Design of molecular structure and synthetic approaches to single-source precursors in the sol-gel technology

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Metal alkoxide and β-diketonate complexes are broadly recognized as versatile precursors of high-purity glass and ceramic materials in the sol-gel technology. By applying reactants containing various metal atoms in the proper ratio and assuring their conservation through sol-gel treatment, single-source precursors (SSP) provide an efficient approach to complex materials. Simple and cost-efficient routes to SSP can be developed by applying the concept of geometrical molecular structure design, which is based on the choice of a type proper of molecular structure and its completion with ligands, providing the necessary number of donor atoms for the chosen core as well as sterical protection.

Key words: *precursor chemistry, single-source precursor, geometric design, solution stability, reactivity control*

1. Introduction

Development of synthetic approaches to new complex materials urges the search for new routes to design and synthesise precursors. The requirements normally put on these compounds, belonging usually to the family of metal alkoxides [1–4], are high solubility in organic solvents, stability in solution, possibility of controlled hydrolysis (most often simply by water without any catalyst), limited sensitivity to moisture (requiring only reasonable precautions in treatment), and last, but far not the least, the accessibility and commercial availability. All these properties are directly determined

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or, like the last one, strongly influenced by the molecular structure of these species. The ability to predict the molecular structure is the key to design the approaches to new precursors. The need in purpose design becomes crucial in approaches to the single source precursors (SSP) – the species permitting to specifically facilitate the formation of the desired material in such aspects as chemical and phase composition, morphology or domain structure via preservation of the chemical composition or structure features of the building blocks from precursor molecule to material. In literature, before recently, one could find two approaches to design of the alkoxide species: the concept of "alkoxosalts" of Meerwein for heterometallic and Bradley's structure theory for homometallic ones. The former considered the heterometallic alkoxides as salts of "ansolvoacids", $H[Al(OR)_4]$, $H[Zr_2(OR)_9]$ and $H[Nb(OR)_6]$, respectively [4, 5]. It predicted successfully the compositions of some of the derivatives of alkali and alkaline earth metals, but failed already in application to derivatives of lanthanides: $La_2Zr_3O(O^iPr)_{16}$ [3] was found instead of $La[Zr_2(O^iPr)_9]_3$ [6], $LaNb_2(O^iPr)_{13}$ [7] instead of $LaNb_3(O^iPr)_{18}$ [8] etc. Bradley's theory predicted the structure of stable oligomeric aggregates to be containing the minimal number of metal atoms providing possibility of formation of stable coordination polyhedra for all of them and turned efficient in prediction of molecular structures for a number of compounds but gave no approach to species with desired size or desired structure.

Having carried out the analysis of available structural data on Ba–Ti system [9–12], we were able to trace the trend to formation of molecules belonging to a limited number of stable structure types, requiring the presence of well-defined number of donor atoms in the ligands. Completing a chosen structure type with additional donor atoms via use of β-diketonate ligands, we were able to prepare a principally new solution-stable precursor of $BaTiO_3$, $Ba_2Ti_2(thd)_4(OEt)_8(EtOH)_2$ [13], belonging to a very common and stable $M_2M'_2X_{16}$ structure type, and formulated a new principle in approach to the complex precursors, the molecular structure design concept (MSDC): to design a new heterometallic alkoxide complex one should choose a desired structure type and complete it with ligands, providing both the necessary number of donor atoms and the sterical protection of the chosen core [14].

We report the successful application of this concept to design and synthesis of new classes of precursors for such materials as spinels, barium and strontium zirconates, zirconia and titania–zirconia.

2. Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk technique or a glove box. Waterfree $M^{II}(acac)_2$, M = Co, Ni, was obtained by sublimation of $M^{II}(acac)_2 \times xH_2O$ (Aldrich Chemical Company Inc.) at 110–145 °C and 1 mm Hg. Waterfree $Zn(acac)_2$ was obtained by refluxing $Zn(acac)_2 \times xH_2O$ (Aldrich Chemical Company Inc.) with dry toluene with subsequent evaporation, repeated twice. $Mg(acac)_2$

was prepared by refluxing magnesium metal with acetylacetone. The slurry and solvent were transferred to a new flask, the solvent was removed by decantation and the crystals were washed with boiling toluene and evaporated to dryness, repeated twice. Titanium and zirconium alkoxides were purchased from Aldrich and used without further purification. $Ta(O^iPr)_5$ and $Nb(O^iPr)_5$ were prepared by anodic oxidation of the metals in methanol and purified according to conventional techniques [7, 8]. $Al(O^iPr)_3$ was obtained by reaction of aluminium foil with isopropanol and purified by recrystallization from toluene. Isopropanol (Merck, p.a.) was purified by distillation over $Al(O^iPr)_3$ and hexane and toluene (Merck, p.a.) by distillation over $LiAlH_4$. The metal ratio in the bimetallic complexes was determined, exploiting the facilities of the Arrhenius Laboratory, Stockholm University, Sweden, on JEOL-820 scanning electron microscope (SEM), supplied with Link AN-10000 energy dispersive spectrometer (EDS). Mass-spectra were recorded using JEOL JMS-SX/SX-102A mass-spectrometer applying electron beam ionization ($U = 70$ eV) with direct probe introduction. UV-Vis spectra were registered for 0.025–0.05 M solutions in toluene using Hitachi U-2001 spectrophotometer. IR spectra of nujol mulls were registered with a Perkin Elmer FT-IR spectrometer 1720 X. ^{1}H NMR spectra were recorded for the $CDCl_3$ solutions on a Bruker 400 MHz spectrometer. The results of microanalysis (C, H) were obtained for all the reported compounds in the Laboratory of Organic Microanalysis of Moscow State University, Russia and Mikrokemi AB, Uppsala, Sweden using the combustion technique.

X-ray single crystal studies were made on SMART CCD 1k diffractometer using SHELXTL-NT program package for computations. X-ray powder diffraction (XRD) patterns of the obtained phases were recorded with a Philips PW 3710 diffractometer with $CuK\alpha_1$ radiation ($\lambda = 1.54056$ Å). The morphology of the films and the particles was investigated with a Hitachi S800 15 kV scanning electron microscope (SEM). The roughness of the film surface was studied with a Picoscan-5 Molecular Imaging atomic force microscopy (AFM). A Topcon EM-002 B Ultrahigh resolution analytical electron microscope was used for the Transmission Electron Microscopy images. Analysis of the composition of the gas phase after thermal decomposition of the precursors was performed using a HP 5973 mass spectrometer coupled with a HP 6890 gas chromatography.

3. Results

In this work, we have carried out a study of structure and stability of the products of modification of zirconium alkoxides $Zr(OR)_4$, R = ^nPr, ^iPr with chelating ligands such as acetylacetone, Hacac, and diethanolamine, $(HOC_2H_4)_2NH$. It turned out that in case of Hacac in the absence of hydrolysis only two types of compounds characterized as $[Zr(OR)_3(acac)]_2$ and $Zr(acac)_3(OR)$ could be formed, none of them being stable in

solution for a long time according to NMR investigation – all of them rearranged slowly yielding Zr(acac)$_4$ as the final product (see Fig. 1).
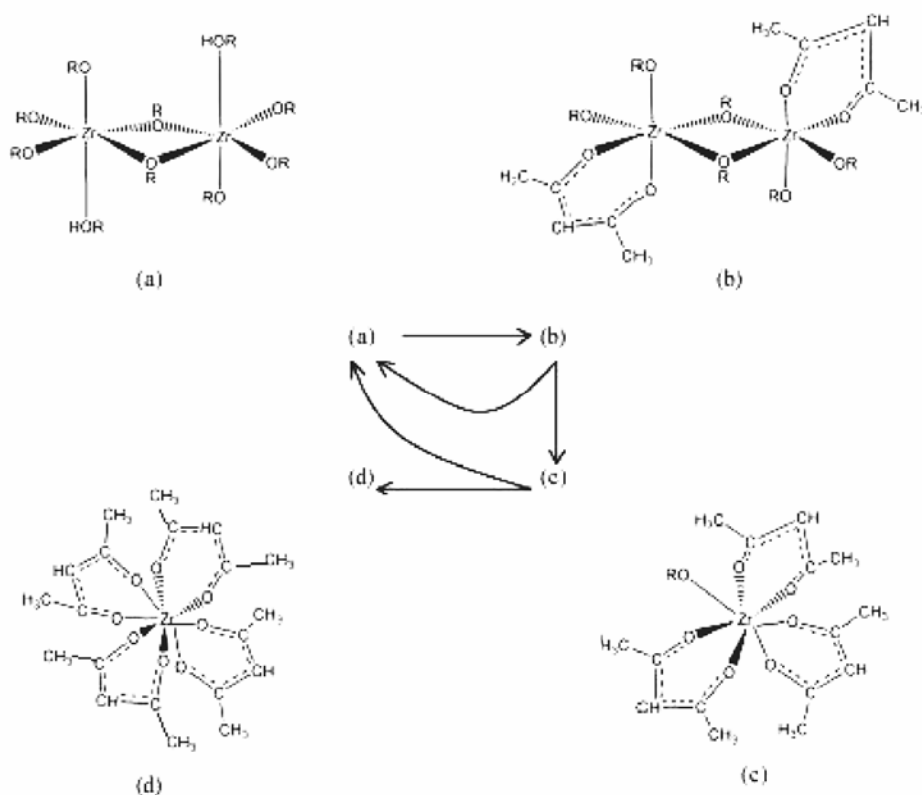

Fig. 1. The proposed mechanism and structures for the stabilization of zirconium propoxide in propanol. Addition of up to 1 mol equivalent Hacac to the initial precursor (a) leads to (b). Addition of more than 1 mol equivalent leads to a reaction of (b) to (a) and (c). Spontaneous rearrangement of (c) gives (d) and (a)

Solution-stable modified species, Zr$_3$(dea)$_3$(O^{i}Pr)$_6$(^{i}PrOH)$_2$ (Fig 2a), were obtained by the reaction of [Zr(O^{i}Pr)$_4$(^{i}PrOH)]$_2$ with diethanolamine (up to 1 eq per mol Zr). This structure contained two types of metal atom positions – nona-coordinated Zr($\mu_2\mu_2\eta^3$-dea)$_3$ in the middle and hexacoordinated Zr(μ_2-dea)$_3$(O^{i}Pr)$_3$ at the ends. It was evident that these could host a different, smaller metal atom and we succeeded in the preparation of a solution-stable bimetallic Zr–Ti analog, ZrTi$_2$(dea)$_3$(O^{i}Pr)$_6$ (Fig. 2b) by modification of a Zr : Ti = 1 : 2 mixture with 3 equivalents of H$_2$dea.

Application of these compounds to prepare mesoporous oxides will be reported separately, but it is important to mention that the Zr–Ti complex with only one type of alkoxide groups (at Zr atoms) opens prospects for approach to oxides from TiO$_2$-ZrO$_2$ systems with uniform distribution of cations in them.
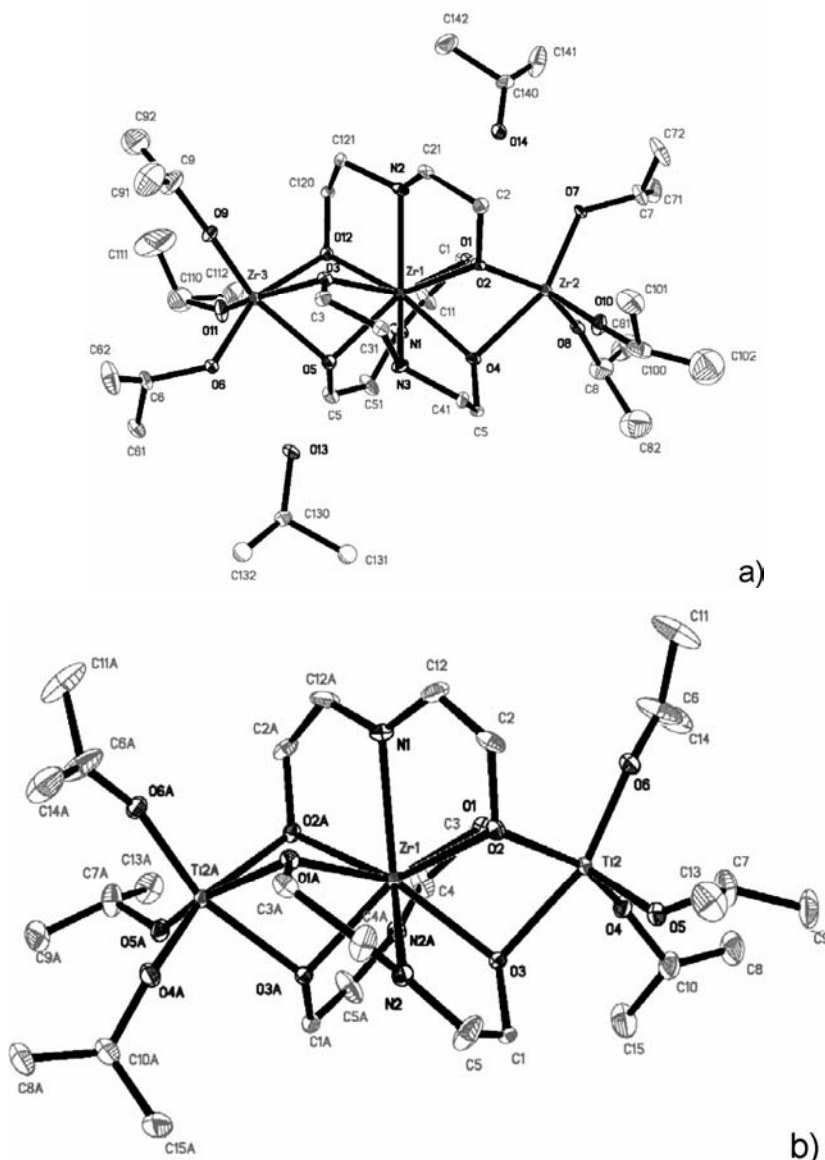
Fig. 2. Molecular structures of $Zr_3(dea)_3(O^iPr)_6(^iPrOH)_2$ (a) and $ZrTi_2(dea)_3(O^iPr)_6$ (b)

Application of MSDC to the synthesis of precursors of ferroelectric materials, $M^{II}ZrO_3$, $M^{II} = Sr$, Ba permitted to develop simple one-batch approaches to hydroxide isopropoxide species (Fig. 3) via partial hydrolysis of solutions of $M^{II}(O^iPr)_2$ and $Zr(O^iPr)_4$ (1:1 ratio) with 1 eq. of water in isopropanol. The Veith et al. idea [1] about the kinetic control in formation of these species was shown to be erroneous and leading to irrationally complicated synthetic approaches.
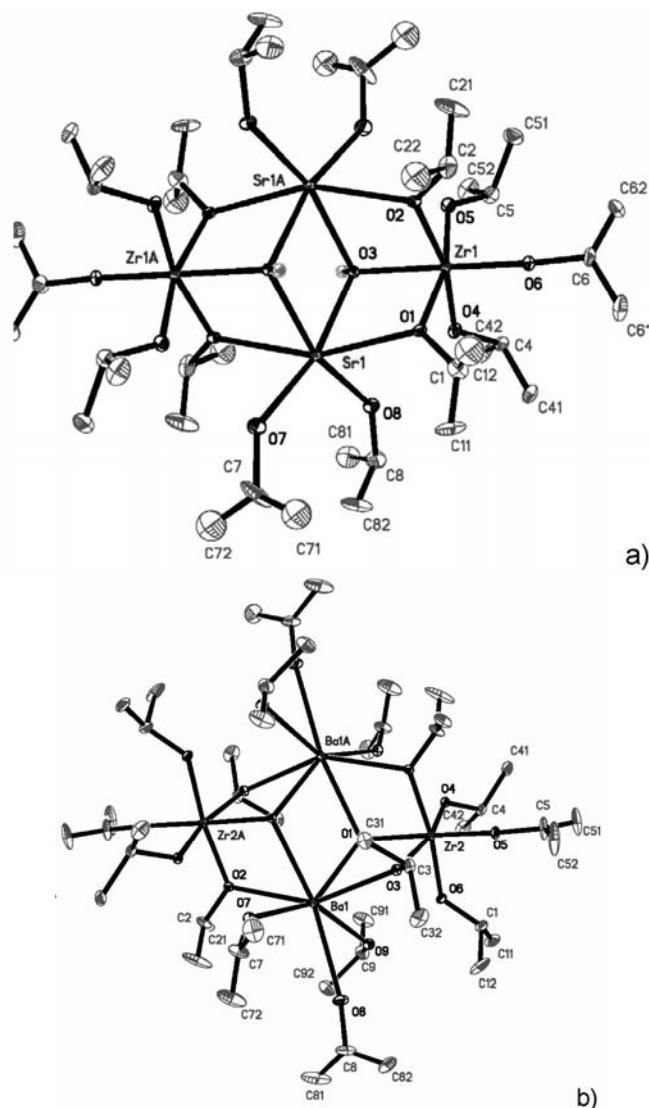
Fig. 3. Molecular structures of $Sr_2Zr_2(OH)_2(O^iPr)_{10}(^iPrOH)_4$ (a) and $Ba_2Zr_2(OH)_2(O^iPr)_{10}(^iPrOH)_6$ (b)

Both these compounds turn out to be unstable in solution, displaying irreproducible solubility in alcohols and decomposition with precipitation of solvated hydroxides, $M^{II}(OH)_2(ROH)_x$, on dissolution in hydrocarbons. Highly soluble solution-stable species were obtained following the same logic as for Ba–Ti precursors, i.e. applying β-diketonate ligands such as 2,2,6,6,-tetramethylheptanedion (Hthd) as modifier (1 eq. for 1:1 mixtures of $M^{II}(O^iPr)_2$ and $Zr(OR)_4$, R= ^nPr, ^iPr) in toluene (see fig. 4).
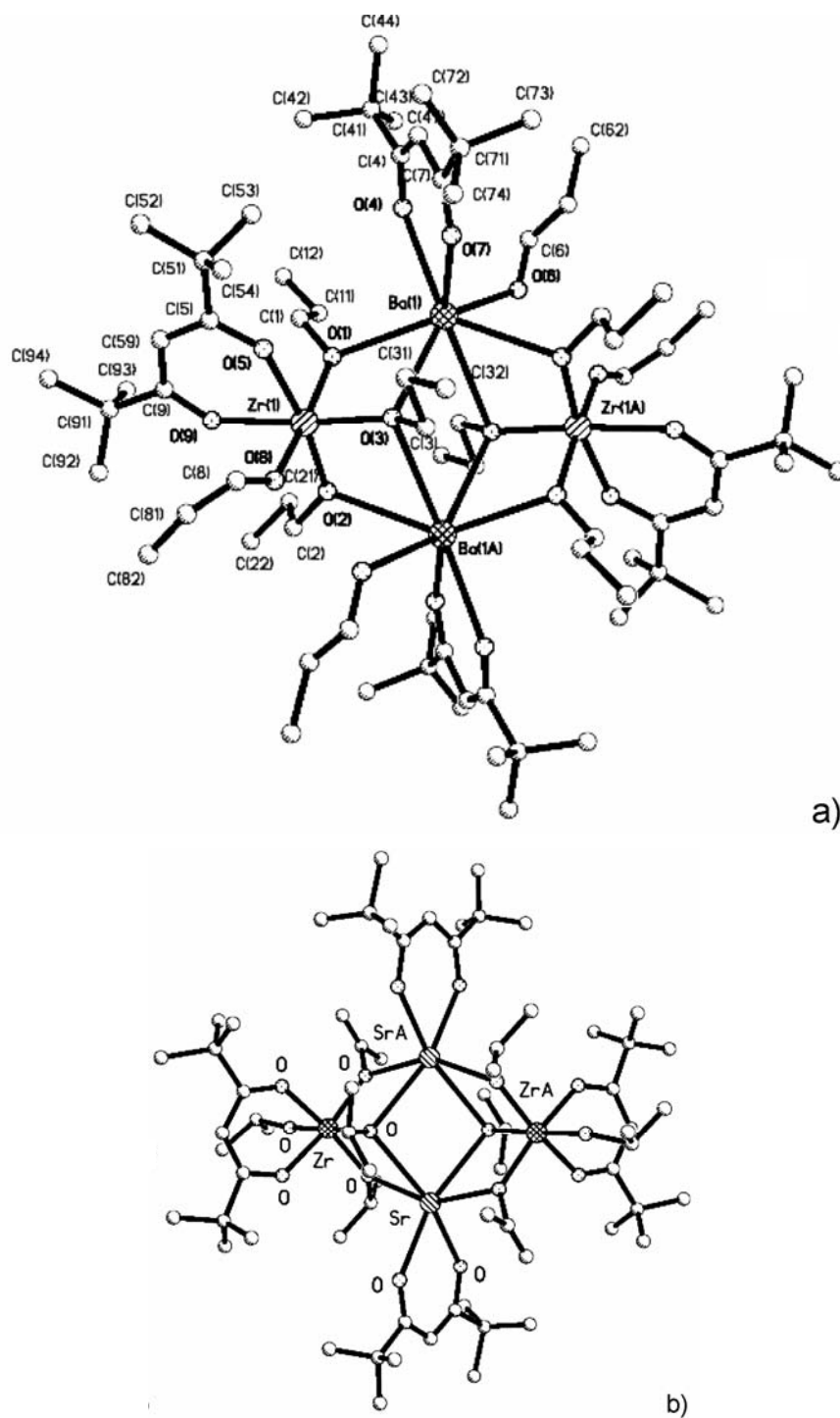
Fig. 4. Molecular structures of $Ba_2Zr_2(thd)_4(O^nPr)_8(^nPrOH)_2$ (a) and $Sr_2Zr_2(thd)_4(O^iPr)_8$ (b)
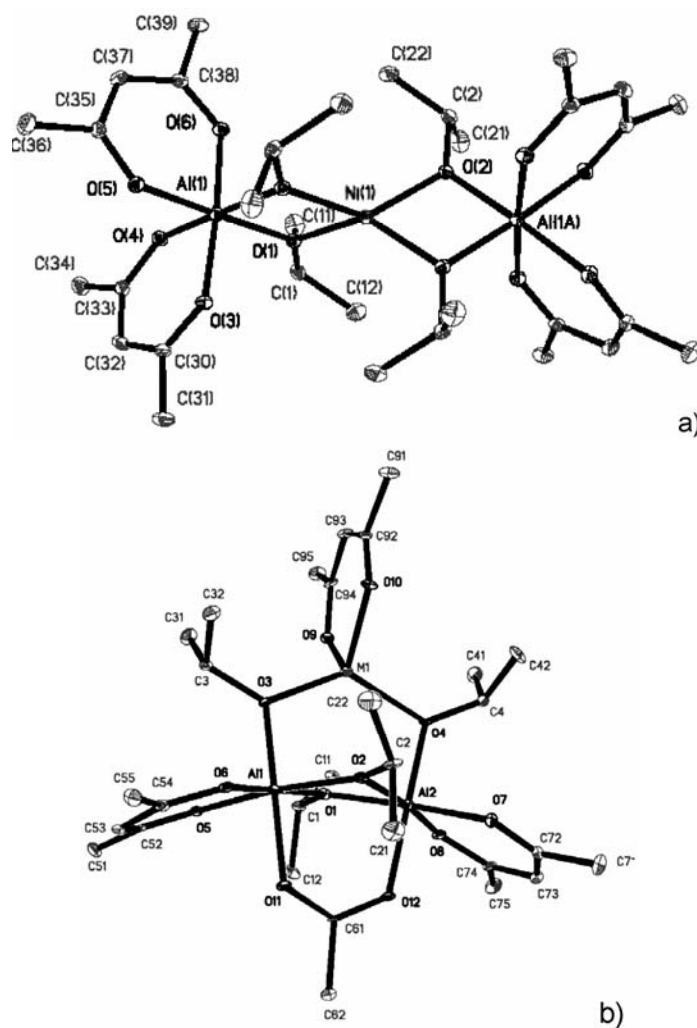
Fig. 5. Molecular structures of $M^{II}Al_2(O^iPr)_4(acac)_4$ (a) and $M^{II}Al_2(O^iPr)_4(acac)_3(OAc)$ (b)

Formation of the $M_2M'_2X_{16}$ structure type is characteristic of the complexes of comparably small cations, such as those of late transition metals and Mg, with normal chain structure ligands (methoxides, ethoxides, *n*-propoxides) or bigger cations, such as Sr or Ba, with iso- or sec- alkoxide derivatives. Complexes of smaller cations and iso- or sec-alkoxide ligands have usually chain structures with two or three alkoxide bridges between the metal atoms [3, 14]. We have applied this knowledge for development of approaches to two new families of spinel precursors, $M^{II}Al_2(acac)_4(O^iPr)_4$, M^{II} = Mg, Mn, Co, Ni, [15] and $M^{II}Al_2(acac)_3(OAc)(O^iPr)_4$, M^{II} = Mg, Mn, Co, Zn, [16] by simple one-batch synthetic techniques:

$$M^{II}(acac)_2 + 2\,Al(O^iPr)_3 + 2\,Hacac \longrightarrow M^{II}Al_2(O^iPr)_4(acac)_4$$

$$M^{II}(acac)_2 + 2\,Al(O^iPr)_3 + Hacac + HOAc \longrightarrow M^{II}Al_2(O^iPr)_4(acac)_3(OAc)$$

The molecular structures of these two new families of precursors (Fig. 5) demonstrate two structure types with analogous formal composition, MM'_2X_{12}, but different geometries: the linear chain one giving easier hydrolysis and less solution stability and the ring-type one with higher solution stability and higher resistance to hydrolysis (due to higher Lewis acidity of Al-fragment involving more ionically bonded acetate ligand).
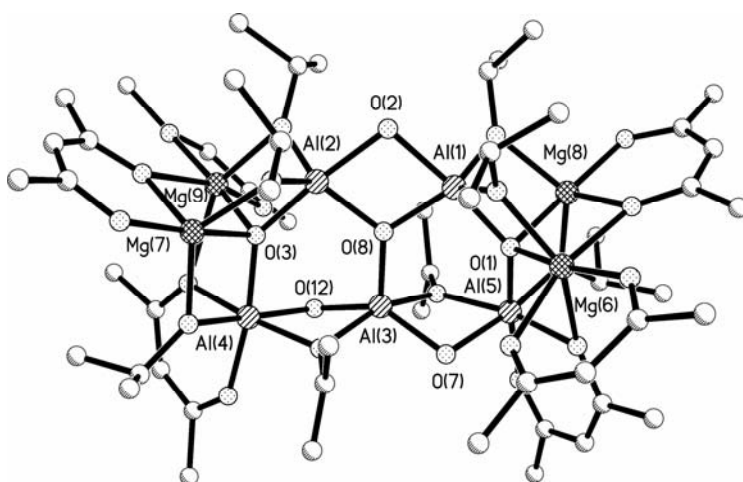

Fig. 6 Molecular structure of $Al_5Mg_4O_3(OH)_3(O^iPr)_8(acac)_6$
formed on microhydrolysis of $MgAl_2(O^iPr)_4(acac)_4$

In sol-gel application of the first of these classes it is important to avoid partial hydrolysis as the solution equilibria for metal alkoxide complexes are leading usually to redistribution of cations in the partially hydrolyzed species [9]. We have carried out a study of partial hydrolysis on $MgAl_2(O^iPr)_4(acac)_4$ and observed also in this case the formation of a complex with changed stoichiometry, $Al_5Mg_4O_3(OH)_3(O^iPr)_8(acac)_6$ (Fig. 6).
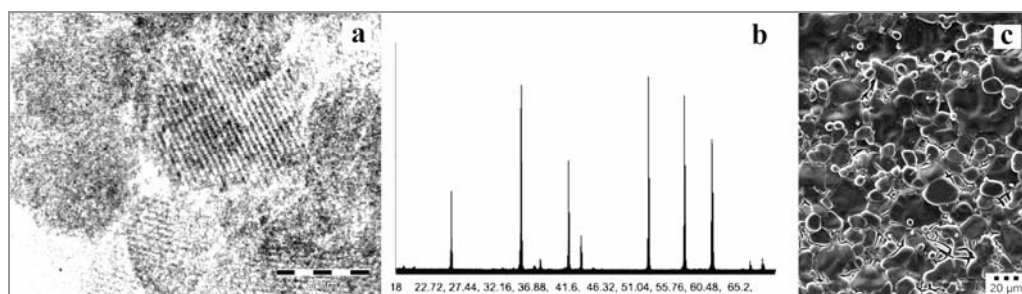
Fig. 7. HREM image of the $CoAl_2O_4$ nanoparticles obtained from $CoAl_2(O^iPr)_4(acac)_3(OAc)$
by sol-gel (a), X-ray powder pattern (b) and SEM image (c) of the $NiAl_2O_4$ film
obtained by dip-coating form solution of $NiAl_2(O^iPr)_4(acac)_4$ in toluene on melted alumina support

Single-phase nanopowders of spinels could successfully be prepared from both classes of precursors by complete hydrolysis (Fig. 7). Single-phase coatings of spinels were obtained from $M^{II}Al_2(O^iPr)_4(acac)_4$ by dip-coating technique in humid atmosphere with intermediate heat treatments at 100 °C and final annealing at 400 °C.

4. Discussion

The present work shows unambiguously that the formation of alkoxide complexes is a result of thermodynamically driven self-assembly and the nature of these compounds, being attractive molecular precursors of materials, including their composition and molecular geometry can be predicted using the molecular structure design concept. The conditions of hydrolysis and subsequent thermal treatment should be carefully investigated in order to support the single-source precursor effect – an erroneous treatment can lead to chemical and phase impurities in the material even when a complex with proper composition is applied as precursor.

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