Molecular structure design and synthetic approaches to the heterometallic alkoxide complexes (soft chemistry approach to inorganic materials by the eyes of a crystallographer)

Vadim G. Kessler

Department of Chemistry, SLU, Box 7015, Uppsala, Sweden. E-mail: Vadim.Kessler@kemi.slu.se; Fax: 46 18 673476; Tel: 46 18 671541

General principles of formation and stability of the hetero-metallic alkoxides existing due to Lewis Acid–Base interaction, isomorphous substitution and heterometallic metal–metal bonds are discussed. The molecular structure design approach based on the choice of a proper molecular structure type and completing it with the ligands, providing both the necessary number of donor atoms and the sterical protection of the metal–oxygen core, is presented. Its applications in prediction of the composition and structure of single source precursors of inorganic materials are demonstrated for such classes of compounds as oxoalkoxides, alkoxide β-diketonates, alkoxide carboxylates, derivatives of functional alcohols, metallatranes and metallasiloxanes.

The development of modern technologies with their appeal for miniaturization and increased performance of the applied materials has urged for already more than 20 years the search for techniques, permitting much better and more versatile control over the composition, structure and morphology of the produced inorganic materials than could be provided by the traditional reactions of solid state synthesis. This search gave rise to a broad variety of synthetic procedures permitting to obtain the desired products under mild conditions, which received the common name of the *Soft Chemistry Approach*. In fact the majority of these techniques, for example, Sol–Gel technology, MOCVD, MOD, involve the application of metal-lorganic compounds or metal complexes with organic ligands, such as alkoxides, β-diketonates, carboxylates *etc*.,—easily hydrolytically or thermally decomposable substances, referred to usually as the Molecular Precursors. The interest in materials with complex composition and nanometer level defined morphology and physical properties focused more recently the attention of researchers on the *Single Source Precursors*

(SSP)—the molecules containing all the necessary elements in the proper ratio and decomposable in a controllable manner under mild conditions.[1] The majority of the SSP known today are the heterometallic and often heteroleptic alkoxide complexes and this paper will make an attempt to present a general concept of preparation of the purposely designed representatives of this family.

Basic principles in formation and structural description of the heterometallic alkoxides

The formation of heterometallic complexes in general can occur due to one of the three following factors:

(1) Lewis Acid–Base interaction (exploiting the difference between two or several metal atoms in electronegativity, which permits to consider one metal center as a stronger acceptor of the electron density and the alkoxide or other ligands at the other as a better donor of it).

(2) Formation of a heterometallic metal–metal bond, which in this case should also obviously be a donor–acceptor interaction.

(3) Isomorphous substitution, which might not lead to formation of the true heterometallic species, but provides in any case the homogenization at the molecular level.

Originally, when Meerwein and Bersin first discovered the heterometallic alkoxides in 1929, their formation was attributed to the Brønsted Acid–Base interaction.[2] The technique applied was simply the titration in the alcoholic media using acid–base indicators for the determination of the equivalence points and the authors were convinced in the existence of the protic *ansolvoacids* like $H[Al(OR)_4]$, $H[HZr(OR)_6]$† and $H[Nb(OR)_6]$ that could be neutralized by the alkoxide anions, OR^-, from the alkali alkoxides. The subsequent studies of the molecular structures of homometallic alkoxides in the solid state and in solution have not confirmed the existence of ansolvoacids. It has been shown that even the complexes obtained in these studies, the so called 'Meerwein salts' (derived from the cations of active metals and anions of the ansolvoacids), are in fact, with some very few exceptions, the molecular compounds with the predominantly covalent bonding between the metal and the oxygen atoms. Their formation was definitely due to the Lewis Acid–Base interaction between the metal atoms and the alkoxide ligands. However, the idea of Meerwein concerning the existence of alkoxometallates has survived, being extremely attractive as the principle for classification of the heterometallic species.[3] Even the recent re-edition of the classical book by Bradley and Mehrotra,[4] discusses the formation and the structural features of the heterometallic derivatives practically exclusively on the basis of this concept, distinguishing the alkoxometallate anions in their molecules and considering the ways in which they are attached to the more electropositive

Vadim G. Kessler graduated with honours from the Moscow State University (MSU) in 1987 and obtained there his Ph.D. degree in 1990 with Dr N. Ya. Turova, being appointed directly after it an Assistant Professor at the Department of Inorganic Chemistry MSU. He spent his first sabbatical year (1992/93) as an associate Researcher of CNRS at the University of Nice with Professor L. G. Hubert-Pfalzgraf and became an Associate Professor at MSU in 1995. The second sabbatical year, 1995/96, he worked as visiting scientist at the University of Stockholm with Professor M. Nygren and moved finally to Sweden, being appointed an Associate Professor at the Department of Chemistry, SLU in 1997. The area of his scientific interests covers all the aspects in search for understanding of the structural and mechanistic reasons of the chemical reactivity of inorganic and organoelement compounds.

metal atoms. This approach turned out to be rather strongly limited in its abilities to predict the compositions of the new heterometallic compounds. The formation and stability of the oxoalkoxides—the products of partial decomposition of the homoleptic species turned out not to find the place in this description. At the same time, it has been shown that these are just the oxoalkoxide derivatives that very often play the role of SSP and can even serve as building blocks in the formation of oxide materials in Sol–Gel technology.[5] A principally new way of description was proposed in 1990 by Caulton and Hubert-Pfalzgraf, who have observed that complexes with a certain ratio of the metal atoms of different kinds in their molecules display usually the molecular structures belonging to a rather limited variety of structural types.[6]

The consequent analysis of the data of more than 1000 X-ray single crystal studies of metal alkoxides (both homo- and heterometallic ones), made until the end of 2000, revealed the existence of a number of stable types of molecular structures that can often be described as fragments of the hexagonal or cubic packing in the metal–oxygen cores (smaller, especially primary ligands, bigger metal atoms) or as chains containing $M(\mu\text{-}OR)_2M$ or $M(\mu\text{-}OR)_3M$ fragments (bigger ligands—secondary, tertiary ones—and smaller metal atoms). This classification has been presented in the most recently published textbook in the Chemistry of Metal Alkoxides.[7] The most fascinating observation was that the size and the number of metal atoms and ligands (donor oxygen atoms) were definitely more important than their chemical nature. For example, the almost analogous trinuclear fragments of the hexagonal packing have been observed in the structures of $LiZr_2(O^iPr)_9(^iPrOH)$[8] and $NaMo_2O_4(O^iPr)_5(^iPrOH)$,[9,10] pairs of such fragments connected by a pair of bridging ligands *via* one corner of the triangle in those of $[BaZr_2(OiPr)_{10}]_2$[11] and $[PbZr_2(OiPr)_{10}]_2$.[12] By far the most widespread structure type for both homo- and heterometallic species turned out to be the one formed by two trinuclear fragments of hexagonal packing fused along one of the edges, first discovered in the structure of titanium methoxide, $Ti_4(OMe)_{16}$[13] (Fig. 1).

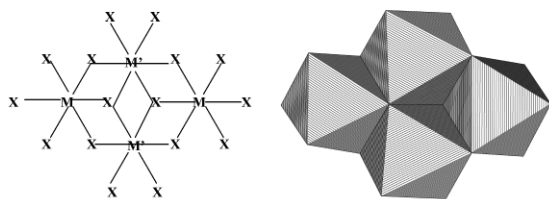**Fig. 1** Bonding scheme and polyhedral presentation for the M_4X_{16} (Ti_4-$(OMe)_{16}$) structure type.

It was observed in the structures of chemically different compounds such as $[NaWO(OEt)_5(EtOH)_2]_2$,[10,14] $[LiNbO\text{-}(OEt)_4(EtOH)]_2$,[15] $[M^IM^{VI}O_2(OC_2H_4OMe)_3]_2$,[10,16] M^I = Li, Na, M^{VI} = Mo, W, and more recently $[MgNbO(O\text{-}Me)_5(MeOH)_2]_2$,[17] $[NaFe(O^tBu)_3(THF)]_2$,[18] $Re_4O_6(O^iPr)_{10}$[19] and $Co_4(OC_2H_4OEt)_6Cl_2$.[20] It is important to mention that the structure type in this case was defined by the number and functions of the bridging ligands in the core, $M_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4$, while the total coordination numbers and thus the coordination polyhedra of the metal atoms were apparently defined by the ratios in the metal and the ligand size.

It is necessary to mention that the heteronuclear metal–metal bond formation and isomorphous substitution have more recently also found application in preparation of the heterometallic alkoxides and will be addressed below.

Molecular structure design concept

The fact that the molecular structures of the stable crystalline heterometallic complexes were following quite simple geometrical principles was opening the prospect of the design of new structures for particular applications. It was speaking strongly in favor of the thermodynamic control in formation of the heterometallic species.‡ A trend to formation of the molecules belonging to a stable structure type might become a decisive factor in formation of the heterometallic complexes. The design approach was then to be based on (1) the choice of the structure type to be used, (2) calculation of the necessary number of the donor atoms, (3) choice of the ligands with proper composition and sterical requirements to be able to provide both the right number of donor functions and the protection of the chosen core of metal and donor atoms (put the metal atoms into the thermodynamically preferred coordination polyhedra).

This concept can be considered as the development of the *Structure Theory* once proposed by D. C. Bradley for the prediction of the structures of homometallic coordination oligomers.[4,22]

It was first applied 10 years ago in the preparation of single-source precursors for the ferroelectric films of $BaTiO_3$. Although quite a number of mixed metal alkoxide species of barium and titanium have been discovered until then, most of them displayed stoichiometries different from that required for $BaTiO_3$. Thus the compounds formed in the $Ba(OEt)_2$–$Ti(OEt)_4$–EtOH system were $BaTi_4(OEt)_{18}$,[23] $BaTi_2(OEt)_{10}(EtOH)_5$ and $Ba_4Ti_2O(OEt)_{14}(EtOH)_8$,[24] which explained quite clearly, why the single-phase films could not be prepared using the ethoxide precursor solutions. No homoleptic alkoxide precursors with the Ba : Ti = 1 : 1 ratio could be found in the isopropoxide or *n*-butoxide systems either, but the oxidation of these solutions or their partial hydrolysis led to the single-source oxo-precursors, $[BaTiO(O^iPr)_4]_4(^iPrOH)_n$ (n = 3, 4)[25] and $[BaTiO(O^nBu)_4]_4(^nBuOH)_x$.[5] The stability of the latter was, however, quite limited urging the continued search for more suitable SSP for this material. Using the principles described above, we have chosen as the model structure type that of $Ti_4(OMe)_{16}$—the one by far best represented for the compounds with 1 : 1 stoichiometry. Its core contains 4 metal atoms (2 + 2 for the 1 : 1 composition) and 16 donor atoms. The donor atoms from only the alkoxide ligands (from barium 2 × 2 and from titanium 2 × 4, 12 in total) were obviously too few to stabilize the chosen core: 4 additional donor atoms were to be introduced. It was clear that these additional donor atoms were to be somehow connected to the other ones bearing the negative charge in the structure and application of the chelating ligands appeared a reasonable solution. Addition of 4 equivalents of a rather bulky β-diketone, tetramethylheptanedione (Hthd), to the solution of the ethoxides in 1 : 1 ratio (in toluene) resulted with rather high yield in the structure corresponding very closely to the predicted one[26] (Fig. 2), but displaying slightly increased coordination numbers for the Ba atoms (due to one extra solvating molecule of ethanol):

$$2\ Ba(OEt)_2 + 2\ Ti(OEt)_4 + 4\ Hthd \rightarrow$$
$$Ba_2Ti_2(thd)_4(OEt)_8(EtOH)_2 + 2\ EtOH$$
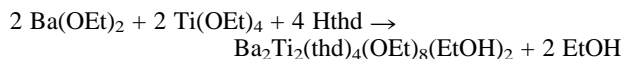
The same product could be obtained *via* interaction of barium β-diketonate with titanium ethoxide in toluene–ethanol mixture:

$$2\ Ba(thd)_2 + 2\ Ti(OEt)_4 + 2\ EtOH \rightarrow$$
$$Ba_2Ti_2(thd)_4(OEt)_8(EtOH)_2$$
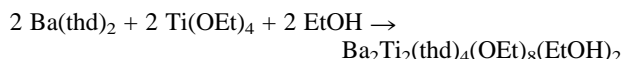
It is important to mention that the first approach was completely unsuccessful in the preparation of the analogous acetylacetonate derivative, but it could in fact be obtained by the reaction of unsolvated barium acetylacetonate with titanium ethoxide in pure toluene:
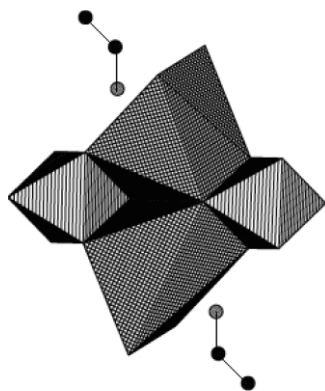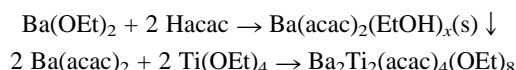
Fig. 2 Polyhedral presentation of the molecular structure of $Ba_2Ti_2(thd)_4$-$(OEt)_8(EtOH)_2$.

$$Ba(OEt)_2 + 2\ Hacac \rightarrow Ba(acac)_2(EtOH)_x(s) \downarrow$$

$$2\ Ba(acac)_2 + 2\ Ti(OEt)_4 \rightarrow Ba_2Ti_2(acac)_4(OEt)_8$$

The latter reaction was obviously displaying an inverted case in the Lewis Acid–Base interaction: the need of barium cation in extra electron density could more efficiently be satisfied with the alcohol molecules than with the alkoxide ligands provided by the titanium ethoxide.

This observation was envisaging the role of the nature of solvent as an important parameter in the synthesis of hetero-metallic alkoxides: it became clear that the donor solvents (Lewis bases) would be able to destroy the heterometallic species *via* formation of the homometallic solvated ones.

Application domains for the molecular structure design concept

The principles of the design concept formulated above can quite successfully be applied for the description of the structure of homoleptic (alkoxide-only) heterometallic complexes, formed by interaction of two homometallic species in solution. The major interest in its application arises, however, in cases when this simple approach does not provide the heterometallic species at all or leads to those possessing 'wrong' compositions. The design becomes crucial in the cases of the chemical modifica-tion and, in the first hand, formation of the heterometallic oxoalkoxides, and also in the reactions resulting in formation of the heteroleptic complexes containing other organic ligands than alkoxides—β-diketonates, carboxylates *etc*. (both *via* the chemical modifications of the homoleptic alkoxides and *via* reactions of a β-diketonate or carboxylate of one metal with an alkoxide of the other). In all these cases the wrong reaction stoichiometry can lead to formation of very complex mixtures of the products, from which it might by very difficult or impossible to isolate the desired SSP.

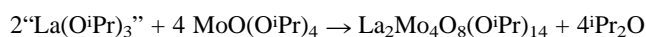## Formation of heterometallic oxoalkoxides

Preparation of oxoalkoxides

The formation of the oxoalkoxide complexes is in fact a general tool leading to strengthening of the interaction between the components in formation of the heterometallic species. It serves to increase the Lewis acidity of the reactants as the formal replacement of two alkoxide group with one oxo-ligand should result in the coordination unsaturation of the species formed. Among the synthetic approaches to the oxoalkoxides it is necessary to mention:

(a) Microhydrolysis—addition of the controlled amounts of water in organic solvents to a solution of one or several alkoxides (the best studied and most widely used one), for example, in formation of aluminium oxoalkoxides:[27]

$$4\ Al(O^iBu)_3 + H_2O \rightarrow Al_4O(O^iBu)_{10}(^iBuOH) + HO^iBu$$

(b) Ether elimination reaction. It is especially characteristic of the derivatives of multivalent early transition elements, such as $Mo(VI)$,[10,28,29] $W(VI)$,[10,14] $Nb(V)$,[30–32] for example:

$$Mo(OMe)_6 \rightarrow MoO(OMe)_4 + Me_2O$$

$$2\text{"}La(O^iPr)_3\text{"} + 4\ MoO(O^iPr)_4 \rightarrow La_2Mo_4O_8(O^iPr)_{14} + 4^iPr_2O$$

This reaction was found to be catalyzed by the acidic reagents, for example:[33,34]

$$MoO(OEt)_4 + H_2O(H^+) \rightarrow$$
$$Et_2O + [H_2Mo_6O_{19}]^{2-}\ (molybdenum\ blue)$$

In the presence of the pronouncedly basic (alkaline, alkaline earth) alkoxides it was found to produce directly the inorganic molybdates or tungstates:[10]

$$MoO(OEt)_4 + 2\ NaOEt \rightarrow Na_2MoO_4 \downarrow + 3\ Et_2O$$
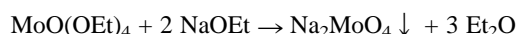
The formation of the oxospecies on reactions of metal alkoxides with aldehydes and ketones:[35]

$$MoO(OEt)_4 + CH_3CHO \rightarrow MoO_2(OEt)_2 + CH_3CH(OEt)_2$$

and that on the thermal treatment on desolvation of zirconium or hafnium alkoxides:[36,37]

$$3\ Zr(O^iPr)_4(^iPrOH) \rightarrow$$
$$Zr_3O(O^iPr)_{10} + CH_3CH=CH_2 + 4\ ^iPrOH$$
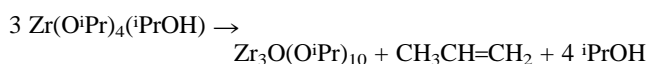
have been supposed to follow the same reaction mechanism.

(c) Reduction of the highly charged metal centers by the β-hydrogen transfer is for the metal alkoxides quite often accompanying other processes such as hydrolysis[38] and ether elimination,[39] for example:

$$VO(OEt)_3 + H_2O \rightarrow V_6O_7(OEt)_{12} + CH_3CHO + \dots$$

$$6MoO(O^iPr)_4 \rightarrow$$
$$Mo_6O_{10}(O^iPr)_{12} + 2\ CH_3COCH_3 + 2\ ^iPrOH + 4\ (^iPr)_2O$$
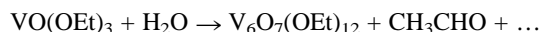
(d) Oxidation of the alkoxide ligand by the traces of oxygen dissolved in applied solvents is especially characteristic of the most basic derivatives, such as those of alkali, alkaline earth and rare earth ones, for example:[40]

$$Ca(OEt)_2(EtOH)_4 + O_2 \rightarrow Ca_6O_2(OEt)_8(EtOH)_{12+2}$$
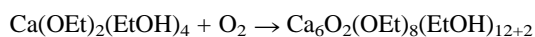
(e) Oxidation of the metal–metal bonds by purposely pro-vided dry oxygen, for example:[41]

$$LiMo_2O_2(OEt)_7 + \tfrac{1}{2}\ O_2 \rightarrow LiMo_2O_4(OEt)_5(EtOH)$$
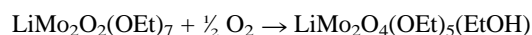
Molecular structure design examples

Developing the application of the molecular structure design concept to the oxoalkoxide complexes we decided to choose the earlier completely unexplored area—derivatives of the pairs of the strongest Lewis acids, such as molybdenum and niobium or molybdenum and tantalum, as the objects. These systems are of interest as precursors of mixed oxide and especially sulfide materials for catalytic applications.[42] As the first model for the new species we have chosen the molecule of $Mo_6O_{10}(O^iPr)_{12}$ (Fig. 3), in the structure of which it was clearly possible to

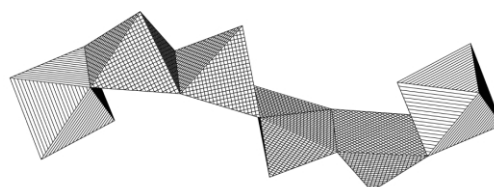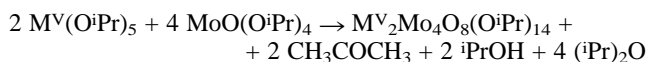**Fig. 3** Polyhedral presentation of the molecular structures of $Mo_6O_{10}(O^iPr)_{12}$ and $M^V_2Mo_4O_8(O^iPr)_{14}$.

distinguish two kinds of building blocks—the pairs of tetra-gonal pyramids, $(\mu\text{-}OR)_2Mo^VO(\mu\text{-}O)_2Mo^VO(\mu\text{-}OR)_2$ (with a

single Mo–Mo bond) and octahedra, $Mo^{VI}O(O^iPr)_5$. As the bond lengths and angles for the Mo(vi) and Nb(v) or Ta(v) were nearly almost identical in the known molecular structures, we hoped to be able to obtain the corresponding heterometallic analogs by mixing $M^V(O^iPr)_5$ and $MoO(O^iPr)_4$ in 1:2 ratio with the subsequent thermal treatment in order to accelerate the reaction described above in (c):

$$2\ M^V(O^iPr)_5 + 4\ MoO(O^iPr)_4 \rightarrow M^V_2Mo_4O_8(O^iPr)_{14} + 2\ CH_3COCH_3 + 2\ {}^iPrOH + 4\ (^iPr)_2O$$

To our great surprise, the product isolated from the first test of this reaction between the molybdenum and tantalum alkoxides had a different structure (see Fig. 4) and composition,
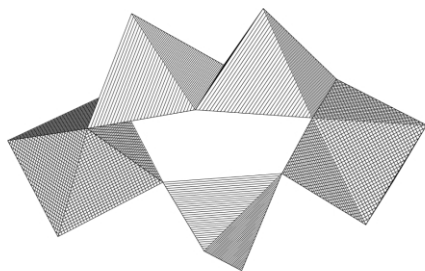
Fig. 4 Polyhedral presentation of the molecular structure of Ta_2-$Mo_3O_8(O^iPr)_{12}$.

$Ta_2Mo_3O_8(O^iPr)_{12}$. In addition to the predicted building blocks it contained also a tetraoxomolybdate anion, indicating the more deep transformation into the oxosubstituted species than the one, following the stoichiometry of the reaction pathway in (c). It turned out that the tantalum isopropoxide, we applied, was contaminated with $Ta_2(OMe)_2(O^iPr)_8$, producing on thermolysis MeOH, which in the presence of molybdenum alkoxides reacted further with acetone (in contrast to the isopropanol, inert due to the sterical hindrance) and provided $(CH_3)_2C(OMe)_2$ along with more oxosubstituted species (see (b) above). Application of the pure $Nb(O^iPr)_5$ or $Ta(O^iPr)_5$ resulted in practically quantitative isolation of the corresponding $M^V_2Mo_4O_8(O^iPr)_{14}$[43–45]—precursors for the materials with M^V : Mo = 1:2 ratio (Fig. 3).

In the search for possible models with a different metal stoichiometry, we turned to the structure of the zinc–tantalum heterometallic alkoxide, $[IZnTa_2O_2(O^iPr)_7]_2$ (Fig. 5a).[46] The
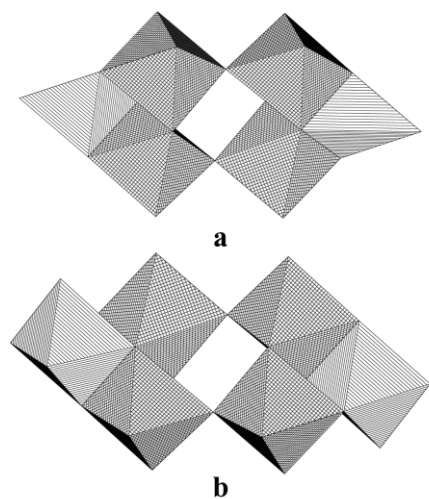

Fig. 5 Polyhedral presentation of the molecular structures of $[IZn$-$Ta_2O_2(O^iPr)_7]_2$ (a) and $Mo_2Ta_4O_8(OMe)_{16}$ (b).

bonding parameters in the tetrahedral arrangement for Zn appeared quite close to those in the octahedral $MoO_2(OR)_4$ fragments, described in refs. 10 and 41. Using the general

analogy between isopropoxide and methoxide derivatives of multivalent early transition metals,[7] we applied the micro-hydrolysis of the mixture of molybdenum and tantalum methoxides in 1:2 ratio in toluene and obtained the predicted product (Fig. 5b) with a high yield:[43,47]

$$2\ MoO(OMe)_4 + 4\ Ta(OMe)_5 + 6\ H_2O \rightarrow Mo_2Ta_4O_8(OMe)_{16} + 12\ MeOH$$
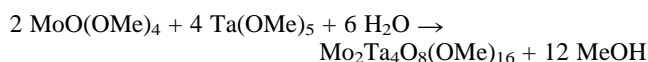
It is necessary to mention that the best technique for the isolation of this compound was the evacuation of the crude product and its recrystallization from toluene. The micro-hydrolysis in the alcohol media was repeated resulting in precipitation of the insoluble $MoO_2(OMe)_2$, confirming the absence of Lewis bases to be a compulsory requirement for such systems.

As chemical modification most often changes the metal stoichiometry in the heterometallic species,[25,26] we have followed the oxidation of the derivatives of molybdenum(v) and niobium and tantalum, $M^V_2Mo_4O_8(O^iPr)$,[14] by the dry oxygen. This reaction was found to lead to the heterometallic species of 1:1 composition with a metal–oxygen core related to the solid-state packing of the ReO_3 type, unknown earlier in the chemistry of metal alkoxides (Fig. 6a):[47]
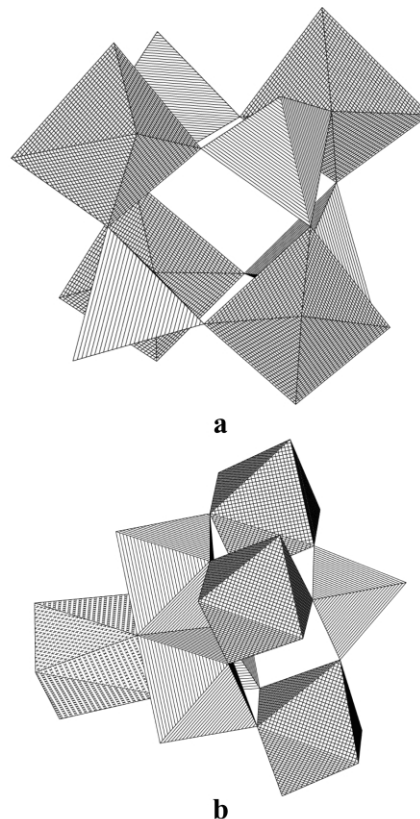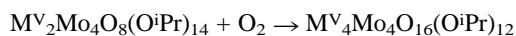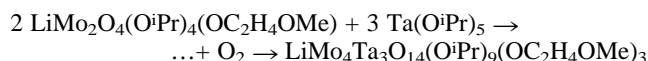
$$M^V_2Mo_4O_8(O^iPr)_{14} + O_2 \rightarrow M^V_4Mo_4O_{16}(O^iPr)_{12}$$

Fig. 6 Polyhedral presentation of the molecular structures of Ta_4-$Mo_4O_{16}(O^iPr)_{12}$ (a) and $LiMo_4Ta_3O_{14}(O^iPr)_9(OC_2H_4OMe)_3$ (b).
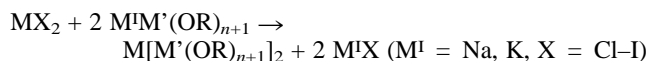
The molecular structure of this compound is built up of four $MoO(\mu\text{-}O)_3$ tetrahedra and four $Ta(OR)_3(\mu\text{-}O)_3$ octahedra alternating with each other. The bonding parameters in the latter were quite close to those for the $Li(OC_2H_4OMe)_3$ trigonal prisms, observed in the structures of Li-M^{VI} 2-methoxyeth-oxides.[41] Using $LiMo_2O_4(O^iPr)_4(OC_2H_4OMe)$ instead of $MoO(O^iPr)_4$ in the synthesis of reduced Mo-Ta species and applying the subsequent oxidation it was possible to isolate the single crystals of the corresponding substitution product (Fig. 6b):[47]

$2 \text{LiMo}_2\text{O}_4(\text{O}^i\text{Pr})_4(\text{OC}_2\text{H}_4\text{OMe}) + 3 \text{Ta}(\text{O}^i\text{Pr})_5 \rightarrow$
$$\ldots + \text{O}_2 \rightarrow \text{LiMo}_4\text{Ta}_3\text{O}_{14}(\text{O}^i\text{Pr})_9(\text{OC}_2\text{H}_4\text{OMe})_3$$

The resulting structure was the subject of compression because of the lower charge of the introduced unit and therefore need in smaller number of bridging oxoligands, but its general motive remained clearly recognizable.

Interaction of metal complexes with chelating ligands and metal alkoxides

The aliphatic alkoxide derivatives of the elements belonging to the end of the 3d transition series, such as Mn, Co, Ni, Cu and Zn, are known as polymeric, insoluble and poorly reactive species. The traditional approach to their heterometallic derivatives is based on the salt elimination reaction,[4,6,7] producing precursors of only strictly given stoichiometry:

$\text{MX}_2 + 2 \text{M}^I\text{M}'(\text{OR})_{n+1} \rightarrow$
$$\text{M}[\text{M}'(\text{OR})_{n+1}]_2 + 2 \text{M}^I\text{X} \ (\text{M}^I = \text{Na, K, X} = \text{Cl–I})$$
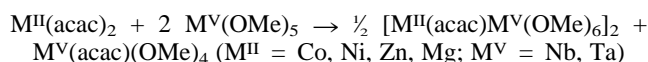
is in some cases technically quite complicated and might produce samples contaminated with alkali metals or halides. The industrial Sol–Gel approaches to these materials are often applying derivatives of these metals and chelating organic ligands, such as β-diketonates[4,7] or aminoalkoxides,[48,49] that are more stable and soluble in organic solvents, for the preparation of precursor solutions. The industrial Sol–Gel approaches to these materials are often applied for the preparation of precursor solutions they are more stable and soluble in organic solvents, derivatives of these metals and chelating organic ligands such as β-diketonates[4,7] or aminoalkoxides.[48,49] It appeared therefore rather interesting to investigate and try to predict the molecular structures originating from the reaction of these species with multivalent metal alkoxides, applied currently as precursors of the other components in related materials.

Derivatives of primary alcohols

With the size of the late transition metal atoms being much smaller than that of barium atoms, it was possible to anticipate in this case the formation of the mixed-metal β-diketonatoalkoxides with a 1:1 metal ratio and the M_4X_{16} structure type (as those found in search for BaTiO_3 precursors above, see Fig. 2). Much smaller chelating ancillary ligands than Hthd were to be used in order not to disturb the core geometry. In fact, the first representative of this family, $\text{Co}_2\text{Zr}_2(\text{acac})_2(\text{O}^n\text{Pr})_{10}$,[50] had already at that point been discovered to be formed with low yield in the interaction of $\text{Co}(\text{acac})_2$ and $\text{Zr}(\text{O}^n\text{Pr})_4$. The latter can be explained by several reasons, such as the $\text{Zr}(\text{O}^n\text{Pr})_4$ being always contaminated with oxo-species, and also by the application of $^n\text{PrOH}$ (a Lewis base) as solvent for this reaction in ref. 50.

The first systems considered were those to be produced *via* the reaction of $\text{M}^V(\text{OMe})_5$ and $\text{M}^{II}(\text{acac})_2$. The metal–oxygen M_4X_{16} core had in this case to have a total negative charge for ligands equal to 14 ($2 \times 2 + 2 \times 5$). This corresponded to the presence of only 2 acac-ligands (to provide 2 additional donor atoms for the total of 16 in the core). That meant that 2 acac ligands, initially present on the late transition metal atoms, were to be replaced by the alkoxide ones and demanded the application of a double access of the metal alkoxide to achieve the complete conversion in this reaction:[51]

$\text{M}^{II}(\text{acac})_2 + 2 \text{M}^V(\text{OMe})_5 \rightarrow \frac{1}{2} [\text{M}^{II}(\text{acac})\text{M}^V(\text{OMe})_6]_2 +$
$$\text{M}^V(\text{acac})(\text{OMe})_4 \ (\text{M}^{II} = \text{Co, Ni, Zn, Mg; M}^V = \text{Nb, Ta})$$

The yields were found to be practically quantitative and the molecular structures of the heterometallic species corresponded

exactly to the expectations (Fig. 7). The following reaction pathway was proposed (for Co-Ta species as an example):
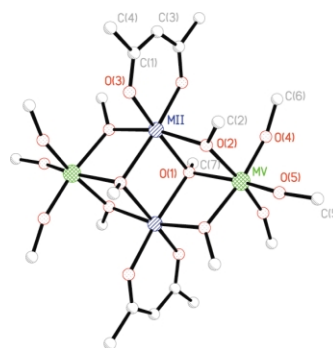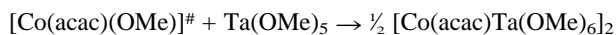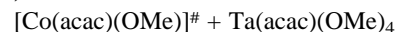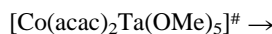

Fig. 7 The molecular structure of $[\text{M}^{II}(\text{acac})\text{M}^V(\text{OMe})_6]_2$.

$$\text{Ta}_2(\text{OMe})_{10} \rightleftharpoons 2 \text{Ta}(\text{OMe})_5$$
$$[\text{Co}(\text{acac})_2]_4 \rightleftharpoons 4 \text{Co}(\text{acac})_2$$
$$\text{Co}(\text{acac})_2 + \text{Ta}(\text{OMe})_5 \rightarrow [\text{Co}(\text{acac})_2\text{Ta}(\text{OMe})_5]^\#$$

$[\text{Co}(\text{acac})_2\text{Ta}(\text{OMe})_5]^\# \rightarrow$
$$[\text{Co}(\text{acac})(\text{OMe})]^\# + \text{Ta}(\text{acac})(\text{OMe})_4$$

$$[\text{Co}(\text{acac})(\text{OMe})]^\# + \text{Ta}(\text{OMe})_5 \rightarrow \frac{1}{2} [\text{Co}(\text{acac})\text{Ta}(\text{OMe})_6]_2$$
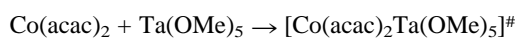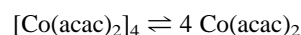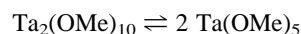
It appeared interesting to develop this approach to be able to prepare the possible derivatives of late transition metals and molybdenum—precursors of selective oxidation catalysts in organic chemistry. As $\text{Mo}(\text{OMe})_6$ is a compound with saturated coordination,[28] it appeared logical to apply the monooxoderivative, $\text{MoO}(\text{OMe})_4$[52]—a structure analog of $\text{M}^V(\text{OMe})_5$—for this purpose. This analogy for the reactants implied naturally the analogy for the reaction stoichiometry and resulted in quantitative preparation of the heterometallic oxo-molybdenum derivatives with M_4X_{16} type structure[53] (Fig. 8):

$\text{M}^{II}(\text{acac})_2 + 2 \text{MoO}(\text{OMe})_4 \rightarrow \frac{1}{2} [\text{M}^{II}(\text{acac})\text{MoO}(\text{OMe})_5]_2$
$$+ \text{MoO}(\text{acac})(\text{OMe})_3, \ \text{M}^{II} = \text{Co, Ni}$$
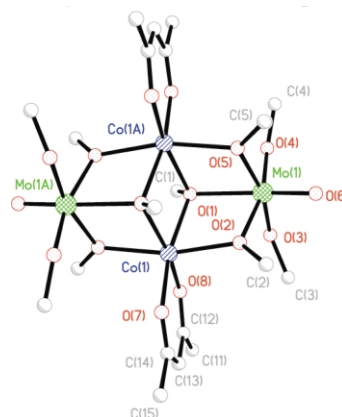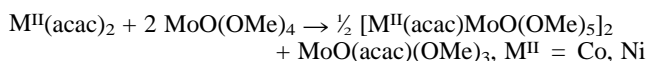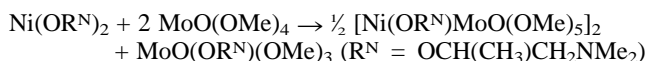

Fig. 8 The molecular structure of $[\text{Co}(\text{acac})\text{MoO}(\text{OMe})_5]_2$.

The only chemical difference between the heterometallic derivatives of niobium and tantalum on one side and those of molybdenum on the other—much lower solubility of the latter in the hydrocarbon solvents—was caused apparently by much stronger charge distribution in its molecules. That was clearly due to the presence of the oxoligands. We sought ways to improve the solubility of the heterometallic species and chose for this purpose the aminoalkoxides as late transition metal reagents, taking into consideration the generally much higher solubility of aminoalkoxides compared to acetylacetonates:

$\text{Ni}(\text{OR}^N)_2 + 2 \text{MoO}(\text{OMe})_4 \rightarrow \frac{1}{2} [\text{Ni}(\text{OR}^N)\text{MoO}(\text{OMe})_5]_2$
$$+ \text{MoO}(\text{OR}^N)(\text{OMe})_3 \ (\text{R}^N = \text{OCH}(\text{CH}_3)\text{CH}_2\text{NMe}_2)$$

The structure of the heterometallic aminoalkoxide complex proved to be analogous to that of the acetylacetonate derivatives by means of EXAFS spectroscopy (no suitable single crystals have been obtained so far).[53]

Another possibility to increase the solubility of heterometallic species was found in the application of the derivatives of a longer chain alcohol than methanol, for example, ethanol. This approach was realized in the preparation of highly soluble derivatives of late transition metals and tantalum (Fig. 9):
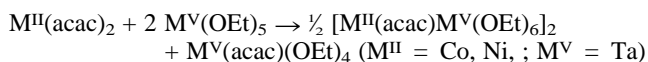
$$M^{II}(acac)_2 + 2 M^V(OEt)_5 \rightarrow \frac{1}{2} [M^{II}(acac)M^V(OEt)_6]_2$$
$$+ M^V(acac)(OEt)_4 \ (M^{II} = Co, Ni, ; M^V = Ta)$$
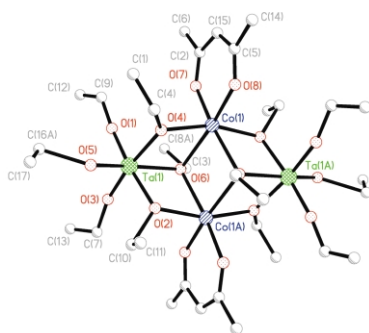
Fig. 9 The molecular structure of $[Co(acac)Ta(OEt)_6]_2$.

An important advantage of the ethoxide derivatives in this case is provided by the relatively high stability of their toluene solutions to uncontrolled microhydrolysis. In the case of methoxides the latter leads to quick precipitation of the poorly soluble in toluene late transition metal acetylacetonatomethoxides, $[M^{II}(acac)(OMe)(MeOH)]_4$.

Derivatives of secondary alcohols

It appeared challenging to investigate, how the different sterical requirements would influence the structure and properties of the reaction products of metal acetylacetonates and metal alkoxides. First essay was the study of interaction of $M^{II}(acac)_2$ and $Ti(O^iPr)_4$ in hexane or pentane (to be able to isolate the products displaying extremely high solubilities). The stoichiometry of this reaction was quite unexpectedly analogous to that with niobium and tantalum methoxides and, supposedly, to that in reaction with $Zr(O^nPr)_4$:

$$Co(acac)_2 + 2 Ti(O^iPr)_4 \rightarrow$$
$$\frac{1}{2} [Co(acac)Ti(O^iPr)_5]_2 + \frac{1}{2} [Ti(acac)(O^iPr)_3]_2$$

The molecular structure of the obtained heterometallic species belonged, however, not to the close packing-derived, but to the linear chain type ones (Fig. 10) with the M_4X_{14}
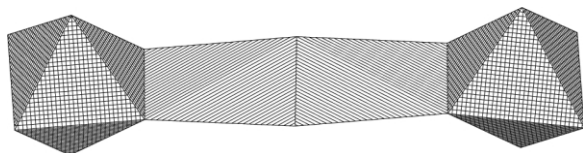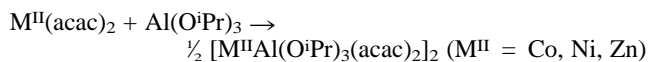

Fig. 10 Polyhedral presentation of the molecular structures of M_4X_{14} type.

formulation.[54] The simple calculation of the total negative charge of ligands in this core showed that it is accessible not only for the heterometallic complexes with tetravalent metals ($2 \times 2 + 2 \times 4 = 12$, 2 additional donor atoms being provided by the two acetylacetonate ligands present), but also with the pentavalent ones ($2 \times 2 + 2 \times 5 = 14$). In this latter case no additional donor atoms would be necessary and the complexes were to be the homoleptic alkoxide species. This permitted the proposal of a principally new synthetic approach to such

species, applying the stoichiometrically necessary access of the pentavalent metal alkoxide:

$$Co(acac)_2 + 3 Ta(O^iPr)_5 \rightarrow$$
$$\frac{1}{2} Co_2Ta_2(O^iPr)_{14} + 2 Ta(acac)(O^iPr)_4$$
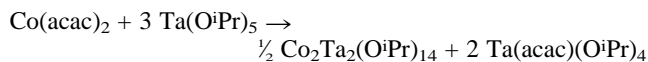
The determined molecular structure of $Co_2Ta_2(O^iPr)_{14}$ corresponded exactly to the expectations (Fig. 10).[54] The same analysis for the trivalent metals ($2 \times 2 + 2 \times 3 = 10$) indicated the need for four additional donor atoms (4 acetylacetonate ligands to be present in the molecule) and required the $1:1$ ratio of the reactants for the complete conversion:

$$M^{II}(acac)_2 + Al(O^iPr)_3 \rightarrow$$
$$\frac{1}{2} [M^{II}Al(O^iPr)_3(acac)_2]_2 \ (M^{II} = Co, Ni, Zn)$$

The reactions proceeded with a quantitative yield (in toluene after 10–30 min on reflux) giving products with molecular structures corresponding to the M_4X_{14} type (Fig. 10).[55]

Looking closer at the polyhedral representation of the structures of M_4X_{14} type, it was possible to distinguish the central fragment, containing two atoms of the more electropositive late transition metals in tetrahedral coordination, and two terminal octahedral fragments with less electropositive atoms in the centers. It was interesting to investigate whether it is possible to construct the structures with only one tetrahedral unit in the center. This was not formed in the reaction of $Co(acac)_2$ with $Ti(O^iPr)_4$ due, supposedly, to the weakness of the titanium alkoxofragments as Lewis acids.[4,7] The necessary facilitation of the electron density donation was achieved *via* combination of two donor fragments. It was then interesting to try the preparation of the representatives of this new structure type with M_3X_{12} formulation (Fig. 11). Application of the
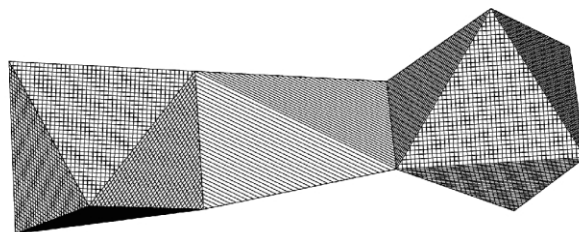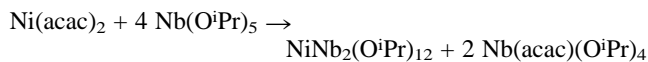

Fig. 11 Polyhedral presentation of the molecular structures of M_3X_{12} type.

corresponding reaction stoichiometry provided the approach to derivatives of the pentavalent metals:[54]

$$Ni(acac)_2 + 4 Nb(O^iPr)_5 \rightarrow$$
$$NiNb_2(O^iPr)_{12} + 2 Nb(acac)(O^iPr)_4$$

The preparation of the corresponding aluminium derivatives required an additional chemical modification as the sum of the charges gave only 8 ($2 + 2 \times 3$) plus two additional donor atoms from the two equivalents of acetylacetonate ligands, provided by the late transition metal reactant. Addition of the two extra equivalents of Hacac to the reaction mixture obtained by reflux of late transition metal acetylacetonate and aluminium alkoxides in $1:2$ ratio provided the species with predicted molecular geometry with quantitative yields:[54]

$$M^{II}(acac)_2 + 2 Al(O^iPr)_3 + 2 Hacac \rightarrow$$
$$M^{II}Al_2(O^iPr)_4(acac)_4 \ (M^{II} = Co, Ni, Mg)$$
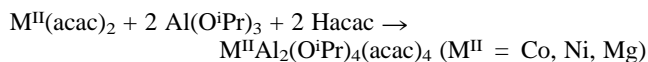
It is important to mention that these easily accessible compounds with $M^{II}:Al = 1:2$ ratio appear to be very attractive precursors of the spinel materials, $M^{II}Al_2O_4$. Very uniform single-phase films of $M^{II}Al_2O_4$ have been obtained on the Al_2O_3 substrates at temperatures as low as 400 °C (Fig. 12).

The same low temperature of formation for the $MgAl_2O_4$ phase from the hydridoalkoxide precursor, $MgAl_2H_4(O^tBu)_4$,
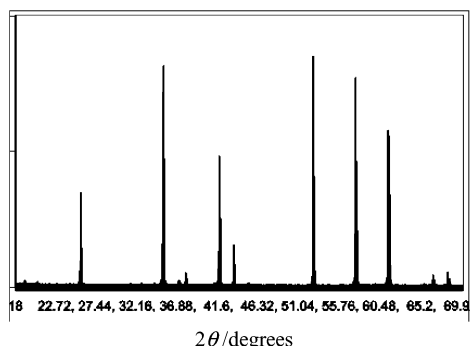
Fig. 12 X-Ray powder pattern of the $NiAl_2O_4$ film obtained from toluene solution of $NiAl_2(acac)_4(O^iPr)_4$ by dip coating and heat treatment at 400 °C.

has recently been attributed by Veith[1] to the specific decomposition mechanism for this latter compound giving rise only to volatile gaseous organic decomposition products. It appears more probable that the low temperature of phase formation reflects in this case the absence of stable intermediate products such as oxocarboxylates or oxocarbonates (that often hinder formation of the complex oxides containing alkaline earth or rare earth elements and requiring temperatures of about 900–1000 °C to be destroyed). An important factor might also be the absence in this case of tar formation, characteristic for the thermal decomposition of the derivatives of bigger organic groups, such as *tert*-butyl, amyl *etc.*

Not unexpectedly, an attempt to obtain the acetylacetonato-alkoxide compound with Zn : Al = 1 : 2 ratio failed, when using the approach described above. The only heterometallic product that could be isolated was $[ZnAl(O^iPr)_3(acac)_2]_2$, which can again, as in the case of the heterometallic derivatives of titanium, be attributed to the small difference in electron acceptor characteristics of aluminium and zinc. This reaction could neither be considered as an attractive approach to manganese derivatives, as the proper drying of the commercial $Mn(acac)_2 \cdot xH_2O$ is quite a complicated task. We have investigated the interaction of manganese(III) acetylacetonate (not requiring further purification) with aluminium alkoxide:[56]

$$Mn(acac)_3 + 3\ Al(O^iPr)_3 \rightarrow MnAl_2(O^iPr)_4(acac)_3(OAc) + ...$$

This reaction led with minor yield to the heteroleptic complex, containing, along with the isopropoxide and acetylacetonate, an acetate ligand. The latter was formed evidently *via* the oxidation of isopropoxide groups. It was apparently the low yield of this latter reaction that was limiting the formation of the heterometallic species in total. The improvement of the reaction stoichiometry *via* addition of only 0.2 extra equivalents of $Al(O^iPr)_3$ (each O^iPr ligand can act normally as 2-electron reducing agent) and one equivalent of HOAc permitted to isolate the $MnAl_2(O^iPr)_4(acac)_3(OAc)$ with 76% yield (when crystallized from toluene). Its molecular structure (Fig. 13) represented a different M_3X_{12} type, which could be derived from the hexagonal packing in the metal–oxygen core. An important feature of it lied also in the presence of strongly electron accepting acetate ligands attached to the aluminium atoms. It gave us hope in approaching the zinc–aluminium precursor by the following reaction:

$$M^{II}(acac)_2 + 2\ Al(O^iPr)_3 + Hacac + HOAc \rightarrow$$
$$M^{II}Al_2(O^iPr)_4(acac)_3(OAc)\ (M^{II} = Co, Zn)$$
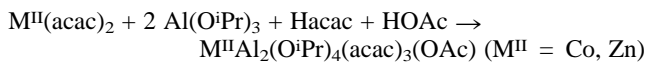
It provided the desired derivatives with more than 90% yield. It is important to note that the initially refluxed mixture of $M^{II}(acac)_2$ and $Al(O^iPr)_3$ in toluene should be cooled down to room temperature before the addition of acetylacetone and especially acetic acid, which will otherwise immediately lead to gelation due to esterification and hydrolysis by the water released in it.[56]
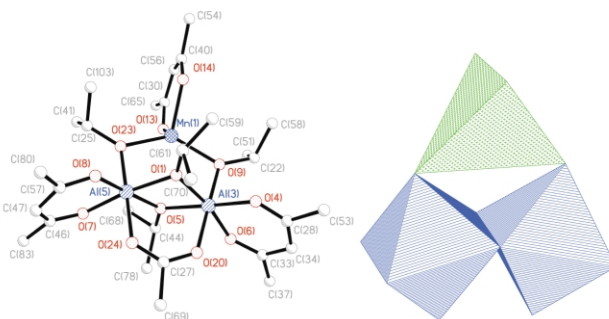

Fig. 13 Molecular structure of $MnAl_2(O^iPr)_4(acac)_3(OAc)$ and its polyhedral presentation.

It appeared challenging to find a way to an SSP for the copper spinel. The coordination geometry for Cu(II) was to be square planar in contrast to the tetrahedral one, preferred by the other 3d late transition metal atoms. The stable coordination geometries for aluminium are both tetrahedral and octahedral. Combination of 2 eq. of $Al(O^iPr)_3$ with one of $Cu(acac)_2$ provided a total of 10 ligand atoms corresponding to the combination of an octahedron in the middle with a tetrahedron and a square plane at the ends of the chain. We have recently succeeded in obtaining this molecule with quantitative yields simply by short-time reflux of these reagents in toluene (Fig. 14).
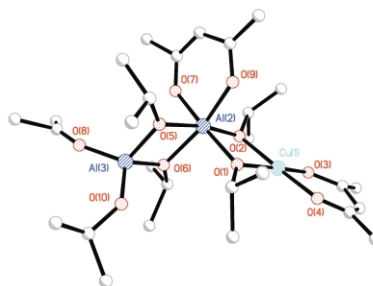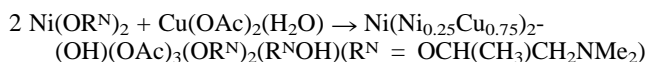

Fig. 14 The molecular structure of $CuAl_2(acac)_2(O^iPr)_6$.

Derivatives of functional alcohols

Interaction of metal carboxylates or β-diketonates with metal alkoxides derived from functional alcohols can provide an approach to heterometallic complexes of two late transition elements, being of interest as precursors of catalytic materials and as potential molecular magnetic materials. The difference in Lewis basicity is almost negligible for the alkoxides of the end of the transition metal series, but the subtle differences in bonding energies to different kinds of donor atoms that can otherwise be referred to as different (in hardness/softness) acidities according to Pearson, may provide a solution. The higher stability is characteristic of the combinations of softer acid–softer base and harder acid–harder base. Mixing of a complex of harder acid–softer base type with that of softer acid–harder base type will provide a trend to ligand exchange and facilitate the aggregation leading possibly to the heterometallic derivatives. This approach was reported to provide access to the nickel–copper carboxylate alkoxide derivatives[57] for example:

$$2\ Ni(OR^N)_2 + Cu(OAc)_2(H_2O) \rightarrow Ni(Ni_{0.25}Cu_{0.75})_2\text{-}$$
$$(OH)(OAc)_3(OR^N)_2(R^NOH)\ (R^N = OCH(CH_3)CH_2NMe_2)$$

The molecular structure of this triangular aggregate can also be seen as derived from a fragment in the dense hexagonal packing (Fig. 15).
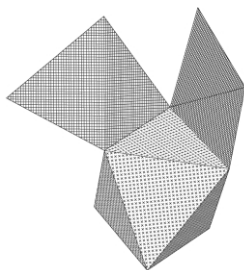
Fig. 15 Polyhedral presentation of the molecular structure of $Ni(Ni_{0.25}\text{-}Cu_{0.75})_2(OH)(OAc)_3(OR^N)_2(R^NOH)$.

## Isomorphous substitution in approach to heterometallic alkoxides

The formation of the mixed-metal species on mixing of the homometallic ones possessing identical molecular geometries was first observed by Hubert-Pfalzgraf and Riess, who isolated and characterized $NbTa(OMe)_{10}$.[58] This trend appears to have a general character and a number of such derivatives has been described since then, for example, $(Mo,W)_2O_2(OMe)_8$[59] or $(Co,Ni)_4(OMe)_4(acac)_4(MeOH)_4$.[60] The distribution of the metal cations is usually statistical in the crystal structures of such compounds, which demands the application of other techniques such as mass-spectrometry and NMR to prove the occurrence of different metal atoms in the same molecule. The uniformity may, however, be easily destroyed by the chemical modification of such species, for example:[60]

$(Co,Ni)_4(OMe)_4(acac)_4(MeOH)_4 + \frac{1}{2} O_2 + 2 OAc^- \rightarrow$
$Co^{III}_2Ni_2(OMe)_4(acac)_4(OAc)_2 + 2 MeOH + 2 OMe^- + H_2O$
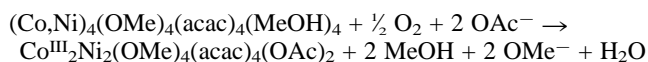
The redistribution of the metal atoms between different positions can in fact be dependent on the individual structural features of the latter. Thus the reaction of $NbTa(OMe)_{10}$ with Re_2O_7 at low temperature provides a modified complex with uniform distribution of metals between the (symmetrically equivalent) positions:[61]

$$NbTa(OMe)_{10} + Re_2O_7 \rightarrow NbTa(OMe)_8(ReO_4)_2$$
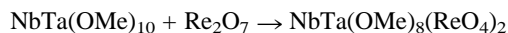
The same reaction but at elevated temperature results in deeper condensation and formation of the tetranuclear species with two structurally different positions:

$$NbTa(OMe)_{10} + Re_2O_7 \rightarrow Nb_2Ta_2O_2(OMe)_{14}(ReO_4)_2$$
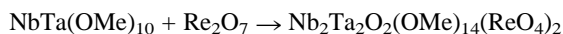
The one surrounded mainly by the alkoxide ligands (σ-bonding) turns out to be occupied preferentially by the tantalum atoms, while that with both oxo- and alkoxide ligands (σ- and π-bonding) preferentially by the niobium ones.

The species, adapting the molecular structure known for only one of the formal homometallic components, constitute a separate and quite unusual class of heterometallic compounds, demonstrating the isomorphous substitution as the construction principle. These are represented by rhenium–molybdenum and rhenium–tungsten derivatives—attractive precursors in the preparation of rhenium alloy nanopowders.[59,62,63] These compounds can be prepared either by the anodic oxidation of rhenium metal in alcohol in the presence of molybdenum alkoxide or by thermally promoted condensation of molybdenum or tungsten alkoxides with Re_2O_7[63]:

$$2 M^{VI}O(OMe)_4 + Re_2O_7 \rightarrow (M^{VI},Re)_4O_{6-x}(OMe)_{12+x}$$
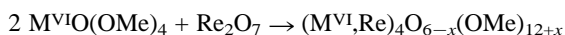
These species adopt the molecular geometry observed for pure rhenium oxomethoxide, but unknown for either molybdenum(VI) or tungsten(VI) homometallic methoxides.

It is interesting to note that in spite of the definite structural equivalence of the $M^{VI}O(OMe)_5$ and $M^V(OR)_6$ octahedra, the reaction of $M^V(OR)_5$ with Re_2O_7 provides, as it has been

mentioned above, only the alkoxide perrhenates,[63–65] which can even demonstrate the same metal–oxygen core structure as the rhenium–molybdenum mixed-metal derivatives. This difference is imposed supposedly by the mechanism of formation of the tetranuclear species, implying condensation of pairs of dinuclear aggregates with a single metal–metal bond (see Scheme 1). The inability of niobium and tantalum atoms to form
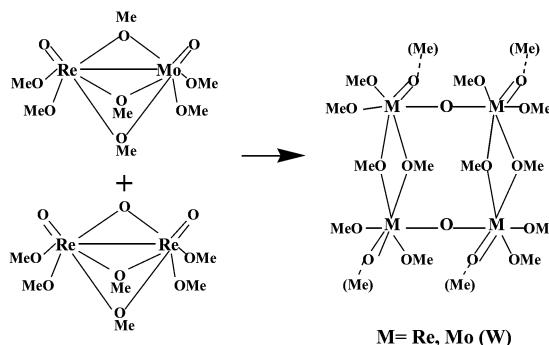
Scheme 1

such heteronuclear bond to a rhenium atom, when surrounded by the π-donor alkoxide ligands, prevents the isomorphous substitution for Re with Nb or Ta in the final product. The same factor (poor stability to oxidation) supposedly hinders the formation of the rhenium–tungsten complex in the course of anodic oxidation of Re in the presence of tungsten alkoxides.[63] The Re–W complexes can be obtained, however, on thermal treatment of the solutions of Re_2O_7 and $WO(OMe)_4$ in toluene favoring the reduction of W(VI) and Re(VII) by the methoxide ligands.

Formation of heterometallic metal–metal bonds

Application of this approach is hindered by the strong π-donor ability of the alkoxide ligands, favoring the stabilization of the higher oxidation state derivatives. Only two representatives of this class of compounds have been reported so far, namely, $Mo_2WO(O^iPr)_{10}$,[66] and $ReMoO_2(OMe)_7$.[67] The latter remains the only reported representative of a compound with dinuclear donor–acceptor metal–metal bond and was obtained *via* the electrochemical generation of Re(V) d^2 species in the presence of Mo(VI) d^0 ones:

$$:ReO(OMe)_3 + MoO(OMe)_4 \rightarrow ReMoO_2(OMe)_7$$

Derivatives of polydentate ligands with confined geometries

The synthesis of truly heterometallic species using polydentate ligands such as triethanolamine and diethanolamine has recently attracted quite strong attention due to the possibility of controlling very strictly the stoichiometry and topology of the species, produced *via* the reactions of inert complexes of one metal with two molecules of these aminoalcohols and the alkoxide of the other metal. This approach was first applied and structurally proven in the preparation of a lanthanum–niobium complex, demonstrating high solubility and even volatility due to the rigidity of its central diatrane core (Fig. 16):[68]

$$H_3[La(tea)_2] + 3 Nb(O^iPr)_5 \rightarrow [La(tea)_2]\{Nb(O^iPr)_4\}_3$$
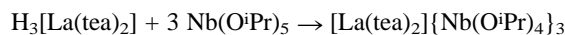
The modern applications of this approach are directed mainly to the production of sterically rigid single molecule magnets.[69] The self-assembled alkoxo-carboxylate and alkoxo-β-diketonate molecular magnets are often very easily influenced by the solvent and temperature changes,[70] which urges the search for
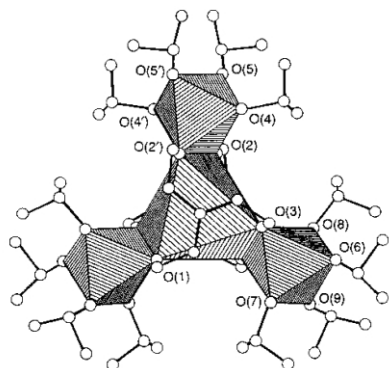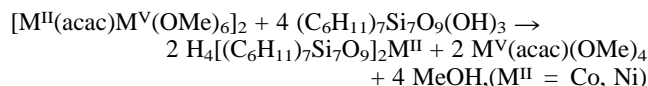
Fig. 16 Polyhedral presentation of the molecular structure of [La-(tea)$_2$]{Nb(O^{i}Pr)$_4$}$_3$.

the geometrically confined structures in the view of possible applications.

The simple geometrical considerations described above can also be useful in describing the structures and developing approaches to the metal derivatives of alkyloligosiloxanes and alkylsilsesquioxanes, which can not be classified really as heterometallic alkoxides. They are of interest as molecular models of heterogeneous applied catalysts and are often used themselves as homogeneous catalysts in organic synthesis. The observed structural units in this case can be related very often to the Si$_4$O$_4$ ring units in the structures of zeolites.[71] The heterometallic heteroleptic alkoxide species have recently been successfully applied in the reactions with alkylsilsesquioxanes as sources of soluble and reactive late transition metal alkoxides, for example:[72]

$$[M^{II}(acac)M^V(OMe)_6]_2 + 4\ (C_6H_{11})_7Si_7O_9(OH)_3 \rightarrow$$
$$2\ H_4[(C_6H_{11})_7Si_7O_9]_2M^{II} + 2\ M^V(acac)(OMe)_4$$
$$+ 4\ MeOH, (M^{II} = Co, Ni)$$

The polyhedral model description (Fig. 17) permits a full explaination of the facility of this reaction, the M^V component
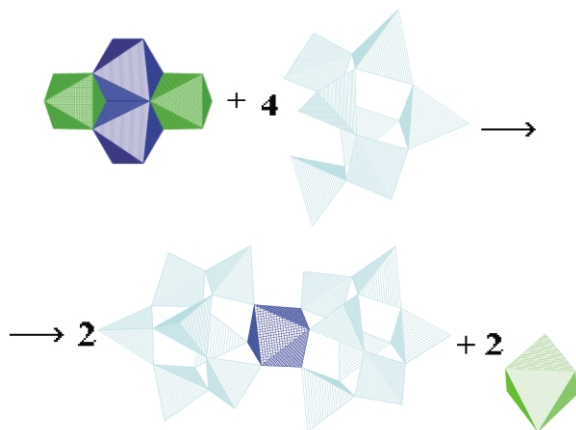

Fig. 17 Polyhedral model description of the interaction of [Co-(acac)M^V(OMe)$_6$]$_2$ with an alkylsilsesquioxane.

being removed in the form of monomeric octahedral molecules with saturated coordination. It is interesting to note that the application of the soluble alkoxide derivatives themselves, for example, M$^{II}_2$Al$_2$(acac)$_4$(O^{i}Pr)$_6$ does not lead to formation of the metallasilsesquioxane complexes in analogous reactions.

Conclusions

The proposed concept relates the molecular structure features and stability of the heterometallic alkoxides to the stable structure types, formed by combination of stable coordination polyhedra. It permits the prediction of the existence and

structure for a broad variety of new species and optimizes the synthetic approaches to them. It is especially important to mention that it permits also to put reasonable doubt on the existence and molecular structure of a long series of compounds that have been reported earlier without convincing structural characterization. It is possible, for example, to reject as unrealistic such formulations[4] as (^{i}PrO)$_3$M^V[Al(O^{i}Pr)$_4$]$_2$, M^V = Nb, Ta (impossibility of coordination number CN = 7 for them with alkoxide ligands), M^{III}[M^V(O^{i}Pr)$_6$]$_3$, M^{III} = Fe, Cr (the central atoms are far too small for three hexaalkoxometallate fragments to be placed around them), M^{II}[Zr$_2$(O^{i}Pr)$_9$]$_2$, M^{II} = Fe, Co, Ni, Cu (the minimum CN that fits this structure is 6, but it cannot exceed 5 for sterical reasons), LaCl$_x$[Zr$_2$(O^{i}Pr)$_9$]$_{3-x}$, where x = 1 or 0 (CN cannot exceed 8 for the lanthanides in alkoxides) *etc*. It is also possible to conclude that metal alkoxides as a family of compounds in their structural chemistry are much closer relatives of the typically inorganic derivatives such as hydroxides and polyoxometallates than of metallorganic substances like metal alkyls, which they resemble in preparation and handling techniques.

Notes and references

† The proper formulation of the composition for the corresponding alkoxometallate anion as Zr$_2$(OR)$_9$$^-$ was provided later by W.G. Bartley and W. Wardlaw in *J. Chem. Soc.*, 1958, 422.

‡ The idea of predominantly kinetic control in reactions leading to formation of heterometallic alkoxides, proposed later by Veith *et al*.[21], stood in fact in open contradiction with the results of this group. Thus, the structures of the [CdM^{II}M$^{IV}_2$(O^{i}Pr)$_{12}$]$_2$, M^{II} = Ca, Sr, Ba, M^{IV} = Sn, Ti, Zr, Hf, did contain the Cd atoms in the more thermodynamically stable tetrahedral, and the M^{II} ones in octahedral coordination arrangements contrary to what should have been observed in the case of kinetic control in their formation.

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