{10} + O_2$	157, 161
Two square pyramids $[M_5(\mu_5\text{-}O)]$ sharing one $[M_2]$ edge			
$[M_8O_2(OPh)_{12}(PhOH)_2L_6]\cdot 2\,PhMe$, $M_8 = Ba_8$ or $[Ba_2Sr_6]$, $L = OP(NMe_2)_3$	$[M_8(\mu_5\text{-}O)_2(\mu_3\text{-}OR)_8(\mu\text{-}OR)_4(\mu\text{-}ROH)_2L_6]$; μ_3-OR groups are above the centres of lateral faces, μ-OR groups are located along the base, CN of Ba are 6, 8	$Ba + PhOH + OP(NMe_2)_3$, $Ba + PhOH + Sr(OPh)_2 + OP(NMe_2)_3 + PhMe$	162
$[Eu_2^{III}Ba_6O_2(OPr^i)_{14}(Pr^iOH)_2(THF)_4]$	groups μ_3-OR are above the centres of lateral faces, μ-OR groups are located along the base, CN of Eu is 6, CN of Ba is 8	$Eu + Ba + Pr^iOH$, THF, Δ	163
Two $[M_4]$ tetrahedra linked by two μ-OR groups			
$[W_8^{III}O_4(OPr^i)_{16}]$	tetrahedra contain two W=W bonds and two W−W bonds, $[W_4(\mu\text{-}O)_2(\mu\text{-}OR)_2(OR)_6]_2$	decomposition of $W_4(OPr^i)_{10}$ $(-C_3H_8)$	164

[a] TMEDA = $(Me_2NCH_2)_2$.

Table 8. Nonanuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
$[Ba_6Li_3O_2(OBu^t)_{11}(THF)_3]$	two $[M_6]$ octahedra sharing a $[Ba_3]$ face	$Ba + Bu^tOH + LiBu^n + THF$	165
$[Bi_9O_7(OC_6F_5)_{13}(THF)_2]$	$[Bi_6(\mu_3\text{-}O)_7(\mu_3\text{-}OAr)[Bi(OAr)_4]_3$; μ_3-O groups on seven faces of the $[Bi_6]$ octahedron, μ_3-OR groups on the eighth face; three of seven μ_3-O groups are coordinated to $[Bi(OR)_4]$	$[Bi(OC_6F_5)_3(PhMe)]_2\cdot 2\,PhMe +$ + THF	166
$[Fe_9O_3(OEt)_{21}]\cdot EtOH$	$[Fe_9(\mu_4\text{-}O)_2(\mu_3\text{-}O)(\mu\text{-}OR)_{15}(OR)_6(ROH)]$; two pentanuclear rings linked by μ_3-O and μ-OR groups and sharing an Fe atom	distillation of $Fe_5O(OEt)_{13}$ (200 °C, 0.01 mm Hg)	167
$H_{18}[Eu_9^{II}O_8(OAr)_{10}L_7][Eu_9O_9(OAr)_{10}L_6]$, Ar = 2,6-$Me_2C_6H_3$, L = THF	two types of monocapped cubes; μ_4-O groups in the centres of faces, three μ-OR groups along the edges	$Eu(OAr)_2(Pr^iOH)$, Δ, vacuum, THF	96

Table 9. Decanuclear oxoalkoxides.

Compound	Structure	Starting compounds, conditions of formation	Ref.
$[K_2(TMEDA)_2Li_8O(OBu^t)_8]$	$[K_2(\eta^2\text{-TMEDA})_2Li_8(\mu_8\text{-}O)(\mu_3\text{-}OR)_8]$	–	168
$[M_{10}(\mu_6\text{-}O)_2X_{26}]$ as structural analogues of $[V_{10}^{V}O_{28}]^{6-}$			
$Na_2[V_8^{IV}V_2^{V}O_{16}(RO_3)_4]\cdot n\,H_2O$, R = $HOCH_2C(CH_2)_3$	anion $[V_{10}(\mu_6\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}O)_{10}(\mu\text{-}OR)_4(OR)_8]^{n-}$, RO_3 groups on the surface of anions	$V_2O_5 + V_2O_3 + NaVO_3$	169
$[NH_4]_4[V_{10}^{IV}O_{16}(RO_3)_4]\cdot 4\,H_2O$ or $[Et_4N][V_{10}^{IV}O_{13}(RO_3)_5]$ [R = $EtC(CH_2)_3$] or $M_2[V_{10}^{IV}O_{14}(OH)_2(RO_3)_4]\cdot 2\,H_2O$ [M = Me_4N, Et_4N, Me_3NH; R = $HOCH_2C(CH_2)_3$]	the same	$R(OH)_3 + MCl + H_2O$, Δ, *P*	170
$M_2^{I}[Mn_{10}O_2(RO_3)_6Cl_8]\cdot 4\,MeOH\cdot 2\,H_2O$, R = $MeC(CH_2)_3$	anion $[Mn_{10}(\mu_6\text{-}O)_2[(OCH_2)_3CMe]_6Cl_8]^{2-}$	–	171
$[Fe_{10}O_2Cl_8(RO_3)_6]$, R = $EtC(CH_2)_3$	$[Fe_{10}(\mu_6\text{-}O)_2Cl_8(RO_3)_6]$	$FeCl_2\cdot 4\,H_2O + R(OH)_3$	146
$[(VO)_2Fe_8O_2Cl_6(RO_3)_6]$, R = $EtC(CH_2)_3$	$[(VO)_2Fe_8(\mu_6\text{-}O)_2Cl_6(RO_3)_6]$, two $[Fe_6(\mu_6\text{-}O)]$ octahedra sharing a $[Fe_2]$ edge	$FeCl_2\cdot 4\,H_2O + R(OH)_3 +$ + V_2O_5	146

Table 9 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Other isopoly compounds			
$[Fe_{10}O_4Cl_8(OMe)_{14}(MeOH)_6]\cdot 2\,MeOH$	$[Fe_5(\mu_4\text{-}O)_2Cl_4(OR)_7(ROH)_3]_2\cdot 2\,ROH$	$FeCl_2$ + NaOMe + + $[NH_3OH]Cl$ + MeOH	172
$[LiTa_9O_{13}(OEt)_{20}(EtOH)]$	$[LiTa_9(\mu_4\text{-}O)(\mu_3\text{-}O)_3(\mu\text{-}O)_9(\mu\text{-}OR)_6(OR)_{15}(\mu_3\text{-}H)]$, Ta octahedra and a Li tetrahedron	by-product of electrochemical synthesis Ta + EtOH + LiCl	173
$[Mg(MeOH)_6]^{2-}[Mg_2Mo_8O_{22}(OMe)_6.$ $.(MeOH)_4]^{2-}\cdot 6\,MeOH$	anion $[Mg_2(Mo^{V,VI}O)_8(\mu_4\text{-}O)_2(\mu_3\text{-}O)_6(\mu\text{-}O)_6(\mu\text{-}OR)_6(ROH)_4]^{2-}$, $Mo^V = Mo^V$ bonds	$MoCl_5$ + $MgCl_2$ + + MeOH + NaOH	174
$[Na_4Zr_6O_2(OEt)_{24}]$	$[Na_2\{Zr(OR)\}_3(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_7]_2$, two $[Na_2Zr_3(\mu_5\text{-}O)]$ trigonal bipyramids sharing a $[Na_2(\mu_3\text{-}O)_4]$ face	'$Zr(OEt)_4$' + $NaOSiMe_3$	44
$[Ba_4Cu^I_6O(OCEt_3)_{12}]$	$[Ba_4Cu_6(\mu_4\text{-}O)(\mu\text{-}OR)_{12}]$, six linear $[Cu(OR)_2]$ groups along edges of the $[OBa_4]$ tetrahedron	$Ba_2Cu^I_4(OCEt_3)_8 + O_2$	175
$[Al_{10}O_4(OEt)_{22}]$	$[Al_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu\text{-}OR)_7(OR)_4]_2$; two pentanuclear rings are linked *via* the $[Al_2(\mu_3\text{-}O)_2]$ ring; CN of Al are 4, 5, 6	$Al(OEt)_3$, PhH, Δ	17
$[Al_{10}O_6(OPr^i)_{18}NH_3]$	$[Al_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}OR)_6(OR)_{12}NH_3]$; CN of Al are 4, 5, 6	$Al(OPr^i)_3 + NH_3$	176
$[Ti_{10}O_8(OEt)_{24}]\cdot PhMe$	$[Ti_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OEt)_{10}(OEt)_{14}]\cdot PhMe$	$Ti_7O_4(OEt)_{20}$ + + $Ti_8O_6(OR)_{20}$ + PhMe	143
$[Sr_6Ti_4O_4(OPr^i)_{20}]$	$[Sr_6Ti_4(\mu_4\text{-}O)_4(\mu_3\text{-}OR)_4(\mu\text{-}OR)_{12}(OR)_4]$; four μ_3-OR groups and four $[OTi(OR)_4]$ groups on eight faces of the $[Sr_6]$ octahedron; the $[SrO_6]$ octahedron	$Sr(OPr^i)_2 + Ti(OPr^i)_4$	102
$[Ni_6Sb_4O_4(OEt)_{16}(EtOH)_4]$	$[Ni_6Sb_4(\mu_4\text{-}O)_4(\mu\text{-}OR)_{16}(ROH)_4]$; Ψ-octahedra $[(\mu_4\text{-}O)Sb(\mu\text{-}OR)_4]$ on four faces of the $[Ni_6]$ octahedron, $[NiO_6]$ octahedra	$NiBr_2 + Sb(OEt)_3 + KOEt$	177
$[Pb_6Nb_4O_4(OEt)_{24}]$	$[Pb_6Nb_4(\mu_4\text{-}O)_4(\mu_3\text{-}OR)_4(\mu\text{-}OR)_{12}(OR)_8]$; four μ_3-OR groups and four $[ONb(OR)_5]$ octahedra on eight faces of the $[Pb_6]$ octahedron; the $[PbO_6]$ trigonal prism	$Pb_4O(OEt)_6 + Nb(OEt)_5$ $(-Et_2O)$	178
$[Me_4N]_4[Mn_{10}\{2,2\text{-}(OC_6H_4)_2\}_4O_4Hal_{12}]$, Hal = Cl, Br	$[Mn_{10}\{\mu,\mu\text{-}2,2\text{-}(OAr)_2\}_4O_4Hal_{12}]^{4-}$ is a structural analogue of adamantyl, CN of Mn are 5, 6	$MnCl_2 + C_6H_4(OH)_2$-2,2 + $[Me_4N]OH\cdot 5\,H_2O$	179

Table 10. Oxoalkoxides with nuclearity higher than 10.

Compound	Structure	Starting compounds, conditions of formation	Ref.
$[Al_{11}O_6(OR)_{21}]$, R = Pr^n, Pr^i	$[Al_{11}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OPr^n)_{10}(\mu\text{-}OPr^i)_2(\mu\text{-}ROH)_2.$ $.(OPr^i)_8(OR)]$; two pentanuclear $[Al_5O_2(OX)_{10}]$ rings are linked *via* the $[Al(\mu_3\text{-}O)_2(\mu\text{-}O)_2(OR)]$ group	$Al(OPr^i)_3 + Ta(OPr^i)_5 + Pr^nOH$	180
$[Mn_7Sb_4O_4(OEt)_{18}(EtOH)_2]$	$[Mn_7Sb_4(\mu_5\text{-}O)_2(\mu_4\text{-}O)_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_{16}(ROH)_2]$	$Mn_2Sb_4(OEt)_{16} + H_2O$	181
$[Zr_3Mo_8O_{24}(OPr^i)_{12}(Pr^iOH)_4]$	$[Zr_3(MoO_2)_4(MoO)_4(\mu_3\text{-}O)_8(\mu\text{-}O)_4(\mu\text{-}ROH)_4(OR)]$	$Zr(OPr^i)_4\cdot Pr^iOH + MoO(OPr^i)_4$ $(-Pr^i_2O)$	182
$[Ti_{11}O_{13}(OPr^i)_{13}(OR)_5]$, R = Et, Pr^i	$[Ti_{11}(\mu_3\text{-}O)_{10}(\mu\text{-}O)_3(\mu\text{-}OR)_7(OR)_6(OEt)_5]$	$Ti(OPr^i)_4 + H_2O$ (h = 0.3 – 0.8)	183 – 185
$[Ti_{12}O_{16}(OPr^i)_{16}]$	$[Ti_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}O)_2(\mu\text{-}OR)_4(OR)_{12}]$	$Ti(OPr^i)_4 + H_2O$, 100°C (h = 1)	183 – 185
$[Ti_{12}O_{16}(OPr^i)_{10}(OEt)_6]$	$[Ti_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}O)_2(\mu\text{-}OR)_4(OR)_6(OEt)_6]$	$Ti(OPr^i)_4$ + AcOH	183 – 185
$[Mn_8Sb_4O_4(OEt)_{20}]$	$[Mn_8Sb_4(\mu_5\text{-}O)_4(\mu_3\text{-}OEt)_4(\mu\text{-}OEt)_{16}]$	$MnCl_2 + NaSb(OEt)_4$	186
$[Zr_{13}O_8(OMe)_{36}]$	$[Zr_{13}(\mu_4\text{-}O)_4(\mu\text{-}O)_4(\mu\text{-}OR)_{24}(OR)_{12}]$; Keggin-type $[Zr_{12}O_{36}]$ structure, the thirteenth Zr atom, $[ZrO_8]$ cube, in the centre; this cube is linked to twelve $[ZrO_2(\mu\text{-}OR)_4(OR)]$ seven-vertex polyhedra	$Zr(OMe)_4$ + MeOH + NaOH	9
$[Y_{14}Cl_{12}O_2(OBu^t)_{28}(THF)_4]$	four $[Y_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_n(THF)_m]$ triangles are linked *via* μ_4-O and μ-Cl ligands and two $[Y(\mu\text{-}OR)_2(\mu\text{-}Cl)_2]$ groups	decomposition of $[Y_3Cl_2(OBu^t)_7(THF)_2]$	187

Table 10 (continued).

Compound	Structure	Starting compounds, conditions of formation	Ref.
Linear chain			
$[Li_8Y_8O_2Cl_4(OBu^t)_{24}]$	$[Li_4Y_4(\mu_4\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_6(\mu\text{-}Cl)_2(OR)_4]_2$, two $[Li_2(\mu\text{-}OR)_2]$ groups in the centre are linked to two 'butterflies' *via* two μ-Cl	$YCl_3 + 2\,LiOBu^t + THF$	188
$[Ti_{16}O_{16}(OEt)_{32}]$	$[Ti_8(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}O)_2(\mu\text{-}OR)_8(OR)_8]_2$	$Ti(OEt)_4$ + EtOH, 100 °C, *P*	142, 189
$[V^{IV}_{16}O_{20}(\eta^3,\mu\text{-}O_3R)_8(H_2O)_4]\cdot 3\,H_2O$, R = $(CH_2)_3CCH_2OH$	$[\{(VO)_6V_2(\mu_5\text{-}O)_2(\eta^3,\mu\text{-}RO_3)_4(H_2O)_2\}_2(\mu\text{-}O)_4]\cdot 3\,H_2O$, four layers of $[V_2V_6]_2$ octahedra	$V_2O_5 + C(CH_2OH)_4 + MCl + H_2O$, Δ, *P*	190
$[Li_8Ta_8O_{14}(OEt)_{20}(EtOH)_8]\cdot 4\,EtOH$	$[Li_8Ta_8H_8(\mu_4\text{-}O)_2(\mu_3\text{-}O)_8(\mu\text{-}O)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_{10}(OR)_{16}]\cdot 4\,ROH$	$LiTa_9O_{10}(OEt)_{20}(EtOH) + LiOEt$	173
$Ti_{17}O_{24}(OPr^i)_{20}$	Keggin-type structure, seventeenth Ti atom in the centre	$Ti(OPr^i)_4$ + AcOH	191
$[Ba_4Ti_{13}O_{18}(OC_2H_4OMe)_{24}]$	$[Ba_4Ti_{13}(\mu_5\text{-}O)_6(\mu_3\text{-}O)_{12}(\eta^2,\mu_3,\mu\text{-}OR)_{12}\,(\eta^1,\mu\text{-}OR)_{12}]$	$Ba(OR)_2 + Ti(OR)_4 + H_2O$ (h = 6)	192
$[Ti_{18}O_{28}(OBu^t)_{16}(Bu^tOH)]$	$[Ti_{18}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{20}(\mu\text{-}O)_4(OR)_{16}(ROH)]$	$Ti(OBu^t)_4 + H_2O$, 100 °C (h = 1.14)	193
$[Cu_{18}O_2(OSiMe_3)_{14}]$	$[Cu_{18}(\mu_4\text{-}O)_2(\mu\text{-}OR)_{14}]$; two intersecting $[Cu_9O_8]$ rings, μ_4-O in the centres	$CuOSiMe_3$, 80 °C, 10^{-3} mm Hg (−R_2O)	194
$Mn_{19}O_{12}(OR)_{14}(ROH)_{10}$, R = OC_2H_4OMe	$[Mn_{19}(\mu_3\text{-}O)_{12}(OR)_{14}(ROH)_{10}]$, CdI_2 structural type, layers of octahedra are linked *via* μ_3-O and μ_3-OR groups	$MnCl_2 + NaOC_2H_4OMe$	195
$[Ni_6Sb_{14}O_{18}(OEt)_{18}(EtOH)_2]$	–	$NiCl_2 + NaSb(OEt)_4$	147, 196
$M_7[Na(H_2O)_3Mo^V_{36}Mo^{VI}_6H_{15}O_{109}\cdot\{(OCH_2)_3CCH_2OH\}_7]$	framework of vertex- and edge-sharing Mo octahedra, the $[Na(H_2O)_3]$ group in the centre, RO_3 groups on the surface	$MoO_3 + Na_2MoO_4 + H_2O +$ $+ C(CH_2OH)_4 + Me_4NCl$, Δ, *P*	197
Polymeric linear chain			
$[Sr_2Sb_4O(OEt)_{14}]$	$[Sr_2Sb_4(\mu_4\text{-}O)(\mu\text{-}OR)_{14}]_\infty$ — a chain of alternating $[Sb(\mu\text{-}OR)_4]$ tetrahedra and $[Sr_2Sb_3(\mu_4\text{-}O)(\mu\text{-}OR)_{10}]$ groups, CN of Sb are 4, 5; CN of Sr is 7	$Sr(OEt)_2 + Sb(OEt)_3$	198

groups at all), the conditions of formation of the latter indicate that various decomposition processes can occur. In most cases, the appearance of oxo groups is associated with uncontrolled decomposition of alkoxides *in situ* in attempting to synthesise these compounds according to conventional methods.

Apparently, the most stable forms of OA exist in each system. For instance, single crystals of $Nb_8O_{10}(OEt)_{20}$ and $Ti_7O_4(OEt)_{20}$ prepared according to two procedures, *viz*., by the reactions of water with ethoxides or upon spontaneous decomposition, were demonstrated to be identical. For example, the $Nb_8O_{10}(OEt)_{20}$ compound was formed upon prolonged storage of liquid samples of $NbO(OEt)_3$ in tubes (the process is accompanied by elimination of Et_2O),[151] whereas $Ti_7O_4(OEt)_{20}$ was prepared by heating solutions of $Ti(OEt)_4$ in an autoclave to 100 °C,[142] *i.e*., in the complete absence of moisture.

Of special note is the synthesis of OA by alcoholysis of metal oxides or the synthesis of oxo metallates by exchange reactions with compounds which already contain oxo groups. Examples are the synthesis of $(MoO)_2O[(CMe_2)_2O_2]_2[O(CMe_2)_2OH]_2$ from MoO_3 and pinacol,[28,29] the formation of $[R_4N]_2\cdot[(MoO_2)_4O_2(OMe)_6]$ by methanolysis of metamolybdate $[Bu_4N]_4Mo_8O_{26}$,[78] the preparation of $[Bu_4N]_3[Nb_2W_4O_{18}(OR)]$ (R = Me, Et, Pr^i, Bu^t, $SiAlk_3$) by alcoholysis of the $[HNb_2W_4O_{19}]^{3-}$ heteropolyanion [118] and the hydrothermal synthesis of numerous hexa- and decanuclear molecular and anionic V(IV,V) and Mo(V,VI) complexes by reactions of metal oxides with MeOH and polyatomic alcohols.[113,115–117,169,170,197]

1. Hydrolysis

Pioneering X-ray diffraction studies of the structures of partial hydrolysis products of alkoxides marked the beginning of systematic studies of this reaction (which was generally monitored by ^{17}O, ^{1}H and ^{13}C NMR spectroscopy). Condensed titanium OA molecules were investigated by Day and co-workers,[42,143,183,193] Mosset and co-workers [142,189] and Sanchez and co-workers.[184,185,191] These molecules contain from three to eighteen metal atoms linked *via* polydentate oxo and alkoxy groups. Hydrolysis of alcoholic solutions at a $[H_2O]:[Ti(OEt)_4]$ ratio varying from 0.5 : 1 to 0.7 : 1 (h = 0.5–0.7) afforded crystals of $[Ti_{16}O_{16}(OEt)_{32}]$ [142,189] along with the above-mentioned $Ti_7O_4(OEt)_{20}$ [7,142] (see Fig. 1 *a*). Oxoisopropoxide $Ti_3O(OPr^i)_{10}$ is formed in solutions at h = 0.05–0.2. However, only the heteroleptic complex $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(OPr^i)_9]$ was isolated in the crystalline state.[42] The octanuclear $[Ti_8O_6(OEt)_{20}]$ molecules exist in an alcoholic solution, but only a derivative of benzyl alcohol with the $[Ti_8O_6]$ core, *viz*., the $[Ti_8O_6(OBn)_{20}]\cdot Et_2O$ complex, was prepared in the crystalline state.[143] The decanuclear $[Ti_{10}O_8(OEt)_{24}]\cdot PhMe$ complex was also prepared from toluene solutions of oxoethoxides. Hydrolysis of $Ti(OPr^i)_4$ in solutions at 100 °C (in an autoclave) afforded a mixture of two isomers with composition $[Ti_{12}O_{16}(OPr^i)_{16}]$. At 20 °C, the solution contains $[Ti_{11}O_{13}(OPr^i)_{18}]$, which crystallises in the presence of EtOH to form $[Ti_{11}O_{13}(OPr^i)_{13}(OEt)_5]$.[183] The largest molecule of this group, *viz*., $[Ti_{18}O_{28}(OBu^t)_{16}(Bu^tOH)]$, was prepared by hydrolysis of $Ti(OBu^t)_4$ (h = 1.14).[193] Condensation of $Ti(OPr^i)_4$ in the presence of acetic acid to form $[Ti_{12}O_{16}(OPr^i)_{16}]$ [183,184] results from the reaction with water (generated in the course of esterification of an excess acid) and alcohol eliminated upon the replacement of OR groups with OAc.

Hydrolysis also gave rise to $[Sn_3O(OBu^i)_{10}(Bu^iOH)_2]$,[40] $[U_3O(OBu^t)_{10}]$,[49] a series of bimetallic complexes, *viz*., $[BiTi_2O(OPr^i)_8]$,[41] $[LiTiO(OPr^i)_3]_4$,[158] $[K_4Zr_2O(OPr^i)_{10}]$,[107] $[Cu_4Zr_4O_3(OPr^i)_{18}]$,[156] $[MoTa_2O_4(OMe)_8]_2$,[133] *etc*. Among these compounds, the barium titanium oxo cellosolve molecule

$[Ba_4Ti_{13}O_{18}(OC_2H_4OMe)_{24}]$ (prepared at $h = 6$) [192] has the maximum size.

Recently, the following oxoalkoxides were synthesised by controlled hydrolysis in alcoholic solutions of aluminium and tantalum alkoxides:[33, 34, 53–55, 103, 152] the tetrahedral $[Al_4(\mu_4\text{-}O)(OR)_{10}(ROH)]$ complexes (R = Bu^i, $h = 0.25$; CF_3CH_2, $h = 0.5$), $Ta_5(\mu_3\text{-}O)_4(\mu\text{-}O)_3(OBu^t)_{11}$ ($h = 1.0$), $Ta_7(\mu_3\text{-}O)_3(\mu\text{-}O)_6(OPr^i)_{17}$ ($h = 0.55$) and $Ta_8(\mu_3\text{-}O)_2(\mu\text{-}O)_8.(OEt)_{20}$ ($h = 0.5-1.0$) with isopolyanion-type structures.

Controlled hydrolysis of aryloxoalkyl derivatives, in which water replaces alkoxy groups, while aryloxy groups remain intact, is also of interest.

$$M(OAr)_nR_m + H_2O \longrightarrow [M(OAr)_nO_{m/2}]_2 + ROH$$

Examples are the $[TiO(OC_6H_3Pr^i_2\text{-}2,6)_2(NC_5H_4\text{-}4\text{-}NC_4H_8)]_2$ (see Ref. 21) and $[NbO(OC_6H_3Pr^i_2\text{-}2,6)_3]_2$ complexes.[22]

2. Oxidation

Many oxo complexes were synthesised by controlled oxidation of alkoxides of metals in the lowest oxidation states. For example, oxoalkoxides $[M^{IV}_3O(OR)_{10}]$ (R = Pr^i, CH_2Bu^t), $[(Mo^VO)_4O_4(OPr^i)_4Py_4]$, $[Mo^{5.3+}_3O_5(OPr^i)_6]_2$, $[Mo^{VI}O_2(OBu^t)_2]$ and $W^{VI}_2O_3(OR)_6$ (R = Pr^i, Bu^t, CH_2Bu^t) were isolated from the reaction products of $M_2(OR)_6$ (M = Mo, W) with oxygen.[46, 47, 80, 199, 200] In the case of $W_2(OR)_6$, NO {in the synthesis of $[W^{IV}_2O(OBu^t)(OSiMe_2Bu^t)_5Py_2]$ [25]} or acetone {in the synthesis of $[W^{IV}_4O_2(OPr^i)_{12}]$ [88]} were used as oxidants.

Oxidation of bimetallic copper(I) alkoxides, *viz*., $Ba_2Cu_4(OR)_8$ and $Cu_2Zr_2(OR)_{10}$, with oxygen produced the oxo ligands $[Ba_4Cu^I_6O(OCEt_3)_{12}]$ and $[Cu^{II}_4Zr_4O_3(OPr^i)_{18}]$, respectively.[156, 161, 175] In the former compound, the oxidation state of copper remained unchanged.

The $MoO_2(OEt)_4$, $WO(OR)_4$ and $NbO(OR)_3$ compounds (R = Me, Et, Bu^n) were prepared by passing dry air through coloured alcoholic solutions of electrolytes, which are anodic oxidation products of molybdenum, tungsten or niobium (which were subjected to partial reduction on the cathode).[136, 201, 202]

Uncontrolled oxidation with oxygen traces present in the gaseous phase or solvents is typical of alkali or alkaline-earth metal alkoxides. The primary reaction products contain peroxide groups OOR or OOH.[203] Decomposition of the latter by a radical mechanism results in the appearance of water molecules, as well as oxo and carboxy groups, in the coordination environment of the metal atom. This process is accompanied by the appearance of a yellow-brown colour, whose intensity sharply increases upon storage of samples or refluxing of their alcoholic solutions. For example, refluxing (in particular, in the course of dehydration of EtOH) of yellow alcoholic solutions of $Ca(OEt)_2$ over a long period of time afforded crystals of the oxo complex $Ca_6O_2(OEt)_8 \cdot 14\,EtOH$ (see Fig. 2 *b*).[16] Apparently, this colour is attributable to the presence of radicals, which was confirmed by ESR spectroscopy of coloured $Ba(OR)_2$ samples. The IR spectra of such products show the following new bands (regardless of the nature of the starting radical): ν(OH) band of ethanol molecules coordinated to OA and ν(COO) and δ(OCO) bands of the formate group generated from peroxides upon their decomposition. The tendency of alkoxides to oxidation increases in the series Li ≪ Cs, Mg ≪ Ba and Et < Bu^n ≪ Pr^i ≪ C_2H_4OMe,[204] which corresponds to the rate of formation of radicals (the rate was determined by ESR spectroscopy, in particular, for LiOR).[205]

Samples of M^IOAlk or $M^{II}(OAlk)_2$, which were prepared by the reactions of metals with a stoichiometric amount of alcohol in a hydrocarbon medium, appeared to be much more resistant to oxidation compared to those synthesised in alcoholic solutions or prepared by desolvation of $M(OR)_n \cdot x\,ROH$. Oxidation of the alkoxides in their synthesis in a hydrocarbon medium is, apparently, hindered by precipitation of the unsolvated $M(OR)_n$ compounds and insolubility of O_2 in hydrocarbons (as opposed to alcohols). Uncontrolled microhydrolysis is favourable for oxidation due, apparently, to the appearance of free alcohol in samples.[3]

An interesting procedure for the synthesis of OA is based on the addition of ketones to certain molecules, in particular, to $Ti(OR)_4$ ('oxolation') giving rise to large cluster molecules.[185]

3. Decomposition (thermolysis and elimination of ethers)

At rather high temperatures, volatile thermolysis products of alkoxides can contain alcohols, ethers, aldehydes, saturated and unsaturated hydrocarbons, *etc*. The structures of crystalline products provide evidence for condensation attendant on this process. For instance, refluxing of $Al(OEt)_3$ under a benzene layer for several days leads to thermal destruction of the polymeric molecules to give products which go into solution, resulting in crystallisation of $[Al_{10}O_4(OEt)_{22}]$ in low yield.[17] The hydrocarbon-soluble 'α form of aluminium ethoxide' (which is, in reality, OA) was synthesised (according to the Meerwein method) by the reaction of the metal with a stoichiometric amount of alcohol in a xylene solution at 140 °C; in this case decomposition of $Al(OEt)_3$ occurs already *in situ*.[206]

The $[Al_8O_2(OH)_2(OBu^i)_{18}]$ [53] and $[Fe_9O_3(OEt)_{21}] \cdot EtOH$ [167] complexes crystallise from vacuum distillation products of the lower-nuclearity oxo complexes $Al_4O(OBu^i)_{10}$ and $Fe_5O(OEt)_{13}$. Copper oxosilane oxide $[Cu_{18}O_2(OSiMe_3)_{14}]$ was prepared by distillation of $CuOSiMe_3$ [the formation of $(Me_3Si)_2O$ was established].[194] Evidently, the process is accompanied by destruction followed by condensation of the resulting fragments. Decomposition of $W_4(OPr^i)_{10}$ to $[W^{III}_4O_2(OPr^i)_8]_2$ occurs with elimination of propane.[164] Thermolysis of bimetallic isopropoxide $KSb(OPr^i)_4$ afforded crystalline $[K_2Sb_2O(OPr^i)_6]_2$ and Pr^i_2O. Refluxing of toluene solutions of $KM^{III}(OBu^t)_4$ (M^{III} = Sb, Bi) over a long period of time resulted in elimination of isobutylene and afforded the oxo complexes $[K_4M^{III}_2O(OBu^t)_8]$. It should be noted that Na-containing compounds with the same composition are generated already in the step of the reaction of $NaOBu^t$ with $M^{III}(OBu^t)_3$.[109]

If decomposition of alkoxides occurs at rather low temperatures, the reaction gives ethers as the major products. For instance, thermolysis of methoxides $Al(OMe)_3$, $Pb(OMe)_2$ and $NaAl(OMe)_4$ (at ~120 °C) afforded dimethyl ether as the only gaseous product.[206–208] Heating of an alcoholic solution of $Ti(OEt)_4$ in an autoclave at 100 °C led to crystallisation of $Ti_{16}O_{16}(OEt)_{32}$ and elimination of Et_2O.[142, 190]

Condensation with elimination of ethers

$$M-OR + RO-M \longrightarrow M-O-M + R_2O$$

proved to be one of the main pathways of spontaneous decomposition of alkoxides. The formation of oxo bridges is, undoubtedly, thermodynamically favourable and, in the case under consideration, is analogous to ageing of oxide hydrates accompanied by condensation of two hydroxy groups with elimination of a water molecule. This type of reaction was first described by Bradley and co-workers,[209] who prepared oxo complexes by transesterification of niobium ethoxide with *tert*-butyl alcohol

$$Nb(OEt)_5 + Bu^tOH \longrightarrow$$
$$\longrightarrow NbO(OBu^t)_3 + Nb_2O(OBu^t)_8 + Bu^t_2O + EtOH.$$

The proposed mechanism involves the heterolytic cleavage of the O–R bond followed by the attack of the resulting carbocation on the M–O bond of another OR group. Ethers (like other volatile decomposition products, for example, unsaturated hydrocarbons) are not always detectable against the background of alcohols.[14]

Evidently, the size ratio of the metal atom and the substituent (as well as the degree of branching of the latter) is an essential factor responsible for the resistance of ortho derivatives to decomposition. As an example, let us consider iron(III) alkoxides. In the known structures of alkoxides {except for $[Fe(OMe)_3 \cdot MeOH]_\infty$ and unstable $[Fe(OEt)_3]_\infty$}, the coordina-

tion environment of Fe atoms always involves oxo groups.[15, 129, 149, 172] However, in the presence of the $CHBu^t_2$, C_6HMe_4-2,3,4,6, $SiMe_3$ (see Ref. 3) or CMe_2Ph [15] substituents, the reactions afford stable structures of alkoxides of the ortho series containing tetrahedrally coordinated metal atoms. Of aluminium derivatives (the atomic radius of aluminium is substantially smaller than that of iron), polymeric alkoxides $Al(OR)_3$ (R = Me, Et) with a layered structure consisting of $[AlO_6]$ octahedra [isostructural with the corresponding $Fe(OR)_3$] appear to be quite stable. The same is true for the crystalline $[Al(OPr^i)_3]_4$ compounds (Al has coordination numbers of 4 and 6) and $[Al(OBu^t)_3]_2$ (containing tetrahedrally coordinated metal atoms). Analogous iron homologues do not crystallise at all and, according to the IR spectroscopic data, contain oxo groups.[3]

Apparently, this type of decomposition is the main pathway in various synthesis reactions of alkoxides resulting in the 'unexplainable' formation of oxo complexes. This decomposition is particularly characteristic of derivatives containing large Ba, Ln, Zr, Mo, W and U atoms. It should be emphasised that their lighter analogues form alkoxides of the ortho series under comparable conditions.

For instance, barium compounds virtually always contain oxo groups even in the presence of large ligands. Examples are $[Ba_5(\mu_5\text{-}O)(OPh)_8(PhOH)(THF)_8]$ [89] and $[Ba_6(\mu_6\text{-}O)(OR)_{10}\cdot(ROH)_4]$ (R = C_2H_4OMe).[105] The Ba atoms in these molecules have coordination numbers from 7 to 9. Analogous Sr or Ca derivatives, *viz*., $[Sr_4(OPh)_8(PhOH)_2(THF)_6]$ [210] and $Ca_9(OR)_{18}\cdot 2\,ROH$,[211] belong to the ortho series. In the latter compounds, the metal atoms are octahedrally coordinated (only in the calcium cellosolve, the peripheral Ca atoms have a coordination number of 7). Even the reaction of barium metal with phenol in the presence of orthophenoxide $[Sr(OPh)_2]_3\cdot 5\,OP(NMe_2)_3$ affords the bimetallic oxo complex $[Ba_2Sr_6(\mu_5\text{-}O)_2(OPh)_{12}(PhOH)_2\cdot\{OP(NMe_2)_3\}_6]$.[162] An increase in the size of metal atoms in going from Sr to Ba leads to an increase in the coordination number. Evidently, stable polyhedra are formed only if one oxo group is involved in the coordination environment of the metal atoms along with large ligands.

The appearance of oxo groups in these compounds is not associated with uncontrolled hydrolysis or oxidation. This is evidenced by high yields of products and good reproducibility of experiments which were carried out by different research groups under various conditions. The corresponding ortho forms $Ba(OAr)_2$ can be prepared only upon their stabilisation by chelation with crown ethers or amino alcohols or after the introduction of one more substituent into the phenoxy group in the *para* position with respect to the OH group.[91, 212–214]

The formation of oxo groups upon coordination of 'small' ligands to the Ba atom can be exemplified by barium alkoxotitanates. The most stable complexes in the $Ba(OR)_2$–$Ti(OR)_4$–ROH systems have the composition $Ba[Ti_2(OR)_9]_2$ (R = Et, Pr^i, Bu^n). In these complexes, the central Ba atom has a coordination number of 8.[215, 216] However, the use of a system consisting of methoxides leads to the formation of the $[Ba_2Ti_4(\mu_3\text{-}O)(OMe)_{18}\cdot(MeOH)_7]\cdot MeOH$ complex,[131] in which the coordination number of Ba increases to 9 due to additional coordination of one oxo group (Fig. 3). Evidently, eight 'small' OMe groups are inadequate to provide a stable polyhedron of the Ba atom, but only an oxygen atom can be coordinated instead of the ninth alkoxy group for steric reasons, resulting in elimination of an ether molecule. It should be emphasised that in all the molecules under consideration, the coordination environment of the metal atom involves only one oxo group.

An analogous situation is observed in the structures of rare-earth metal alkoxides, which can be exemplified by methyl cellosolves (R = C_2H_4OMe). Cerium-group metals form seven- and eight-vertex polyhedra involving oxo atoms: $[Pr_4(\mu_4\text{-}O)_2\cdot(OR)_8(OPMe_3)]_2$ (see Ref. 150) and $[Gd_6(\mu_4\text{-}O)(OR)_{16}]$.[130] By contrast, derivatives of yttrium-group metals $[M(OR)_3]_{10}$ (M = Y, Dy) contain no oxo ligands and occur as planar decanuclear rings with seven-coordinate metal atoms.[217, 218]

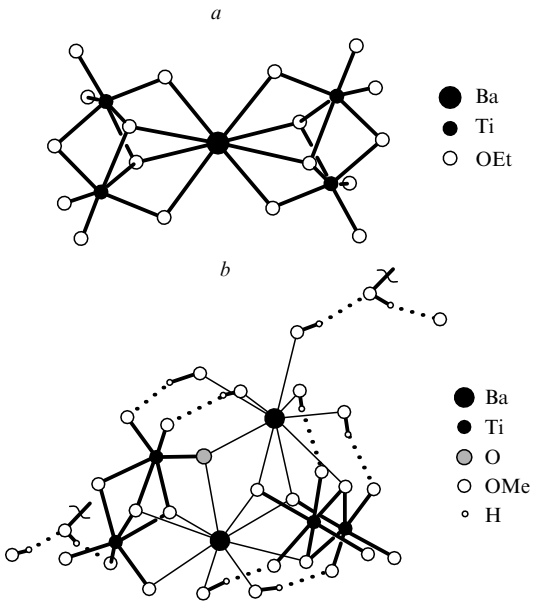


Figure 3. Metal–oxygen cores in the structures of $Ba[Ti_2(OR)_9]_2$ (*a*) [216] and $[Ba_2Ti_4(\mu_3\text{-}O)(OMe)_{18}(MeOH)_7]\cdot MeOH$ (*b*).[131]

Desolvation of the solvates $Ln(OR)_n\cdot m\,L$ (L = ROH, THF) is always attended by the formation of oxo groups. In certain cases, elimination of the corresponding ethers was observed.

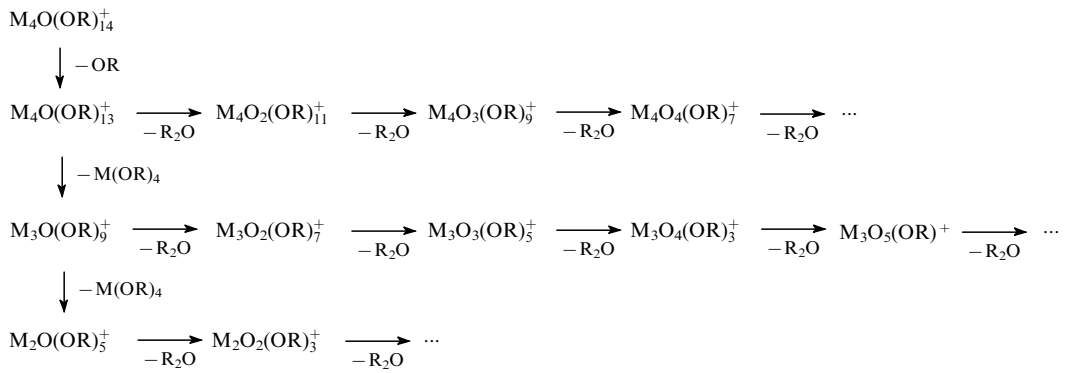
Solvate	Reaction conditions	Reaction product	Ref.
$[La_3(OBu^t)_9L_2]$, L = Bu^tOH, THF	PhMe, Δ	$La_5O(OBu^t)_{13}$	219
$[Nd(OPr^i)_3(Pr^iOH)]_4$	25 °C, vacuum	$Nd_6O_5(OR)_8$	220
$[Ce(OBu^t)_4(THF)_2]$	20 °C, 72 h	$Ce_3O(OBu^t)_{10}$	221
$[Ce(OPr^i)_4(Pr^iOH)]_2$	70 °C, 10^{-3} mm Hg	$Ce_4O(OPr^i)_{14}$	57

The extremely unstable praseodymium solvate $Pr_3(OPr^i)_9\cdot(Pr^iOH)_2$ decomposes to $Pr_5O(OPr^i)_{13}$ already at low temperatures (in the course of drying).[92] Taking into account that the ortho forms $Ln(OAlk)_n$ (n = 3, 4) exist only as solvates with alcohols, THF or Py, it can be hypothesised that the widely occurring form of oxoalkoxides $Ln_5O(OR)_{13}$ (R = Pr^i, Bu^t) is generated as a result of desolvation of unstable solvates. Transesterification of the solvate $[Ce(OPr^i)_4(Pr^iOH)]_2$ with pinacol giving rise to $Ce_2O[O(CMe_2)_2O]_2[O(CMe_2)_2OH]_2$ (see Ref. 75) can also be assigned to this type of reaction.

Decomposition with elimination of ethers (detected) is very typical of lead and bismuth alkoxides. For example, polymeric $Pb(OPr^i)_2$ readily undergoes oligomerisation to form $Pb_4O\cdot(OPr^i)_6$, $Pb_6O_4(OPr^i)_4$ and $Pb_7O_2(OPr^i)_{10}$.[127, 144, 222, 223] In this connection, the complex formation of these compounds with other alkoxides is generally accompanied by the formation of the oxo complexes $[Pb_2Ti_2O(OPr^i)_{10}]$,[60] $[Pb_3Zr(\mu\text{-}O)(OBu^t)_8]$ [62] and $[Pb_6Nb_4(\mu_4\text{-}O)_4(OEt)_{24}]$ [178] [for Sn(II) alkoxides, only oxomethoxide, which was prepared by hydrolysis, is known [123]].

In various synthesis reactions and subsequent transformations, bismuth alkoxides also give oxo complexes. The exchange reactions of $BiCl_3$ with alkali metal alkoxides produce $[NaBi_4O_2(OC_6F_5)_9(THF)_2]$, $[Na_2Bi_4O_2(OC_6F_5)_{10}(THF)_2]$, $[NaBi_3O(OC_6F_5)_8(THF)]$ and $[Bi_6O_3(OC_6F_5)_{12}(THF)_2]$.[64] The complex formation of bismuth and sodium alkoxides affords $[Na_4Bi_2O(OBu^t)_8]$ [109] and $[Na_4Bi_2O(OC_6F_5)_8(THF)_4]$.[111] Alco-

Scheme 1



M = Zr, Hf; R = Et, Pr^i, Bu^n, Bu^i, Bu^t.

holysis of $BiPh_3$ or $Bi[N(SiMe_2)_2]_3$ is accompanied by the formation of $[Bi_6O_3(OC_6H_3Cl_2\text{-}2,6)_{12}]$[132] and $[Bi_4O_2(OBu^t)_8]$.[73] Transsolvation of $[Bi(OC_6F_5)_3(C_6H_6)]_2$ with tetrahydrofuran gives $[Bi_9O_7(OC_6F_5)_{13}(THF)_2]$.[166] Even hydrolysis of $Bi(OEt)_3$ in benzene occurs with elimination of ether.[224] Due to the high sensitivity of bismuth derivatives to moisture traces, the results of the synthesis of particular compounds depend on the origin of the starting reagents. For example, the reaction of $BiCl_3$ with $NaOC_6F_5$ in phenol purchased from Aldrich affords $[NaBi_3O(OC_6F_5)_8(THF)]$, whereas the reaction with the use of phenol purchased from Strem gives rise to $[NaBi_4O_2(OC_6F_5)_9(THF)_2]$ and $[Na_2Bi_4O_2(OC_6F_5)_{10}]$, which are products of deeper decomposition.[64]

Unexpectedly, it was found that zirconium and hafnium 'isopropoxides' (commercial reagents) prepared by desolvation of $[M(OPr^i)_4 \cdot Pr^iOH]_2$ contain several types of oxo complexes [for example, $M_3O(OR)_{10}$ and $M_4O(OR)_{14}$]. These samples also contain impurities of the undecomposed starting solvates. Hence, their empirical composition corresponds to the formula '$M(OR)_4$'. The presence of oxo complexes was detected by ^1H NMR spectroscopy and mass spectrometry of the $M(OR)_4 \cdot ROH$ compounds, in which fragmentation of all oligomers is attended by elimination of ether (Scheme 1).[225]

Crystals of $Zr_3O(OBu^t)_{10}$ and $[Hf_3O(OEt)_{10}(EtOH)]_2$ were grown by allowing electrolytes, which were prepared by anodic dissolution of metals in the corresponding alcohols,[45] to stand for a long period of time (Fig. 4).

Recently, the crystalline ortho form $[Zr(OPr^n)_4]_4$ has been isolated from commercial reagents containing primarily $Zr_3O(OPr^n)_{10}$ by vacuum distillation with unprecedented protection against moisture[226] [it should be noted that alkoxides $Ti(OAlk)_4$, unlike Zr and Hf derivatives, are quite stable]. In the study,[226] it was hypothesised that the formation of numerous oxoalkoxides $Ln_5O(OPr^i)_{13}$ is also associated with extremely high hygroscopicity of the corresponding ortho forms.

Condensation with elimination of ether is very typical also of rhenium,[227] molybdenum and, to a somewhat lesser extent, tungsten alkoxides. Of compounds belonging to the $Mo(OR)_6$ series, only highly unstable methoxide was isolated.[228–230] All oxoalkoxides $MoO(OR)_4$ are very prone to decomposition both in the free state and solutions to form polymeric compounds $MoO_2(OR)_2$ and ethers R_2O.[231] Numerous attempts to synthesise $W(OBu^t)_6$ led only to the formation of $WO(OBu^t)_4$, Bu^t_2O being detected among the reaction products.[232–234] Storage of the oily $MoO(OPr^i)_4$ compounds over a long period of time afforded crystalline $[Mo_3^{5,3+}O_5(OPr^i)_6]_2$ and Pr^i_2O (along with alcohol and acetone) as a result of a redox reaction.[141]

To summarise, it can be hypothesised that this type of decomposition is associated with the fact that metal atoms, which are coordinated only by alkoxy ligands and have no space for a new OR group, are coordinatively unsaturated. Hence, stable polyhedra are formed only in the presence of 'small' ligands, *viz*., an oxo group or solvate molecules (THF, ROH, MeCN, Py, *etc*.), in the coordination environment.

Decomposition of bimetallic alkoxides to oxo alkoxo metallates $M_mM'_nO_p(OR)_q$ containing heterometallic M–O–M′ bridges is of most importance among the reactions under consideration. Many complexes of this type are formed as a result of complexation of two alkoxides (*i.e*., decomposition occurs *in statu nascendi*). Attempts to isolate compounds devoid of oxo groups failed.

In most cases, alkali or alkaline-earth metal alkoxide is involved as one of the components. Examples are $[Li(MgTHF)_4O(\mu\text{-}OC_6H_4Me\text{-}2)_7]$,[98] $[LiTiO(OPr^i)_3]_4$,[158] $Sr(Pr^iOH)_2[Ti_2O(OPr^i)_7]_2$,[102] $[Sr_6Ti_4O_4(OPr^i)_{20}]$,[102] $[Na_2Zr_3O.(OEt)_{12}]_2$,[44] $[M_4Sb_2O(OBu^t)_8] \cdot n\,THF$[109] (M = Na, K; n = 0, 1, 4), $[Na_4Bi_2O(OBu^t)_8]$,[109] $[MgNbO(OMe)_5(MeOH)_2]_2$,[76] $[LiTa_9O_{10}(OEt)_{20}(EtOH)]$[173] and $Na_4[Mo_8O_{24}(OMe)_4] \cdot 8\,MeOH$.[153] However, processes are known where decomposition attends the complex formation of alkoxides of two transition metals, for instance, $[La_2(MoO)_4O_4(OPr^i)_{14}]$,[128] $[Zr_3Mo_8O_{24}.(OPr^i)_{12}(Pr^iOH)_4]$[182] (in these two cases, elimination of ether was observed), $[TaMo^V_2O_4(OPr^i)_7]_2$,[104] $[Er_2Ti_4O_2(OEt)_{18}.(EtOH)_2]$[140] and $[Cu_4Zr_4O(OPr^i)_{18}]$.[156]

The reactions of Ba and Nb (or Ta) ethoxides give rise to crystals of $[BaM^VO(OEt)_5(EtOH)_n]_4$ (M = Nb, Ta), although bimetallic complexes with composition $BaM^V_2(OEt)_{12}$ exist in freshly prepared solutions. By contrast, isopropoxides $[BaM^V_2(OPr^i)_{12}(Pr^iOH)_2]$ are not prone to decomposition and exist in the crystalline state.[85,160,235] The compound $[Ba_4Ti_4O_4(OPr^i)_{16}(Pr^iOH)_4]$ slowly crystallises from solutions of barium and titanium isopropoxides in isopropyl alcohol[159] [as mentioned above, the complexes in all solutions have the composition $BaTi_4(OR)_{18}$ (see Ref. 215)].

The influence of the nature of the substituent (steric factors) is observed, in particular, in the complexation of titanium and thallium(I) alkoxides. The reaction of two ethoxides and isopropoxides affords the octahedral $[Tl_4Ti_2O(OR)_{10}]$ molecules. However, even the partial introduction of OCH_2Bu^t groups gives rise to the ortho forms $TlTi_2(OR)_5(OCH_2Bu^t)_4$ (R = Et, Pr^i).[122]

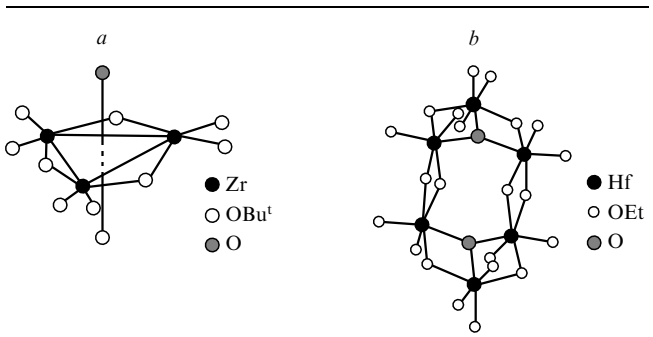


Figure 4. Metal–oxygen cores in the structures of $Zr_3O(OBu^t)_{10}$ (*a*) and $[Hf_3O(OEt)_{10}(EtOH)]_2$ (*b*).[45]

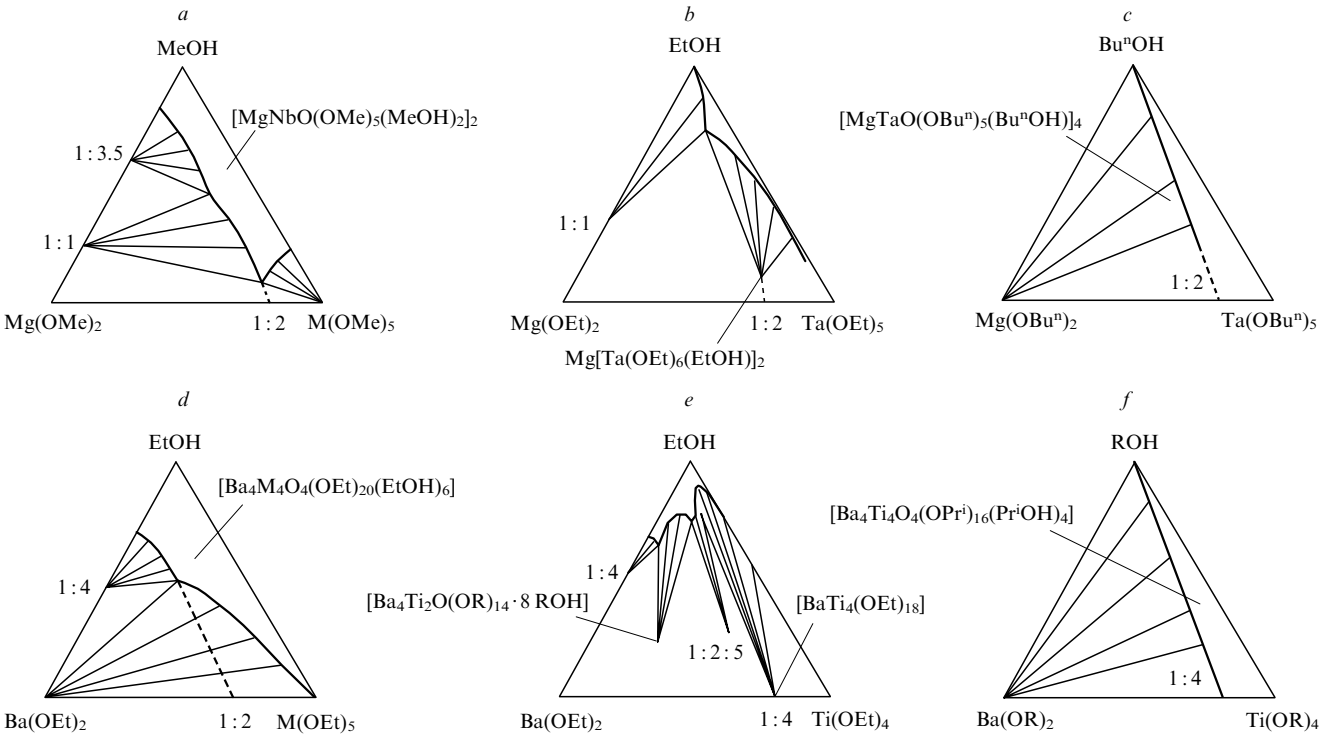


Figure 5. Solubility (20 °C) and the formation of bimetallic oxo complexes [76, 85, 159, 160] in the $Mg(OMe)_2-M(OMe)_5-MeOH$ (M = Nb, Ta) (*a*), $Mg(OEt)_2-Ta(OEt)_5-EtOH$ (*b*), $Mg(OBu^n)_2-Ta(OBu^n)_5-Bu^nOH$ (*c*), $Ba(OEt)_2-M(OEt)_5-EtOH$ (M = Nb, Ta) (*d*),[85, 235] $Ba(OEt)_2-Ti(OEt)_4-EtOH$ (*e*) and $Ba(OR)_2-Ti(OR)_4-ROH$ ($R = Pr^i$, Bu^n) (*f*)[215] systems.

Attempts to reveal a particular dependence of the decomposition pathway on the nature of metals and substituents failed. However, a comparison of the results of physicochemical analysis of the $M(OR)_m-M'(OR)_n-ROH$ systems (Fig. 5) with the results of structural studies of bimetallic oxo complexes demonstrated that crystallisation of OA occurs in systems (or concentration regions) where these compounds are least soluble. In these cases, $M_mM'_n(OR)_p$ are readily soluble or uncrystallisable products.

Molybdenum and tungsten derivatives are particularly prone to decomposition in the presence of alkali metal alkoxides. Judging from conductometric titration curves, the first step of the reactions of $MoO(OR)_4$ with NaOR in alcoholic solutions affords the addition products $NaMoO(OR)_5$ ($R = Et$, Pr^i). However, $[NaMo_2O_4(OR)_5(ROH)]_2$ [compounds of the $MoO_2(OR)_2$ series] crystallise from these solutions even if the reagents are present in a ratio $Na : Mo \leqslant 1 : 2$. In the presence of an excess of NaOR (compared to 1 : 2), the formation of Na_2MoO_4 is observed, and the crystallisation rate of this compound sharply increases with increasing concentration of NaOR. The process occurs with elimination of ether (which was detected chromatographically).[137, 138] Analogous results were obtained in the reactions of M^IOR with $WO(OR)_4$ or $WO_2(OR)_2$, but the rates of these reactions are substantially lower than that observed for $MoO(OR)_4$.[137]

The formation of oxo complexes [along with $M(OR)_n$ or instead of them] in the electrochemical synthesis of alkoxides is, apparently, attributable to decomposition of $M(OR)_n$ in the cathode compartment (presumably, due to local warming). Examples are the syntheses of $[M_5O(OPr^i)_{13}]$ (M = Sc, Y, La),[11, 93] $[Pb_6O_4(OPr^i)_4]$,[127] $[Hf_3O(OEt)_{10}(EtOH)]_2$,[45] $Ta_2O(OPr^i)_8 \cdot (Pr^iOH)$,[33, 34] $[LiTa_9O_{10}(OEt)_{20}(EtOH)]$,[173] a series of rhenium alkoxides $\{[Re_2^V(OMe)_8]_2O_2$,[71] $[Re_4^{VI}O_6(OMe)_{12}]$[72] and $[Re_4^{V,VI}O_6(OPr^i)_{10}]\}$[84] and numerous methyl cellosolves.[236]

Apparently, the above-described type of decomposition has a rather general character. For example, the synthesis of silane oxides $M(OSiMe_3)_2$ (M = Hg, Pb) by transesterification of $M(OR)_n$, alcoholysis of MCp_n or metathesis of $Pb[N(SiMe_3)_2]_2$ with Bu^tNCO is complicated by the formation of the oxo derivatives $Pb_4O(OSiPh_3)_6 \cdot PhH$,[59] $[Pb_7O_2(OSiMe_3)_{10}]$[145] and HgO[237] [with elimination of $(R_3Si)_2O$].

Heteroleptic complexes, in particular, alkoxo carboxylates, are even more prone to this type of decomposition[238, 239] than homoleptic alkoxides.

$$Sn(OR)_4 + Cd(OAc)_2 \longrightarrow$$
$$\longrightarrow Cd_4Sn_4O_2(OR)_{10}(OAc)_{10} + AcOR$$

$R = CH_2Bu^t$.

Since such complexes readily eliminate ester, they were proposed as precursors in the synthesis of complex oxides from the gaseous phase (CVD method):[240]

$$MM'_nO_x(OR)_y(R'COO)_z \longrightarrow MM'_nO_m + R'COOR.$$

Other examples of processes where the appearance of oxo groups cannot be related to the above-mentioned decomposition pathways of alkoxides, can be cited. In particular, transesterification of $Nb(OR)_5$ with pinacol affords $[Nb_3O_2\{O(CMe_2)_2O\}_5 \cdot \{O(CMe_2)_2OH\}]$ and $[Nb_4O_4\{\eta^2,\mu\text{-}O(CMe_2)_2O\}_2(OPr^i)_8]$.[52] By contrast, transesterification with ethylene glycol and methyl cellosolve gave rise to niobium compounds belonging to the ortho series.[241]

The formation of $[Al_4O(OBu^i)_{10}(Bu^iOH)]$,[53] $[Al_{10}O_6(OPr^i)_{18}NH_3]$[176] and $[K(18\text{-}C\text{-}6)_2]^+[Mo_4O(OCH_2 \cdot Bu^t)_{11}]^-$ (see Ref. 69) in the reactions with bases, such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), NH_3 or KOH, may be associated with elimination of β-hydrogen atoms in radicals attended by elimination of alkenes.

Alcoholysis of chlorides, *viz.*, Lewis acids, can be accompanied by side reactions giving rise to HCl and water, which are responsible for the appearance of oxo groups {for example, in the $[Nb_2Cl_4(OEt)_2(THF)_2]_2O_2$ (see Ref. 70) and $[Th_4O \cdot \{(OC_2H_4)_4O\}_3Cl_8] \cdot 3MeCN$[63] molecules}. Presumably, the

same is also true for the formation of oxo complexes in numerous exchange reactions of chlorides in alcoholic solutions, where alcoholysis of MCl_n cannot be suppressed. Examples are the syntheses of $[IZnTa_2O_2(OPr^i)_7]_2$ [by the reaction of ZnI_2 with $KTa(OR)_6$],[134] $[Ti_3OCl(OCH_2Bu^t)_9]$ (from $TiCl_4$ and NaOR)[43] and $[Al_4O(OPr^i)_6Cl_4(Pr^iOH)]$ [from $AlCl_3$ and $Al(OR)_3$].[18]

Unfortunately, by-products of decomposition accompanied by the formation of OA have been thoroughly examined only in a few studies. The question about the relation between individual reactions is very complicated, particularly because oxidation and elimination of ethers are catalysed by water traces.

III. Properties of oxoalkoxides

Oxo complexes differ from alkoxides of the ortho series primarily in that the former compounds are not necessarily soluble in alcohols and hydrocarbons and they are much more prone to crystallisation. Numerous examples are known, where insoluble polymeric $M(OR)_n$ compounds undergo oligomerisation due to uncontrolled hydrolysis or oxidation. Solubility of these compounds sharply increases in alcohols and non-polar organic solvents. For instance, the replacement of OR groups in polymeric $Ba(OBu^n)_2$ up to the composition $BaO_{0.05}(OBu^n)_{1.9}$ leads to an increase in solubility in alcohols from 0% to ~40%.[204]

Crystalline oxo complexes go into an alcoholic solution only upon weak warming (or after mechanical grinding under an alcoholic layer). Cooling of such solutions generally leads to very slow crystallisation of $MO_m(OR)_n$ (even in the presence of a bottom phase), and crystals never precipitate in quantitative yields. Vacuum distillation of the mother liquor usually gives rise to a non-crystalline substance, which is compositionally different from crystals. In no case were the equilibrium values attained in the determination of the solubility of oxo complexes in alcohols. Polytherms measured on heating and cooling of solutions show a hysteresis.[151] The only exception is $Ta_2O(OPr^i)_8 \cdot Pr^iOH$, whose binuclear molecules apparently exist in an alcoholic solution.[33,34] These facts indicate that oxo complexes undergo solvolytic decomposition when going into solution to form fragments with different compositions and structures, and these fragments are involved in complex poly(oligo)merisation processes.

Certain information on the structures of fragments existing in the gaseous phase or alcoholic solutions can be obtained by their 'reconstruction' from the crystal structures of polynuclear complexes. For example, fragments of tetra-, penta- and hexanuclear oxo complexes can readily be distinguished in the $Al_{10}O_4(OEt)_{22}$ molecule (see Fig. 2 *c*).[17] These fragments were detected by mass spectrometry. The average degree of association [with respect to monomeric $Al(OR)_3$] is ~4.4. It should be noted that this value was obtained from the results of both mass spectrometry and cryoscopy in benzene, from which the decanuclear complex crystallises.[242] Analogously, the structures of molecules in amorphous $[NbO(OEt)_3]_n$ samples can be reconstructed from the data on the crystal structure of $Nb_8O_{10}(OEt)_{20}$ (see Fig. 1 *b*).[151]

The possibility of crystallisation of alkoxides of the ortho series from solutions containing oxo complexes is yet another consequence of the presence of particles with different compositions (including particles containing no oxo groups) in solutions of OA. For example, the starting solvate crystallises in low yield from an alcoholic solution of desolvation products of $[Zr(OPr^i)_4 \cdot Pr^iOH]_2$ containing, as mentioned above, $Zr_3O(OR)_{10}$ and $Zr_4O(OR)_{14}$.[225] Bimetallic alkoxides $ZrAl_2(OPr^i)_{10}$ and $LaNb_2(OPr^i)_{10}$ were prepared from solutions of the $Al(OPr^i)_3 - ZrO_n(OPr^i)_{4-2/n} - Pr^iOH$[243] or $Nb(OPr^i)_5 - La_5O(OPr^i)_{13} - Pr^iOH$ systems,[85] respectively, because they are apparently the least soluble of all the components and complexes present in these systems. In the presence of $Ti(OEt)_4$ or $Nb(OEt)_5$ (which add oxo groups), polymeric $Fe(OEt)_3$ precipitates from a solution containing iron oxoethoxide.[244]

Since oxoalkoxides undergo thermal destruction on heating, they are not, as a rule, transformed into the gaseous state. In some cases, mass spectra show low-intensity ions corresponding to fragmentation of the most stable molecules, for example, $[Ln_5O(OPr^i)_{13}]$[93,11,245] and $[Al_{10}O_4(OEt)_{22}]$.[17] The $[Na_4M_2O.(OBu^t)_8]$ complexes (M = Bi or Sb) sublime without decomposition at 180 and 120 °C (10^{-2} mm Hg), respectively.[109] In many cases, heating is accompanied by disproportionation of OA to form volatile $M(OR)_n$ and polymeric products containing a larger number of oxo groups per metal atom. This is the reason why $Ta(OPr^i)_5$ can be prepared by sublimation from the product of electrochemical synthesis $[Ta_2O(OPr^i)_8(Pr^iOH)]$[33] or by distillation of $Nb(OEt)_5$ from $[Nb_8O_{10}(OEt)_{20}]$.[151]

In conclusion, it should be noted that the reactivity increases substantially in going from alkoxides to oxo complexes. In many cases, high stability of one or both orthoalkoxides hinders their complexation. The replacement of inactive $M(OR)_n$ with the corresponding oxo complex substantially increases the reaction rate. For example, the reaction of $Ti(OPr^i)_4$ with partial hydrolysis products of polymeric $Pb(OPr^i)_2$ or $Bi(OPr^i)_3$ instead of these compounds as such proceeds rapidly at 20 °C to give $[Pb_2Ti_2O(OPr^i)_{10}]$[60] and $[BiTi_2O(OPr)_9]$, respectively.[41] Polymeric $Ba(OBu^n)_2$ reacts with alcoholic solutions of $Ta(OBu^n)_5$ only in the presence of traces of uncontrolled oxidation products to form highly soluble bimetallic oxo complexes. This allows one to prepare solutions of these two butoxides with different concentrations and any component ratio.[232] Under the same conditions, the reaction with $Ti(OBu^n)_4$ affords solutions with a ratio $Ba : Ti \gg 1 : 4$ (Fig. 5 *f*).[204] Zirconium, hafnium or tantalum isopropoxides react with $Al(OPr^i)_3$ only upon prolonged refluxing of alcoholic solutions, which is apparently accompanied by the appearance of OA particles.[243,246] Presumably, preliminary activation is not needed in reactions with M^IOR or $M^{II}(OR)_2$ due to the virtually unavoidable presence of microamounts of oxo groups in the samples.

IV. Structural types of oxoalkoxides

Since oxoalkoxides have various structures, it is convenient to consider these compounds in order of increasing nuclearity in their oligomeric molecules.

1. Binuclear OA

Binuclear oxoalkoxides (see Table 1) are represented by molecules consisting of two tetrahedra {$[(OsO)O(OCMe_2CH_2NHBu^t)]_2$,[19] $[Nd_2O(OCH_2Bu^t)_4]$[20]}, two five-vertex polyhedra, *viz*., trigonal bipyramids and tetragonal pyramids sharing a $(\mu\text{-O})_2$ edge {for example, $[Nb(\mu\text{-O})(OC_6H_3Pr^i_2\text{-}2,6)_3]_2$ (see Ref. 22)}, two octahedra sharing a μ-O vertex $[(MoO)_2O[O(CMe_2)_2O]_2.[O(CMe_2)_2OH]_2$[28]], sharing a $(\mu\text{-O})_2$ edge ($[(WO)O.(RO_2)(OROH)]_2$ (see Ref. 30), sharing a $[(\mu\text{-O})(\mu\text{-OR})]$ edge {$[Ta_2O(OPr^i)_8(Pr^iOH)]$[33,34]} or sharing a $[(\mu\text{-O})(\mu\text{-X})_2]$ face (X = OR, Cl) {for example, $[Ta_2OCl_3(OC_6H_3Pr^i_2\text{-}2,6)_5]$[35]}. The bonds between metals and oxo bridges are shorter than the M—(μ-OR) bonds and, in some cases, shorter than the terminal M—OR bonds. In the $[M_2(\mu\text{-OR})_2]$ rings of dimeric alkoxides, the M—(μ-OR)—M angles remain virtually constant (107–112°) and are independent of the nature of the metal atom, the substituent and the coordination polyhedron, whereas the M—(μ-O)—M angles in oxo complexes vary within a broad range {from 80.1° in the $[Mo^{III}_2O(OCH_2Bu^t)_4(PMe_3)_4]$ molecule[27] to 154–161° in the $[(WO)O(RO_2)(OROH)]_2$ molecule[30]}.

In the $[Ta_2O(OPr^i)_8(Pr^iOH)]$ complex,[33,34] the presence of one strong $Pr^iO\cdots HOPr^i$ hydrogen bond between the terminal ligands leads to a decrease in the distance between these ligands [O···O(H), 2.52 Å] and 'pushing off' of the OPr^i groups located on the opposite side of the equatorial plane (Fig. 6). Binuclear derivatives of metals in the lowest oxidation states, such as $[W^{IV}_2(\mu\text{-O})(\mu\text{-OBu}^t)(OSiMe_2Bu^t)_5Py_2]$,[25] $[Re^{VI}_2O_2(\mu\text{-O})(\mu\text{-OMe})_2.(OMe)_4]$[39] and $[(Mo^VO)(\mu\text{-O})(OC_6F_5)_2]^-_2$,[23] contain bridging groups along with M = M bonds (2.49–2.56 Å).

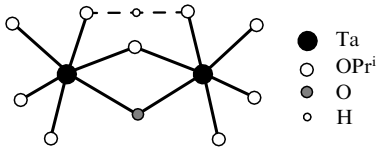


Figure 6. Metal–oxygen core in the structure of $[Ta_2O(OPr^i)_8.(Pr^iOH)]$.[33,34]

2. Trinuclear OA

Trinuclear oxoalkoxides (see Table 2) are represented by two types of triangles. In one type, the $[M_3]$ triangle is centred by a μ_3-O group on one side of the equatorial plane. In another (more widespread) type, there is not only a μ_3-O group but also a μ_3-X group located on the opposite side of the equatorial plane (X = OR, OH, Cl), resulting in the formation of the $[M_3(\mu_3\text{-}O).(\mu_3\text{-}X)(\mu\text{-}OR)_3]$ trigonal bipyramids (see Fig. 4 *a*) flattened along the threefold axis. In the $[Ti_3O(OMe)(OPr^i)_9]$ molecule,[42] the $(\mu_3\text{-}O)-Ti-(\mu_3\text{-}OMe)$ angles are 69°. In the $[W_3(\mu\text{-}O)_2(OBu^t)_8]$ molecules, the bonds in the triangle occur not only *via* the bidentate oxo groups but also *via* W–W single bonds and W=W double bonds (2.93 and 2.45 Å, respectively).[50]

In addition to triangular structures, there are also chain molecules, such as linear $[UO_2][U(\mu\text{-}O)(OBu^t)_5]_2$ (see Ref. 51) (as a result of the *trans* arrangement of two terminal groups in the central octahedron) and angular $[Nb_3O_2\{O(CMe_2)_2O\}_5.\{O(CMe_2)_2OH\}]$.[52]

3. Tetranuclear OA

Tetranuclear oxoalkoxides (see Table 3) are represented by two main groups, *viz*., tetrahedra and planar rhombuses consisting of four octahedra linked *via* two μ_3-ligands and four μ-ligands $[Ti_4(OMe)_{16}$ type [3]]. Apparently, a regular tetrahedron is present only in the $[Pb_4(\mu_4\text{-}O)(\mu\text{-}OSiPh_3)_6]$ molecule,[59] in which six μ-OR groups are located along its edges (Fig. 7 *a*). Taking into account the absence of one or several μ-OR groups in the $[Al_4.(\mu_4\text{-}O)(\mu\text{-}OR)_5X_5(ROH)]$ [X = OPr^i, Cl, OBu^i, OCH_2CF_3 (see Fig. 2 *d*)],[18,54,55] $[Pb_3Zr(\mu_4\text{-}O)(\mu_3\text{-}OBu^t)(\mu\text{-}OBu^t)_5(OBu^t)_2]$[62] and $[Ce_4^{3.75+}(\mu_4\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(Pr^iO)_7(Pr^iOH)]$[61] structures, these compounds can be assigned to 'butterfly-type' molecules, in which the wings are additionally linked *via* an oxo group. In solvates of these molecules with alcohols, the wings are linked not only *via* an oxo group but also *via* a very short hydrogen bond between the terminal OR and ROH groups. In the distorted $[W_4(\mu\text{-}O)(\mu\text{-}OPr^i)_2(OPr^i)_7Cl]$ tetrahedron, the central μ_4-O group is absent, and the tungsten atoms are linked to each other *via* μ-OR and μ-O bridges and W=W and W–W bonds (2.45 and 2.9 Å, respectively).[66]

In $Ti_4(OMe)_{16}$-type molecules, four sides of the $[M_4]$ rhombus are additionally linked *via* μ groups, and two $[M_3]$ triangular fragments are linked by μ_3 ligands located on the opposite sides of the plane of the rhombus. These molecules involve two types of metal atoms. Metal atoms of one type are coordinated by two μ_3 groups, whereas metal atoms of another type are coordinated by only one μ_3 group (in Fig. 7 *b*, these atoms are denoted M^1 and M^2, respectively). The oxo ligands are generally located in μ_3 positions. Examples are the $[Bi_4(\mu_3\text{-}O)_2(OBu^t)_8]$[73] and $[(MoO)_4(\mu_3\text{-}O)_2(OEt)_4Cl_4(EtOH)_2]$[81] molecules. However, the reverse situation is observed in the $[(VO)_4O_4(OMe)_4(bipy)_2]$ (bipy is 2,2′-bipyridyl)[74] and $[(MoO_2)_4O_2(OMe)_4(Me_2CNOH)]$[77] complexes and the $[(MoO_2)_2(MoO)_2O_4(OMe)_2(C_6H_4O_2\text{-}1,2)_2]^-$ anion,[78,79] in which the OMe groups are in μ_3 positions, whereas the oxo groups are bidentate.

In the $[LiNbO(OEt)_4(EtOH)]_2$ (see Ref. 85) and $[MgNbO(OMe)_5(MeOH)_2]_2$ molecules,[76] the oxo ligands are terminal and are involved in the 'niobyl' groups (these groups occupy the M^1 and M^2 positions in two molecules, respectively).

Compounds containing more than four metal atoms occur, as a rule, as conglomerates of smaller stable fragments described above. However, there are several more types of penta-, hexa- and octanuclear associates (often *closo*) with high symmetry.

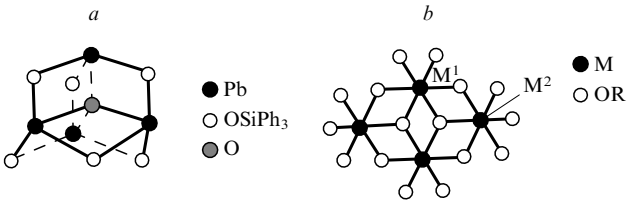


Figure 7. Metal–oxygen cores in the structures of $[Pb_4(\mu_4\text{-}O)(\mu\text{-}OSiPh_3)_6]$[59] (*a*) and $M_4(\mu_3\text{-}O)_2(\mu\text{-}OR)_4(OR)_n$ $[Ti_4(OMe)_{16}$ type] (*b*).

4. Pentanuclear complexes

Pentanuclear complexes (see Table 4) are represented by two main structural types, *viz*., clusters containing the $[M_5(\mu_5\text{-}O)]$ core and combinations of two $[M_2M']$ triangles.

In the molecules of isopropoxides $[Ln_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_5]$ (Ln = Sc, Y, Er, Yb, [Y_4Pr], In),[10–14,92,93] the $[M_5O]$ group can be described as a tetragonal pyramid, in which four μ_3-OR ligands are located above the centres of lateral faces, and four μ-OR groups are located along the edges of the base (see Fig. 2,*a*). The $[Al_5O(OBu^i)_{13}]$ and $[Fe_5O(OEt)_{13}]$ molecules have the structure of $[M_5(\mu_5\text{-}O)(\mu\text{-}OR)_8(OR)_5]$ and differ from the above-described molecules in that they contain no μ_3-OR groups. In these molecules, eight μ-OR groups are located along all edges of the pyramid.[15,53]

In the $[Ln_5O(OPr^i)_{13}]$ molecules with the group $[M_5]$ = $[Sm_4Ti]$, the $[(Tb_{0.9}Eu_{0.1})_4Ti]$ molecule and the $[Nd_5(\mu_5\text{-}O)(OPr^i)_{13}(Pr^iOH)_2]$ solvate, the 'cluster' has a trigonal-bipyramidal structure. In these molecules, two μ_3-OR groups are located above faces of two different pyramids, whereas six μ-OR groups serve as bridges between two axial metal atoms and three equatorial metal atoms.[10,13,99–101] In the tetragonal-pyramidal molecules $[Sr_5(\mu_4\text{-}O)(OCH_2Bu^t)_8(Bu^tCH_2OH)(THF)_4]$[95] and $[Eu^{III}Eu^{II}_4O_5(OAr)(ArOH)_5(MeCN)_8]$ (Ar = $C_6H_3Pr^i_2$-2,6),[96] the oxo group is located in the centre of the base and is coordinated in a tetradentate fashion. Aggregates of this type are very stable, exist in solutions and the gaseous phase and have low reactivity, in particular, in complex formation with other metal alkoxides.

A combination of two corner-sharing triangles is observed exclusively in bimetallic complexes, the more electropositive metal atom being common to two triangles. In the $[NaBi_4(\mu_3\text{-}O)_2(\mu\text{-}OC_6F_5)_7(OC_6F_5)_2]$ molecule, the $[NaBi_2]$ triangles are centred by μ_3-O groups.[64] The $[Mo^V_2Mo^{VI}Ta_2O_8(OPr^i)_{10}]$ complex is the first example of molecule in which all five metal atoms are involved in a non-planar ring containing a Mo=Mo bond (2.58 Å) along with μ-O and μ-OR groups.[104]

5. Hexanuclear OA

Many compounds belonging to this group of mono- and bimetallic complexes (see Table 5) contain μ_6-O-centred or non-centred $[M_6]$ octahedral 'clusters'. In the $[Ba_6(\mu_6\text{-}O)(OC_2H_4OMe)_{10}.(MeOC_2H_4OH)_4]$,[105] *trans*-$[Na_2Gd_4(\mu_6\text{-}O)(OBu^t)_{12}]$[106] and *trans*-$[K_4Zr_2(\mu_6\text{-}O)(OPr^i)_{10}]$ molecules,[107] the μ_3-OR ligands are located on eight faces of the octahedron. Structural analogues of the 'large octahedron' $[M_6O_{19}]^{n-}$ = $[M_6(\mu_6\text{-}O)(\mu\text{-}O)_{12}O_6]$ (M = Nb, Ta, Mo, W), in which twelve μ-O groups are located along the edges and six μ-O groups are terminal, are also well known. Among them are numerous oxo alkoxo vanadates,[113–117] $[V^{IV,V}_6(\mu_6\text{-}O)(\mu\text{-}OEt)_{12}O_6]$, which is a microhydrolysis product of $VO(OEt)_3$ (see Ref. 112) and the $[Fe_6(\mu_6\text{-}O)\{MeC(CH_2O)_3\}_6]^{2-}$ and $[Fe_6(\mu_6\text{-}O)(OMe)_{18}]^{2-}$ anions[120,121] (Fig. 8 *a*).

Among octahedral clusters containing no μ_6-O groups, the $[M_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4]$ compounds (M = Sn, Pb; R = Me, Pr^i) with

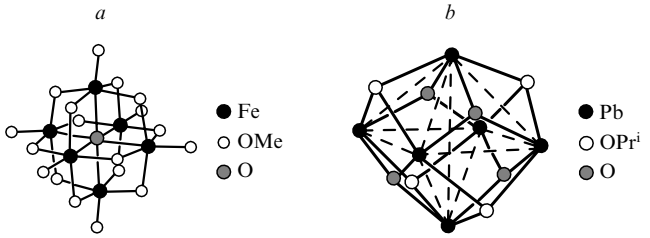


Figure 8. Metal–oxygen cores in the structures of $[Fe_6(\mu_6\text{-}O)(OMe)_{18}]^{2-}$ (*a*) [149] and $[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OPr^i)_4]$ (*b*).[127]

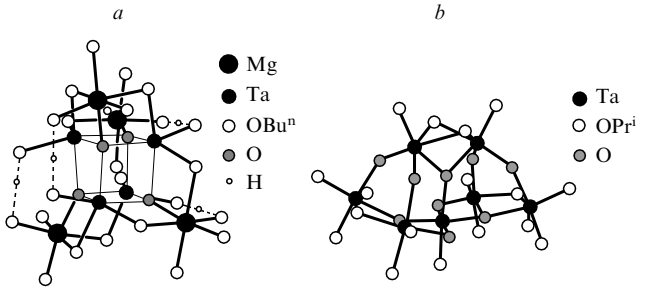


Figure 9. Metal–oxygen cores in the structures of $[Mg_4Ta_4O_4(OBu^n)_{20}(Bu^nOH)_4]$ (*a*) [160] and $[Ta_7O_9(OPr^i)_{17}]$ (*b*).[33, 103]

alternating oxo and OR ligands above the centres of the faces [124–127] [structural analogues of hydroxides of the same metals (see Fig. 8 *b*)] and the bimetallic $[La_2(MoO)_4(\mu_4\text{-}O)_4(\mu\text{-}OPr^i)_8(OPr^i)_6]$ complex,[128] in which four $[Mo_2La_2(\mu_4\text{-}O)]$ groups are located inside the octahedron, are of interest.

In yet another large group of hexanuclear complexes, two $[M_3(\mu_3\text{-}O)]$ triangles are linked to each other to form a ring *via* bidentate O or OR bridges. Examples are $[(MoO_2)Ta_2(\mu_3\text{-}O)(\mu\text{-}OMe)_3(\mu\text{-}O)(OMe)_5]_2$,[133] $[IZnTa_2(\mu_3\text{-}O)(\mu\text{-}OPr^i)_3(\mu\text{-}O)(OPr^i)_4]_2$ (see Ref. 134) and $[Hf_3(\mu_3\text{-}O)(\mu\text{-}OEt)_4(OEt)_6(EtOH)]_2$ (see Ref. 45, Fig. 4 *b*). In the $[Gd_3(OC_2H_4OMe)_8]_2(\mu_4\text{-}O)$ molecule, two triangles, which are perpendicular to each other, are linked *via* a tetradentate oxo group.[130]

In the bimetallic $[Er_2Ti_4O_2(OEt)_{18}(EtOH)_2]$ [140] and $[(NaTHF)_2Bi_4(\mu_3\text{-}O)_2(\mu\text{-}OC_6F_5)_{10}]$ [64] complexes, the $[Ti(\mu_3\text{-}OR)(\mu\text{-}OR)_2(OR)_2]$ and [NaTHF] groups, respectively, are additionally bound to two μ_3-O ligands of the core {$[Ti_4(OMe)_{16}]$ type}. Only the $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4]\cdot 14\,EtOH$ molecule [16] contains two cuboidal tetramers sharing the $[Ca_2(\mu_4\text{-}O)_2]$ face (see Fig. 2 *b*). The $[Fe_6(\mu_4\text{-}O)_2(\mu\text{-}OMe)_8(OMe)_4.\{N(C_2H_4NH_2)_3\}_2]^{2+}$ cation [129] consists of two $[M_4]$ tetrahedra sharing the $[M_2]$ edge {the $[Fe_2(\mu_4\text{-}O)_2]$ group in the centre}. In the molecules $[(MoO)_3(\mu\text{-}O)_2(OPr^i)_6]_2$ (see Refs 46 and 141) and $[M^V(MoO)_2(\mu\text{-}O)_2(OPr^i)_7]_2$ (M^V = Nb, Ta),[104] the zigzag hexanuclear chains are linked *via* μ-O groups.

6. Oligomeric oxoalkoxides with nuclearity higher than six

The following structural types were found for oligomeric oxoalkoxides with nuclearity higher than six (see Tables 6–10): closed polyhedra, in which all atoms are bound to no more than two oxo groups; rings; condensed structures related to inorganic isopolyanions (metal atoms in the latter are coordinated by several oxo groups).

Among closed polyhedra, oxo complexes involving cuboidal cores (see Table 7) are of particular interest. The $[Li_4Ti_4(\mu_5\text{-}O)_2.(\mu_3\text{-}O)_2(OPr^i)_{12}]$ molecule consists of two cuboidal cores $[Li_2Ti_2O_3(OR)]$, which share the $[Ti_2(\mu_5\text{-}O)_2]$ face and are additionally linked *via* the 'external' trigonal bipyramids $[TiO(OR)_4]$.[158] A larger number of molecules contain one cube $[M^{II}_4(\mu_4\text{-}O)_4]$ in the centre. Examples are the $[Mg_4Ta_4O_4(OBu^n)_{20}(Bu^nOH)_4]$ (Fig. 9 *a*), $[Sr_4Ta_4O_4.(OMe)_{20}(MeOH)_{10}]$,[160] $[Ba_4M_4O_4(OEt)_{20}(EtOH)_6]$ (M = Nb, Ta) [85, 160] and $[Ba_4Ti_4O_4(OPr^i)_{16}(Pr^iOH)_{3.5}]$ [159] complexes.†

The M^{II} atoms are linked to the 'external' $[M'(OR)_m]$ groups (M' = Ti, Nb, Ta) *via* oxo ligands and two or more μ-OR groups. The coordination environment of the M^{II} atom also involves alcohol solvate molecules. In spite of the different nature (and even valence) of M' and R, these compounds are structurally very similar. The only difference is the orientation of the $[M'O(OR)_m]$ groups with respect to the cuboidal core. These groups can be located as continuations of edges (Mg–Ta), diagonals of faces (Ba–Nb) or body diagonals (Ba–Ti). It is reasonable to expect that the above-described structure would be observed also in other oxoalkoxides with a ratio $M^{II}:M^n = 1:1$. The complex $[Mg_4Ta_4O_4(OBu^n)_{20}(Bu^nOH)_4]$ is the first structurally characterised n-butoxide. Evidently, the cuboidal core (a matrix, on which an OA molecule is formed) prevents the hydrocarbon chain from knotting, which generally hinders crystallisation.

The same situation is observed in decanuclear molecules (see Table 9). In such molecules, the $[M_6]$ octahedral 'clusters' are located in the centre and the μ_3-OR and μ_4-O groups alternate on eight faces. The latter are involved in the $[(\mu_4\text{-}O)M'(OR)_5]$ octahedra. Examples are the $[Pb_6Nb_4O_4(OEt)_{24}]$,[178] $[Sr_6Ti_4O_4(OPr^i)_{20}]$ [102] and $[Ni_6Sb_4O_4(OEt)_{16}(EtOH)_4]$ [177] complexes. In all these complexes, the central octahedron is formed by more positive metals, *viz*., Pb, Sr and Ni, respectively. The $[Ba_4Cu_6(\mu_4\text{-}O)(\mu\text{-}OCEt_3)_{12}]$ molecule, in which the edges of the central $[(\mu_4\text{-}O)Ba_4]$ tetrahedron are linked *via* six linear $[Cu(\mu\text{-}OR)_2]$ groups,[175] can be considered as a tetrahedral analogue of the above-described structures. In the $[Fe_7O(OH)\{(OCH_2)_3CCH_2OH\}_4Cl_6(MeCN)_2]$ molecule,[146] the central $[Fe_6(\mu_6\text{-}O)]$ octahedron is linked to one $[Fe(OH)(MeCN)_2]$ group (see Table 6). In the $[Na_2Fe_6O(OMe)_{18}(MeOH)_6]$ complex [149] (with axial Fe atoms), the central octahedron is linked to two $[Na(ROH)_3]$ groups (see Table 7). In the structure of $[Bi_6(\mu_3\text{-}O)_7(\mu_3\text{-}OC_6F_5)[Bi(OC_6F_5)_4]_3(THF)_2]$,[166] the μ_3-O groups are located on seven faces of the $[Bi_6]$ octahedron {three of these groups are coordinated to $[Bi(OR)_4]$} and the eighth face is occupied by the μ_3-OR ligand (see Table 8).

Hepta-, octa-, deca- and octadecanuclear alkoxides (see Tables 6, 7, 9 and 10) form rings. The tetrahedral oxygen atom in the $[\{Cu_2Zr_2(OPr^i)_9\}_2(\mu_4\text{-}O)]$ molecule serves as a bridge between two eight-membered rings, each ring containing two linear $[CuO_2]$ groups and $[Zr(\mu\text{-}OR)_3Zr]$ octahedra.[156] One centrosymmetric ring, which consists of four $[Mo_2(\mu_3\text{-}O)]$ triangles linked to each other *via* μ-OH groups, is observed in the $[(MoO)_4O_2(OEt)_2(OH)_3Cl_3(EtOH)_2]_2$ molecule.[81, 157] The spherical $[Cu_{18}O_2(OSiMe_3)_{14}]$ molecule is formed by two intersecting μ_4-O-centred $[Cu_9O_8]$ rings.[194]

The pentanuclear $[M_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu\text{-}OR)_6(OR)_4]$ rings, which differ only in the mode of binding to each other, were found in the structures of aluminium OA with nuclearity from 9 to 11. In the $[Al_{10}O_4(OEt)_{22}]$ molecule,[17] these rings are linked *via* the central $[Al_2(\mu_3\text{-}O)_2]$ group. In the $[Al_{11}O_6(OR)_{21}]$ complex (R = Pr^i, Pr^n), the rings are linked *via* the $[Al(\mu_3\text{-}O)_2(\mu\text{-}O)_2(OR)]$ group. In the $[Al_5Mg_4O_3(OH)_3(OPr^i)_8(acac)_6]$ molecule [180] (acac is acetylacetonate) and its structural analogue $[Fe_9O_3(OEt)_{21}]\cdot EtOH$,[167] the rings share the $[M(\mu_3\text{-}O)]$ edge and are additionally linked to each other *via* a μ-OH group. The $[Al_8O_2(OH)_2(OBu^i)_{18}]$ molecule [53] can be considered as a derivative of decanuclear oxoethoxide lacking one Al atom, which is not bound to the μ_4-O group, in each half of the molecule. Therefore, there is a homologous series of aluminium oxoalkoxides, including from octa- to undecanuclear molecules (Fig. 10).

† Taking into account the exceptionally short Ti–O bonds (1.71 and 1.79 Å), this structure can be considered as a combination of four ionic pairs $[Ba(ROH)]^{2+}_4[TiO(OR)_4]^{2-}_4$. In solution this complex, unlike molecular alkoxo titanates $Ba[Ti_2(OPr^i)_9]_2$, $[BaTi_2(OPr^i)_{10}]_2$ and $[BaTi_3.(OPr^i)_{14}]$,[247] can apparently exist as isolated ions or their associates.

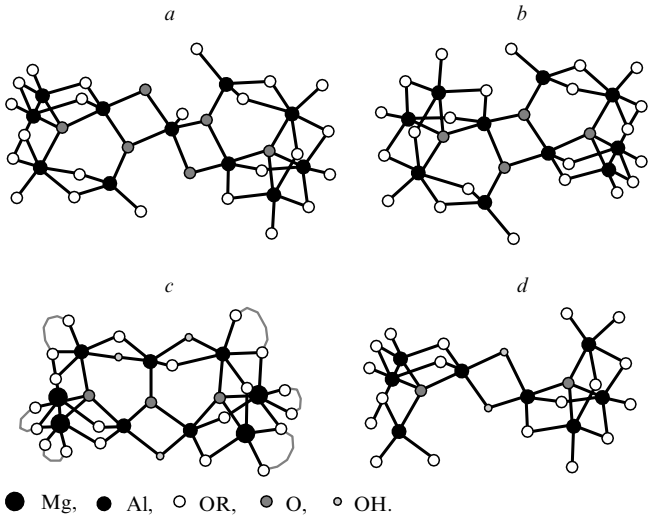


Figure 10. Comparison of the metal–oxygen skeletons in the molecules of undeca-, deca-, nona- and octanuclear aluminium oxoalkoxides — $[Al_{11}O_6(OPr^n)_{10}(OPr^i)_{10}(OR)(ROH)_2]$ (R = Pr^i, Pr^n) (*a*),[180] $[Al_{10}O_4(OEt)_{22}]$ (*b*),[17] $[Al_5Mg_4O_3(OH)_3(OPr^i)_8(acac)_6]$ (*c*)[180] and $[Al_8O_2(OH)_2(OBu^i)_{18}]$ (*d*).[53]

Many known oxo alkoxo complexes containing more than six metal atoms belong to condensed structures related to inorganic isopolyanions. All oxo groups in these compounds (except for 'yl' O atoms) serve as bridges (from bi- to hexadentate), and OR groups are either terminal ligands or bidentate bridges. Oxo alkoxo molybdates(VI) and (V,VI) and vanadates(IV), (V) and (IV,V), which are characterised by the closest packing of edge- and vertex-sharing octahedra, are worthy of notice. These compounds are analogous to metamolybdate $[Mo_8O_{26}]^{4-}$ (see Refs 154 and 155) and decavanadate $[V_{10}O_{28}]^{6-}$.[169, 170] Alkoxy groups of mono- or, more often, polyatomic alcohols $RC(CH_2O)_3$ are located on the surface of these compounds. Examples are the $[(MoO_2)_6(MoO)_2O_{10}(OMe)_4]^{4-}$ (see Ref. 153) and $[V^{IV}_{10}O_{13}\{EtC(CH_2O)_3\}_5]^-$ anions.[169] The $[Ta_7(\mu_3\text{-}O)_3(\mu\text{-}O)_6.(OPr^i)_{17}]$ molecule[33, 34, 103] consists of two vertex-sharing $[Ta_4]$ tetrahedra, which are additionally linked to each other *via* one μ_3-O group and two μ-OR groups (see Fig. 9 *b*). The structure of $[LiTa_9O_{13}(OEt)_{20}(EtOH)]$[173] contains Li atoms and two layers of rings consisting of the $[Ta_3O_7(OR)_6]$ and $[Ta_6O_6(OR)_{15}]$ octahedra, which are linked to each other *via* μ-O bridges. Apparently, the product of hydrothermal synthesis with composition $M_7[Na(H_2O)_3Mo^V_{36}Mo^{VI}_6H_{15}O_{109}\{(OCH_2)_3CCH_2OH\}_7]$[197] has the maximum size. The $[Na(H_2O)_3]$ group located in the centre of this molecule is surrounded by the $[Mo^V_6O_{24}]$ ring and the framework of the $[Mo^{V,VI}O]$ octahedra (see Table 10).

The spherical $[Zr_{13}O_8(OMe)_{36}]$[9] and $[Zr_3Mo_8O_{24}(OPr^i)_{12}.(Pr^iOH)_4]$[182] molecules also belong to the class of compounds under consideration. In these molecules, the $[ZrO_8]$ groups are located in the centre and OR groups are located on the surface (in the former complex, twelve OR groups serve as bridges). The $[Ba_4Ti_{13}O_{18}(OC_2H_4OMe)_{24}]$ molecule containing one central and twelve peripheral Ti octahedra {a structural analogue of the known $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ion}[192] and the $[Mn_8Sb_4O_4(OEt)_{20}]$ molecule with the symmetry S_4 and two Mn octahedra in the centre belong to the same class of compounds (see Table 10).[186]

Unlike the structures with the closest packing of metal–oxygen polyhedra, the 'loose' $M_8O_{10}(OEt)_{20}$ molecules (M = Nb and Ta)[100, 148, 149] (see Fig. 1 *b* and Table 8) contain a cavity surrounded by pairs and triads of octahedra sharing a vertex and linked to each other *via* single octahedra.

Let us consider titanium oxoalkoxides, which have no analogues in inorganic chemistry, in more detail. The $Ti_7O_4(OEt)_{20}$ molecule, which is the first crystalline hydrolysis product of titanium ethoxide, can be considered as a condensation product of the $[Ti_4(OEt)_{16}]$ molecules and the $Ti(OEt)_2[(\mu\text{-}OEt)_2Ti(OEt)_3]_2$ trimer (the latter is present in solution).[248] This compound contains the linear $[Ti(\mu_4\text{-}O)(\mu\text{-}O)_2Ti]$ chain with the $[Ti(\mu_3\text{-}O).(\mu\text{-}O)Ti]$ groups located above and below this chain[7, 142] (see Fig. 1 *a* and Table 6). An analogous situation is observed in the structures of the large $[Ti_8O_6(OCH_2Ph)_{20}]\cdot Et_2O$, $[Ti_{10}O_8(OEt)_{24}]\cdot\cdot PhMe$,[143] $[Ti_{17}O_{24}(OPr^i)_{20}]$[191] and $[Ti_{18}O_{28}(OBu^t)_{16}(Bu^tOH)]$[193] molecules (first examples of Keggin-type structures containing Ti atoms). In these structures, chains composed of pairs or triads of edge-sharing octahedra are linked to each other *via* μ_4-O, μ_3-O and μ-OR bridges. The $[Ti_{16}O_{16}(OEt)_{32}]$ molecule[142, 189] contains two mutually perpendicular blocks consisting of eight octahedra. In each block, six octahedra form a NiAs-type layer, one octahedron is located above the layer, one octahedron is located below the layer, and a tetrahedral cavity is located in the centre of the molecule (see Table 10).

In summary, it can be concluded that most molecules belonging to the class of oxoalkoxides contain 4–10 metal atoms. A rather small number of dinuclear molecules have been described, and polymeric molecules are few in number, as opposed to alkoxides $M(OR)_n$, the majority of which belong to one of the latter two groups. Evidently, the reason is that OR bridges are, as a rule, bidentate (except for μ_3-OR groups on the surface of *closo*-aggregates $[M_n]$), whereas oxoalkoxide molecules contain oxo ligands with high dentate numbers (up to 8) responsible for coordination of metal atoms.

It should be noted that no cuboidal molecules of the $[M_4(\mu_3\text{-}X)_4]$ type were found in the class of tetranuclear oxo complexes {the only exception is $[(MoO)O(OSiMe_3)(Me_2NH)]_4$ (see Ref. 67)}, as opposed to orthoalkoxides, for which such molecules are very typical and these molecules are stable.

In many cases, the accumulated data allow one to predict the structures of unknown compounds of the ortho series with high probability.[3] At the same time, oxoalkoxides, on the whole, are characterised by high variability and unpredictability of molecular structures.

V. Oxoalkoxides as true precursors of oxide phases

It is quite apparent that oxo complexes (mono- and bimetallic) play a considerable role in the phase formation of simple and complex oxides and are true precursors. The M—O—M bridges in bimetallic oxo complexes provide homogeneity of the newly formed oxide phases at the molecular level.

The above-considered differences in the composition, stoichiometry, solubility and reactivity of ortho- and oxoalkoxides are widely used in the sol–gel synthesis of a series of very important composites. The synthesis of $BaTiO_3$ is the most prominent example. For the latter compound to be prepared, the starting solution must contain a precursor with a metal ratio of 1 : 1, which is attained only upon decomposition of $BaTi_4(OR)_{18}$ into oxoalkoxides $BaTiO_n(OR)_{6-2n}$. Otherwise the sol–gel synthesis affords a mixture of phases containing not only $BaTiO_3$ but also polytitanates and Ba_2TiO_4. The latter fact is attributable to the presence of free $Ba(OR)_2$ (along with a complex with 1 : 4 composition) in solutions containing Ba and Ti in a ratio of 1 : 1.[159, 215, 216] Therefore, for single-phase bimetallic oxides to be synthesised, it is necessary that the solution should contain not only components in a required ratio but also a complex with a specified stoichiometry.

Yet another aspect of the use of oxo complexes in the synthesis of crystalline oxide phases is associated with spontaneous decomposition of alkoxides at 20 °C accompanied by elimination of ethers (this method does not belong to the sol–gel technology). This procedure was employed for the preparation of Na_2MoO_4, Na_2WO_4, Li_2MoO_4, Li_2WO_4, γ-Bi_2MoO_6 and cubic solid solutions (δ* phase) of the Bi_2O_3–WO_3 system.[137, 224, 249] Alterna-

tively, the latter can be prepared by solid-phase synthesis. However, this method requires annealing at temperatures >700 °C over a long period of time. Crystallisation of oxide phases directly from solutions in organic solvents is unambiguously indicative of elimination of ether, whereas products prepared by the sol–gel method are amorphous and their crystallisation occurs only after dehydration by annealing.

References

1. K A Andrianov *Metal-Organic Polymers* (New York: Wiley, 1965)
2. D C Bradley, in *Inorganic Polymers* (Eds F G A Stone, W A G Grham) (New York: Academic Press, 1962)
3. N Ya Turova, E P Turevskaya, V G Kessler, M I Yanovskaya *The Chemistry of Metal Alkoxides* (Boston, Dordrecht, London: Kluwer Academic, 2002)
4. C J Brinker, G W Scherer *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing* (San Diego, CA: Academic Press, 1990)
5. L C Klein (Ed.) *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes* (Park Ridge, NY: Noyes, 1988)
6. L C Klein (Ed.) *Sol-Gel Optics: Proceedings and Applications* (Boston, Dordrecht, London: Kluwer Academic, 1994)
7. K Watenpaugh, C N Caughlan *J. Chem. Soc., Chem. Commun.* 76 (1967)
8. D C Bradley, M B Hursthouse, P F Rodesiler *J. Chem. Soc., Chem. Commun.* 1112 (1968)
9. B Morosin *Acta Crystallogr., Sect. B* **33** 303 (1977)
10. O Poncelet, W J Sartain, L G Hubert-Pfalzgraf, K Folting, K G Caulton *Inorg. Chem.* **28** 263 (1989)
11. E P Turevskaya, A I Belokon, Z A Starikova, A I Yanovsky, E N Kiruschenkov, N Ya Turova *Polyhedron* **19** 705 (2000)
12. G Westin, M Kritikos, M Wijk *J. Solid State Chem.* **141** 168 (1998)
13. M Kritikos, M Moustiakimov, M Wijk, G Westin *J. Chem. Soc., Dalton Trans.* 1931 (2001)
14. D C Bradley, H Chudzynska, D M Frigo, M E Hammond, M B Hursthouse, M A Mazid *Polyhedron* **9** 719 (1990)
15. B J O'Keefe, S M Monnier, M A Hillmyer, W B Tolman *J. Am. Chem. Soc.* **123** 339 (2001)
16. N Ya Turova, E P Turevskaya, V G Kessler, A I Yanovsky, Yu T Struchkov *J. Chem. Soc., Chem. Commun.* 21 (1993)
17. A I Yanovsky, N Ya Turova, N I Kozlova, Yu T Struchkov *Koord. Khim.* **13** 242 (1987) [a]
18. N Ya Turova, A I Yanovsky, V G Kessler, N I Kozlova, Yu T Struchkov *Zh. Neorg. Khim.* **36** 2497 (1991) [b]
19. W P Griffith, N T McManus, A C Skapski *Inorg. Chim. Acta* **103** L15 (1985)
20. J Yingtai *J. Chin. Rare Earth Soc.* **11** 17 (1993)
21. J E Hill, P E Fanwick, I P Rotwell *Acta Crystallogr., Sect. C* **47** 541 (1991)
22. V M Visciglio, P E Fanwick, I P Rothwell *Acta Crystallogr., Sect. C* **50** 900 (1994)
23. R G Abbott, F A Cotton, L R Falvello *Inorg. Chem.* **29** 514 (1990)
24. F L Phillips, A C Skapski *J. Chem. Soc., Dalton Trans.* 2587 (1975)
25. M H Chisholm, C M Cook, K Folting, W E Streib *Inorg. Chim. Acta* **198–200** 63 (1992)
26. S K Park, S M Koo, Y E Lee *Polyhedron* **19** 1037 (2000)
27. T A Budzichowski, M H Chisholm, K Folting, K S Kramer *Polyhedron* **15** 3085 (1996)
28. C Knobler, B R Penfold, W T Robinson, C J Wilkins, S H Yong *J. Chem. Soc., Dalton Trans.* 248 (1980)
29. A J Matheson, B B Penfold *Acta Crystallogr., Sect. B* **35** 2707 (1979)
30. A Lehtonen, R Sillanpää *J. Chem. Soc., Dalton Trans.* 2119 (1994)
31. B A Borgias, S R Cooper, Y B Koh, K N Raymond *Inorg. Chem.* **23** 1009 (1984)
32. B A Cartwright, W P Griffith, M Schröder *J. Chem Soc., Chem. Commun.* 853 (1978)
33. N Ya Turova, A V Korolev, D E Tchebukov, A I Belokon, A I Yanovsky, Yu T Struchkov *Polyhedron* **15** 3869 (1996)
34. A I Yanovsky, N Ya Turova, A V Korolev, D E Chebukov, Yu T Struchkov *Izv. Akad. Nauk, Ser. Khim.* 125 (1996) [c]
35. G R Clark, A J Nielson, C E F Rickard *Polyhedron* **6** 1765 (1987)
36. J C Bollinger, M H Chisholm, D R Click, K Folting, C M Hadad, D B Tiedtke, P J Wilson *J. Chem. Soc., Dalton Trans.* 2074 (2001)
37. V V Tkachev, L O Atovmyan *Koord. Khim.* **2** 110 (1976) [a]
38. W Clegg, R J Errington, K A Fraser, D G Richards *J. Chem. Soc., Chem. Commun.* 1105 (1993)
39. P G Edwards, G Wilkinson, M.B.Hursthouse, K M Abdul Malik *J. Chem. Soc., Dalton Trans.* 2467 (1980)
40. H Reuter, M Kremser *Z. Anorg. Allg. Chem.* **615** 137 (1992)
41. S Parola, R Papiernik, L G Hubert-Pfalzgraf, S Jagner, M Hakansson *J. Chem. Soc., Dalton Trans.* 4631 (1997)
42. V W Day, T A Eberspacher, Y Chen, J Hao, W G Klemperer *Inorg. Chim. Acta* **229** 391 (1995)
43. T J Boyle, T M Alam, E R Mechenbier, B L Scott, J W Ziller *Inorg. Chem.* **36** 3293 (1997)
44. W J Evans, M A Ansari, J W Ziller *Polyhedron* **17** 869 (1998)
45. Z A Starikova, E P Turevskaya, N I Kozlova, N Ya Turova, D V Berdyev, A I Yanovsky *Polyhedron* **18** 941 (1999)
46. M H Chisholm, K Folting, J C Huffman, C C Kirkpatrick *Inorg. Chem.* **23** 1021 (1984)
47. M H Chisholm, K Folting, M Scheer *Polyhedron* **17** 2931 (1998)
48. F A Cotton, D O Marler, W Schwotzer *Inorg. Chim. Acta* **95** 207 (1984)
49. V G Kessler, N Ya Turova, A N Panov, Z A Starikova, A I Yanovsky, Yu T Struchkov *Polyhedron* **17** 4189 (1998)
50. M H Chisholm, C M Cook, K Folting *J. Am. Chem. Soc.* **114** 2721 (1992)
51. C J Burns, A P Sattelberger *Inorg. Chem.* **27** 3692 (1988)
52. L G Hubert-Pfalzgraf, V Abada, J Veissermann, J Roziére *Polyhedron* **18** 845 (1999)
53. I Abrahams, D C Bradley, H Chudzynska, M Motevalli, R A Sinclair *J. Chem. Soc., Dalton Trans.* 259 (2002)
54. R A Sinclair, W B Gleason, R A Newmark, J R Hill, S Hunt, P Lyon, J Stevens, in *Chemical Proceedings of Advanced Materials* (Eds L Hench, J K West) (New York: Wiley, 1992) p. 207
55. S A Sangokoya, W T Rennigton, J Byers-Hill, G H Robinson, R D Rogers *Organometallics* **12** 2429 (1993)
56. W J Evans, T J Boyle, J W Ziller *J. Am. Chem. Soc.* **115** 5084 (1993)
57. C Sirio, L G Hubert- Pfalzgraf, C Bois *Polyhedron* **16** 1129 (1997)
58. R Anwander, F C Munck, T Priermeier, W Scherer, O Runte, W A Herrmann *Inorg. Chem.* **36** 3545 (1997)
59. C Gaffney, P G Harrison, T J King *J. Chem. Soc., Chem. Commun.* 1251 (1980)
60. S Daniele, R Papiernik, L G Hubert-Pfalzgraf, S Jagner, M Hakansson *Inorg. Chem.* **34** 628 (1995)
61. K Yunlu, P S Gradeff, N Edelstein, W Kot, G Shalimoff, W E Streib, B A Vaartstra, K G Caulton *Inorg. Chem.* **30** 2317 (1991)
62. D J Teff, J C Huffman, K G Caulton *J. Am. Chem. Soc.* **118** 4030 (1996)
63. R D Rogers, A H Bond, M M Witt *Inorg. Chim. Acta* **182** 9 (1991)
64. K H Whitmire, C M Jones, M D Burkart, J C Hutchison, A L McKnight *Mater. Res. Soc. Symp. Proc.* **271** 149 (1992)
65. W A Herrmann *Angew. Chem., Int. Ed. Engl.* **34** 2187 (1995)
66. M H Chisholm, Ch E Hammond, J C Huffman, J D Martin *Polyhedron* **9** 1829 (1990)
67. G S Kim, D A Keszler, C W DeKock *Inorg. Chem.* **30** 574 (1991)
68. M H Chisholm, Y Yang, E Lobkovsky, J C Huffman *J. Cluster Sci.* **3** 151 (1992)
69. T A Budzichowski, M H Chisholm, K Folting, W E Streib, M Scheer *Inorg. Chem.* **35** 3659 (1996)
70. F A Cotton, M P Diebold, W J Roth *Inorg. Chem.* **24** 3509 (1985)
71. V G Kessler, A V Shevelkov, G V Khvorykh, G A Seisenbaeva, N Ya Turova, D V Drobot *Zh. Neorg. Khim.* **40** 1477 (1995) [b]
72. G A Seisenbaeva, V G Kessler, A V Shevelkov *J. Sol-Gel Sci. Technol.* **19** 285 (2000)

73. N N Sauer, E Garcia, R R Ryan *Mater. Res. Soc. Symp. Proc.* **180** 920 (1990)
74. I Cavaco, J C Pessoa, M T Duarte, P M Matias, R T Henriques *Polyhedron* **12** 1231 (1993)
75. L G Hubert-Pfalzgraf, V Abada, J Veissermann *Polyhedron* **18** 3497 (1999)
76. V G Kessler, E P Turevskaya, A I Belokon, N Ya Turova *Polyhedron* **21** 1629 (2002)
77. A Proust, P Gouzerh, F Robert *J. Chem. Soc., Dalton Trans.* 819 (1994)
78. H Kang, S Liu, S N Shaikh, T Nicholson, J Zubieta *Inorg. Chem.* **28** 920 (1989)
79. S Liu, S N Shaikh, J Zubieta *Inorg. Chem.* **26** 4303 (1987)
80. M H Chisholm, J C Huffman, C C Kirkpatrick, J Leonelli, K Folting *J. Am. Chem. Soc.* **103** 6093 (1981)
81. C Limberg, A J Downs, A J Blake, S Parsons *Inorg. Chem.* **35** 4439 (1996)
82. J A Beaver, M G B Drew *J. Chem. Soc., Dalton Trans.* 1376 (1973)
83. A J Zozulin, D C Moody, R R Ryan *Inorg. Chem.* **21** 3083 (1982)
84. P A Shcheglov, G A Seisenbaeva, D V Drobot, V G Kessler *Inorg. Chem. Commun.* **4** 227 (2001)
85. E P Turevskaya, N Ya Turova, A V Korolev, A I Yanovsky, Yu T Struchkov *Polyhedron* **14** 1531 (1995)
86. H Kumagai, M Endo, S Kawata, S Kitagawa *Acta Crystallogr., Sect. C* **52** 1943 (1996)
87. P A Shcheglov, D V Drobot, G A Seisenbaeva, S Govil, V G Kessler *Chem. Mater.* **14** 2378 (2002)
88. T P Blatchford, M H Chisholm, K Folting, J C Huffman *J. Chem. Soc., Chem. Commun.* 1295 (1984)
89. K G Caulton, M H Chisholm, S R Drake, K Folting, *J. Chem. Soc., Chem. Commun.* 1349 (1990)
90. H Vincent, F Labrise, L G Hubert-Pfalzgraf *Polyhedron* **13** 3323 (1994)
91. P Miele, J-D Foulon, N Hovnanian *Polyhedron* **12** 209 (1993)
92. G Westin, M Wijk, M Moustiakimov, M Kritikos *J. Sol-Gel Sci. Technol.* **13** 125 (1998)
93. N I Kozlova, N Ya Turova, E P Turevskaya *Koord. Khim.* **8** 639 (1982) [a]
94. K M Fromm, E D Gueneau, H Goesmann *Chem. Commun.* 2187 (2000)
95. T J Boyle, P G Clem, M A Rodriguez, B A Tittle, M D Heagy *J. Sol-Gel Sci. Technol.* **16** 47 (1999)
96. W J Evans, M A Greci, J W Ziller *Inorg. Chem.* **39** 3213 (2000)
97. G G Nunes, D M Reis, P Amorim, E L Sa, A S Mangrich, D J Evans, P B Hitchcock, G J Leigh, F S Nunes, J F Soares *New J. Chem.* **26** 519 (2002)
98. K W Henderson, R E Mulvey, F B M Reinhard, W Clegg, L Horsburgh *J. Am. Chem. Soc.* **116** 10 777 (1994)
99. G Helgesson, S Jagner, O Poncelet, L G Hubert-Pfalzgraf *Polyhedron* **10** 1559 (1991)
100. S Daniele, L G Hubert-Pfalzgraf, J-C Daran, S Halut *Polyhedron* **13** 927 (1994)
101. M Moustiakimov, M Kritikos, G Westin *Acta Crystallogr., Sect. C* **54** 29 (1998)
102. A I Yanovsky, Z A Starikova, M I Yanovskaya, N M Kotova, N Ya Turova *Zh. Neorg. Khim.* **48** 1456 (2003) [b]
103. I Abrahams, D C Bradley, H Chudzynska, M Motevali, P O'Shaughnessy *J. Chem. Soc., Dalton Trans.* 2685 (2000)
104. A Johansson, M Roman, G A Seisenbaeva, L Kloo, Z Szabo, V G Kessler *J. Chem. Soc., Dalton Trans.* 387 (2000)
105. K G Caulton, M H Chisholm, S R Drake, K Folting, J C Huffman, W E Streib *J. Chem. Soc., Chem. Commun.* 1498 (1990)
106. H Schumann, G Kociok-Köhn, J Loebel *Z. Anorg. Allg. Chem.* **581** 69 (1990)
107. B A Vaartstra, W E Streib, K G Caulton *J. Am. Chem. Soc.* **112** 8593 (1990)
108. W J Evans, M A Ansari, J W Ziller *Inorg. Chem.* **38** 1160 (1999)
109. M Veith, E C Yu, V Huch *Chem.-Eur. J.* **1** 26 (1995)
110. M Baier, P Brissinger, J Blümel, H Schmidbaur *Chem. Ber.* **126** 947 (1993)
111. J I Jolas, S Hoppe, K H Whitmire *Inorg. Chem.* **36** 3335 (1997)
112. V G Kessler, G A Seisenbaeva *Inorg. Chem. Commun.* **3** 203 (2000)
113. Q Chen, D P Goshorn, C P Scholes, X L Tan, J Zubieta *J. Am. Chem. Soc.* **114** 4667 (1992)
114. A Müller, J Meyer, H Bogge, A Stammler, A Bolgi *Z. Anorg. Allg. Chem.* **621** 1818 (1995)
115. D Hou, G-S Kim, K S Hagen, C L Hill *Inorg. Chim. Acta* **211** 127 (1993)
116. M I Khan, Q Chen, J Zubieta, D P Goshorn *Inorg. Chem.* **31** 1556 (1992)
117. M I Khan, Q Chen, H Höpe, S Parkin, C J O'Connor, J Zubieta *Inorg. Chem.* **32** 2929 (1993)
118. W Clegg, M R J Elsegood, R J Errington, J Harvelock *J. Chem. Soc., Dalton Trans.* 681 (1996)
119. V W Day, W G Klemperer, C Schwartz. *J. Am. Chem. Soc.* **109** 6030 (1987)
120. K Hegetschweiler, H Schmalle, H M Streit, W Schneider *Inorg. Chem.* **29** 3625 (1990)
121. A Cornia, D Gatteschi, K Hegetschweiler, L Hausherr-Primo, V Gramlich *Inorg. Chem.* **35** 4414 (1996)
122. T J Boyle, C A Zechmann, T M Alam, M A Rodriguez, C A Hajar, B L Scott *Inorg. Chem.* **41** 946 (2002)
123. J A Hollingshead, R E McCarley *J. Am. Chem. Soc.* **112** 7402 (1990)
124. P G Harrison, B J Haylett, T J King *J. Chem. Soc., Chem. Commun.* 112 (1978)
125. Y Sasaki, N Miyazawa *Kin. Daigaku Rik. Kenk. Hokuku* **28** 237 (1992)
126. A M Domingos, G M Sheldrick *Acta Crystallogr., Sect. B* **30** 519 (1974)
127. A I Yanovsky, N Ya Turova, E P Turevskaya, Yu T Struchkov *Koord. Khim.* **8** 153 (1982) [a]
128. V G Kessler, N Ya Turova, A N Panov, A I Yanovsky, A P Pisarevsky, Y T Struchkov *Polyhedron* **15** 335 (1996)
129. V S Nair, K S Hagen *Inorg. Chem.* **31** 4048 (1992)
130. S Daniele, L G Hubert-Pfalzgraf, J-C Daran *Polyhedron* **15** 1063 (1996)
131. Z A Starikova, A I Yanovsky, N M Kotova, M I Yanovskaya, N Ya Turova, D Benlian *Polyhedron* **16** 4347 (1997)
132. S C James, N C Norman, A G Orpen, M J Quayle, U Weckenmann *J. Chem. Soc., Dalton Trans.* 4159 (1996)
133. A Johansson, V G Kessler *Polyhedron* **19** 1791 (2000)
134. S Boulmaaz, L G Hubert-Pfalzgraf, S Halut, J-C Daran *J. Chem. Soc., Chem. Commun.* 601 (1994)
135. C Limberg, S Parsons, A J Downs *J. Chem. Soc., Chem. Commun.* 497 (1994)
136. V G Kessler, A N Panov, N Ya Turova, Z A Starikova, A I Yanovsky, F M Dolgushin, A P Pisarevsky, Yu T Struchkov *J. Chem. Soc., Dalton Trans.* 21 (1998)
137. N Ya Turova, V G Kessler, S I Kucheiko *Polyhedron* **10** 2617 (1991)
138. V G Kessler, N Ya Turova, A I Yanovsky, Yu T Struchkov, M A Fedotov *Zh. Obshch. Khim.* **60** 2769 (1990) [d]
139. P A Shcheglov, G A Seisenbaeva, S Gohil, D V Drobot, V G Kessler *Polyhedron* **21** 2317 (2002)
140. G Westin, R Norrestam, M Nygren, M Wijk *J. Solid State Chem.* **135** 149 (1998)
141. V G Kessler, A V Shevelkov, L A Bengtsson-Kloo *Polyhedron* **17** 965 (1998)
142. R Schmid, A Mosset, J Galy *J. Chem. Soc., Dalton Trans.* 1999 (1991)
143. V W Day, T A Eberspacher, W G Klemperer, C W Park, F S Rosenberg *J. Am. Chem. Soc.* **113** 8190 (1991)
144. D J Teff, K G Caulton *Inorg. Chem.* **38** 2240 (1999)
145. C S Weinert, I A Guzei, A L Rheingold, L R Sita *Organometallics* **17** 498 (1998)
146. R Finn, J Zubieta *J. Cluster Sci.* **11** 461 (2000)
147. U Bemm, R Norrestam, M Nygren, G Westin *Inorg. Chem.* **31** 2050 (1992)
148. J J H Edema, S Gambarotta, J J Smeets, A L Spek *Inorg. Chem.* **30** 1380 (1991)
149. K Hegetschweiler, H Schmalle, H M Streit, V Gramlich, H U Hund, I Erni *Inorg. Chem.* **31** 1299 (1992)

150. L G Hubert-Pfalzgraf, S Daniele, A Bennaceur, J-C Daran, J Veissermann *Polyhedron* **16** 1223 (1997)
151. V G Kessler, N Ya Turova, A I Yanovsky, A I Belokon, Yu T Struchkov *Zh. Neorg. Khim.* **36** 1662 (1991) [b]
152. E P Turevskaya, N Ya Turova, A I Belokon, D E Chebukov *Zh. Neorg. Khim.* **43** 1065 (1998) [b]
153. E M McCarron III, R L Harlow *Acta Crystallogr., Sect. C* **40** 1140 (1984)
154. L Ma, S Liu, J Zubieta *J. Chem. Soc., Chem. Commun.* 440 (1989)
155. S Liu, J Zubieta. *Polyhedron* **8** 537 (1989)
156. J A Samuels, W-C Chiang, J C Huffman, K L Trojan, W E Hatfield, D V Baxter, K G Caulton *Inorg. Chem.* **33** 2167 (1994)
157. A J Blake, A J Downs, C Limberg, S Parsons *J. Chem. Soc., Dalton Trans.* 3263 (1995)
158. R Kuhlman, B A Vaartstra, W E Streib, J C Huffman, K G Caulton *Inorg. Chem.* **32** 1272 (1993)
159. A I Yanovsky, M I Yanovskaya, V K Limar, V G Kessler, N Ya Turova, Yu T Struchkov *J. Chem. Soc., Chem. Commun.* 1605 (1991)
160. Z A Starikova, A I Yanovsky, D E Chebukov, E P Turevskaya, N Ya Turova *Zh. Neorg. Khim.* **43** 1308 (1998) [b]
161. J A Samuels, B A Vaartstra, J C Huffman, K L Trojan, W E Hatfield, K G Caulton *J. Am. Chem. Soc.* **112** 9623 (1990)
162. K G Caulton, M H Chisholm, S R Drake, K Folting, J C Huffman *Inorg. Chem.* **32** 816 (1993)
163. W J Evans, D G Griorikos, M A Greci, J W Ziller *Eur. J. Inorg. Chem.* 453 (2002)
164. M H Chisholm, K S Kramer, W E Streib *J. Cluster Sci.* **6** 135 (1995)
165. H Bock, T Hauck, C Näther, N Rösch, M Staufer, O D Häberlen *Angew. Chem., Int. Ed. Engl.* **34** 1353 (1995)
166. C M Jones, M D Burkart, R E Bachman, D L Serra, S J Hwa, K H Whitmire *J. Chem. Soc., Chem. Commun.* 1638 (1992)
167. M Veith, F Grätz, V Huch *Eur. J. Inorg. Chem.* 367 (2001)
168. F M Mackenzie, R E Mulvey, W Clegg, L Horsburgh *Polyhedron* **17** 993 (1998)
169. M I Khan, Q Chen, D P Goshorn, J Zubieta *Inorg. Chem.* **32** 672 (1993)
170. M I Khan, Q Chen, D P Goshorn, H Höpe, S Parkin, J Zubieta *J. Am. Chem. Soc.* **114** 3341 (1992)
171. M Cavaluzzo, Q Chen, J Zubieta *J. Chem. Soc., Chem. Commun.* 131 (1993)
172. S Asirvatham, M A Khan, K M Nicholas *Inorg. Chem.* **39** 2006 (2000)
173. Z A Starikova, N Ya Turova, D E Chebukov, A I Yanovsky *Zh. Neorg. Khim.* **48** 1275 (2003) [b]
174. M Yu Antipin, L P Didenko, L M Kachapina, A E Shilov, A K Shilova, Yu T Struchkov *J. Chem. Soc., Chem. Commun.* 1467 (1989)
175. A P Purdy, C F George *Polyhedron* **17** 4041 (1998)
176. U M Tripathi, A Schier, H Schmidbaur *Z. Naturforsch. B* **53** 434 (1998)
177. U Bemm, R Norrestam, M Nygren, G Westin *Inorg. Chem.* **32** 1597 (1993)
178. R Papiernik, L G Hubert-Pfalzgraf, J-C Daran, Y Jeannih *J. Chem. Soc., Chem. Commun.* 695 (1990)
179. D P Goldberg, A Caneschi, S J Lippard *J. Am. Chem. Soc.* **115** 9299 (1993)
180. Z A Starikova, V G Kessler, N Ya Turova, D E Tcheboukov, E V Suslova, G A Seisenbaeva, A I Yanovsky *Polyhedron* **23** 109 (2004)
181. U Bemm, R Norrestam, M Nygren, G Westin *J. Solid State Chem.* **134** 312 (1997)
182. V G Kessler, A N Panov, A Yu Borissevitch, N Ya Turova *J. Sol-Gel Sci. Technol.* **12** 81 (1998)
183. V W Day, T A Eberspacher, W G Klemperer, C W Park *J. Am. Chem. Soc.* **115** 8469 (1993)
184. N Steunou, F Robert, F Ribot, K Boubekeur, C Sanchez *Inorg. Chim. Acta* **279** 144 (1998)
185. N Steunou, F Ribot, K Boubekeur, J Maquet, C Sanchez *New J. Chem.* **23** 1079 (1999)
186. U Bemm, R Norrestam, M Nygren, G Westin *Inorg. Chem.* **34** 2367 (1995)
187. W J Evans, M S Sollberger *Inorg. Chem.* **27** 4417 (1988)
188. W J Evans, M S Sollberger, T P Hanusa *J. Am. Chem. Soc.* **110** 1841 (1988)
189. A Mosset, J Galy *C.R. Acad. Sci., Ser. 2* **307** 1747 (1988)
190. M I Khan, Y-S Lee, C J O'Connor, J Zubieta *J. Am. Chem. Soc.* **116** 5001 (1994)
191. N Steunou, G Kickelbick, K Boubekeur, C Sanchez *J. Chem. Soc., Dalton Trans.* 3653 (1999)
192. J F Campion, D A Payne, H K Chae, J K Maurin, S R Wilson *Inorg. Chem.* **30** 3244 (1991)
193. C F Campana, Y Chen, V W Day, W G Klemperer, R A Sparks *J. Chem. Soc., Dalton Trans.* 691 (1996)
194. T Greiser, O Jarchow, K-H Klaska, E Weiss *Chem. Ber.* **111** 3360 (1978)
195. I A M Pohl, G Westin, M Kritikos *Chem.-Eur. J.* **7** 3438 (2001)
196. G Westin, M Nygren *J. Mater. Chem.* **4** 1275 (1994)
197. M I Khan, J Zubieta *J. Am. Chem. Soc.* **114** 10 058 (1992)
198. U Bemm, K Lashgari, R Norrestam, M Nygren, G Westin *J. Solid State Chem.* **108** 243 (1994)
199. M H Chisholm *Polyhedron* **2** 681 (1983)
200. M H Chisholm, K Folting, J C Huffman, C C Kirkpatrick, A L Ratermann *J. Am. Chem. Soc.* **103** 1305 (1981)
201. V G Kessler, E P Turevskaya, S I Kucheiko, N I Kozlova, N Ya Turova, I E Obvintseva, M I Yanovskaya, in *Better Ceramics through Chemistry VI (MRS Proceedings), Boston, 1994* Vol. 346, p. 3
202. V G Kessler, S Yu Vasil'ev, A I Belokon, N Ya Turova *Zh. Obshch. Khim.* **60** 2629 (1990) [d]
203. T G Brilkina, V A Shushunov *Reaktsii Metalloorganicheskikh Soedinenii s Kislorodom i Perekisyami* (Reactions of Organometallic Compounds with Oxygen and Peroxides) (Moscow: Nauka, 1966)
204. N Ya Turova, E P Turevskaya, M I Yanovskaya, N M Kotova, R R Shifrina *Zh. Neorg. Khim.* **38** 1137 (1993) [b]
205. E C Ashby, A B Goel, J N Argyropoulos *Tetrahedron Lett.* **23** 2273 (1982)
206. N Ya Turova, N I Kozlova, M I Yanovskaya *Koord. Khim.* **6** 508 (1980) [a]
207. E Amberger, R Hönigschmidt-Grossich *Chem. Ber.* **98** 3795 (1965)
208. M I Karpovskaya, N Ya Turova, A V Novoselova *Koord. Khim.* **3** 1296 (1977) [a]
209. D C Bradley, B N Chakravarti, A K Chatterjee, W Wardlaw, A Whitley *J. Chem. Soc.* 99 (1958)
210. S R Drake, W E Streib, M H Chisholm, K G Caulton *Inorg. Chem.* **29** 2707 (1990)
211. S C Goel, M A Matchett, M Y Chiang, W E Buhro *J. Am. Chem. Soc.* **113** 1844 (1991)
212. K G Caulton, M H Chisholm, S R Drake, K Folting, J C Huffman, W E Streib *Inorg. Chem.* **32** 1970 (1993)
213. K G Caulton, M H Chisholm, S R Drake, K Folting *Inorg. Chem.* **30** 1500 (1991)
214. S R Drake, D J Otway, M B Hursthouse, K M A Malik *Polyhedron* **11** 1995 (1992)
215. E P Turevskaya, M I Yanovskaya, V K Lymar', N Ya Turova *Zh. Neorg. Khim.* **38** 609 (1993) [b]
216. E P Turevskaya, V G Kessler, N Ya Turova, A I Yanovsky, Yu T Struchkov *J. Chem. Soc., Chem. Commun.* 2303 (1994)
217. O Poncelet, L G Hubert-Pfalzgraf, J-C Daran, R Astier *J. Chem. Soc., Chem. Commun.* 1846 (1989)
218. L G Westin, M Kritikos, A Caneschi *Chem. Commun.* 1012 (2003)
219. S Daniele, L G Hubert-Pfalzgraf, J Vaissermann *Polyhedron* **17** 4249 (1998)
220. O Poncelet, L G Hubert-Pfalzgraf *Polyhedron* **8** 2183 (1989)
221. W J Evans, T J Deming, J M Olofson, J W Ziller *Inorg. Chem.* **28** 4027 (1989)
222. R Papiernik, L G Hubert-Pfalzgraf, M C Massiani *Inorg. Chim. Acta* **165** 1 (1989)
223. R Papiernik, L G Hubert-Pfalzgraf, M C Massiani *Polyhedron* **10** 1657 (1991)

224. E P Turevskaya, V B Bergo, M I Yanovskaya, N Ya Turova *Zh. Neorg. Khim.* **41** 721 (1996) [b]
225. E P Turevskaya, N I Kozlova, N Ya Turova, A I Belokon, D V Berdyev, V G Kessler, Yu K Grishin *Izv. Akad. Nauk, Ser. Khim.* 752 (1995) [c]
doi> 226. V W Day, W G Klemperer, M M Pafford *Inorg. Chem.* **40** 5738 (2001)
227. A M Bol'shakov, M A Glushkova, Yu A Buslaev *Koord. Khim.* **4** 1075 (1978) [a]
doi> 228. E Jacob *Angew. Chem., Int. Ed. Engl.* **21** 142 (1982)
doi> 229. G A Seisenbaeva, L Kloo, P Werndrup, V G Kessler *Inorg. Chem.* **40** 3815 (2001)
230. G Tatzel, M Greune, J Weidlein, E Jacob *Z. Anorg. Allg. Chem.* **533** 83 (1986)
231. N Ya Turova, V G Kessler *Zh. Obshch. Khim.* **60** 113 (1990) [d]
232. D C Bradley, M H Chisholm, M W Extine, M E Stager *Inorg. Chem.* **16** 1794 (1977)
233. F A Cotton, W Schwotzer, E S Shamshoum *Inorg. Chem.* **23** 4111 (1984)
234. C I Kucheiko, N Ya Turova, N I Kozlova *Koord. Khim.* **11** 1656 (1985) [a]
235. D E Chebukov, N Ya Turova, A V Korolev, A I Belokon *Zh. Neorg. Khim.* **42** 1642 (1997) [b]
236. N Ya Turova, E P Turevskaya, V G Kessler, N I Kozlova, A I Belokon *Zh. Neorg. Khim.* **37** 50 (1992) [b]
237. H Schmidbaur, M Bergfeld, F Schindler *Z. Anorg. Allg. Chem.* **363** 73 (1968)
doi> 238. C D Chandler, G D Fallon, B O West *J. Chem. Soc., Chem. Commun.* 1063 (1990)
doi> 239. D C Bradley, I M Thomas *J. Chem. Soc., A* 3404 (1959)
doi> 240. J Caruso, M J Hampden-Smith *J. Sol-Gel Sci. Technol.* **8** 35 (1997)
doi> 241. L G Hubert-Pfalzgraf, V Abada, J Waissermann *J. Chem. Soc., Dalton Trans.* 2407 (1999)
242. H Ulich, W Nespital *Z. Phys. Chem.* **165** 294 (1933)
doi> 243. E P Turevskaya, D V Berdyev, N Ya Turova, Z A Starikova, A I Yanovsky, Yu T Struchkov, A I Belokon *Polyhedron* **16** 663 (1997)
244. T V Rogova, N Ya Turova, N I Kozlova *Koord. Khim.* **12** 762 (1986) [a]
doi> 245. D C Bradley, H Chudzynska, M B Hursthouse, M Motevalli *Polyhedron* **10** 1049 (1991)
246. D E Chebukov, N Ya Turova, A I Belokon *Zh. Neorg. Khim.* **44** 869 (1999) [b]
doi> 247. M Veith, S Mathur, V Huch *Inorg. Chem.* **36** 2391 (1997)
248. W R Russo, W H Nelson *J. Am. Chem. Soc.* **92** 1521 (1970)
249. I E Obvintseva, M I Yanovskaya, S I Kucheiko, N Ya Turova, R R Shifrina *Neorg. Mater.* **24** 790 (1988) [e]

[a] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[b] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[d] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[e] — *Inorg. Mater. (Engl. Transl.)*