Interaction of some divalent metal acetylacetonates with Al, Ti, Nb and Ta isopropoxides. Factors influencing the formation and stability of heterometallic alkoxide complexes†

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Interaction of Co(acac)$_2$ with 2 eq. of Ti(O^{i}Pr)$_4$ in hexane leads to an equimolar mixture of the new heterometallic complex [Co$_2$Ti$_2$(acac)$_2$(O^{i}Pr)$_{10}$] (**1**) and the known heteroleptic alkoxide Ti$_2$(acac)$_2$(O^{i}Pr)$_6$. When redissolved in ^{i}PrOH **1** is destroyed, forming [Co$_2$(acac)$_4$(^{i}PrOH)$_2$] (**2**) as the only isolable crystalline product. Reaction of Co(acac)$_2$ with 3 eq. of Ta(O^{i}Pr)$_5$ gives [Co$_2$Ta$_2$(O^{i}Pr)$_{14}$] (**3**) together with Ta(acac)(O^{i}Pr)$_4$. Reaction of Ni(acac)$_2$ with 4 eq. of Nb(O^{i}Pr)$_5$ produces the heterometallic complex [NiNb$_2$(O^{i}Pr)$_{12}$] (**4**). Reactions of M(acac)$_2$ (M = Co, Ni, Mg and Zn) with Al(O^{i}Pr)$_3$ in 1 : 2 ratios provides access to [MAl$_2$(O^{i}Pr)$_4$(acac)$_4$] [M = Co (**5**), Ni (**6**), Mg (**7**)] and [Zn$_2$Al$_2$(O^{i}Pr)$_6$-(acac)$_4$] (**8**) respectively. When redissolved in ^{i}PrOH, [NiAl$_2$(O^{i}Pr)$_4$(acac)$_4$] (**6**) is destroyed, forming a mixture of [Ni$_2$(acac)$_4$(^{i}PrOH)$_2$] (**9**), Al(O^{i}Pr)$_3$ and Al(acac)$_3$. Interaction of M(acac)$_2$, (M = Co, Ni) with metal isopropoxides in ^{i}PrOH as well as their recrystallization from ^{i}PrOH give **2** and **9** respectively. **5–7** are unstable in the hydrocarbon solution on heating, decomposing with formation of [M$_2$Al$_2$(O^{i}Pr)$_6$(acac)$_4$], along with Al(acac)$_3$ and heterometallic alkoxide species. Mg(acac)$_2$ was found to recrystallize unchanged from the solutions of Ti(O^{i}Pr)$_4$ in toluene. The solution structure and stability of the heterometallic complexes has been investigated by UV-Vis spectroscopy and NMR, and the details of their decomposition on sublimation by mass-spectroscopy. The factors influencing the formation and stability of heterometallic complexes originating from the reactions of divalent metal acetylacetonates with metal isopropoxides are discussed.

Introduction

Heterometallic alkoxides of late transition elements, and of cobalt in particular, are of interest as precursors of materials for catalytic applications.[1] The common approach to bimetallic derivatives based on interaction of the alkoxides of two metals is not applicable in this case as the homometallic complexes of late transition metals are polymeric solids displaying very low reactivity.[2] A promising route to the heterometallic compounds appears to be offered by the interaction of late transition metal β-diketonates with early transition metal alkoxides which was earlier reported to provide access to Zr$_2$Co$_4$(μ$_6$-O)(μ-OC$_3$H$_7$)$_8$(OC$_3$H$_7$)$_2$(acac)$_4$[3] and Zr$_3$Fe$_4$(μ$_4$-O)-(μ-OC$_3$H$_7$)$_6$(OC$_3$H$_7$)$_4$(acac)$_3$[4] and recently also to M$_2^{II}$M$_2^V$-(acac)$_2$(OMe)$_{12}$, [M^{II} = Co, Ni, Zn, Mg; M^V(OMe)$_5$, M^V = Ta, Nb].[5] As application of solutions containing metal β-diketonates together with early transition metal isopropoxides represents a rather common approach in sol–gel technology, it was interesting to find out what chemical reactions occur under their preparation and what kind of species can be present in these systems. It is to be mentioned that a considerable number of acetylacetonato-isopropoxides, and in particular NiAl$_2$-(acac)$_4$(O^{i}Pr)$_4$, have been reported by Mehrotra[6] to be formed on treatment of the corresponding heterometallic isopropoxides with acetylacetone, but very little structural characterization was provided for these species. No unequivocal data have been presented so far on their stability in solution and on transition into the gas phase.

Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk techniques or a glove box. Waterfree M^{II}-(acac)$_2$ (M = Co, Ni) was obtained by sublimation of M^{II}-(acac)$_2$·xH$_2$O (Aldrich Chemical Company Inc.) at 110–145 °C and 1 mmHg. Waterfree Zn(acac)$_2$ was obtained by refluxing Zn(acac)$_2$·xH$_2$O (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. Ta(O^{i}Pr)$_5$ and Nb(O^{i}Pr)$_5$ were prepared by anodic oxidation of the metal in isopropanol and purified according to conventional techniques.[7,8] Ti(O^{i}Pr)$_4$ was purchased from Aldrich and distilled prior to use. Al(O^{i}Pr)$_3$ was obtained by reaction of aluminium foil and isopropanol and purified by recrystallization from toluene. Isopropanol (Merck, p.a.) was purified by distillation over Al(O^{i}Pr)$_3$ 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 a JEOL-820 scanning electron microscope (SEM), supplied with a Link AN-10000 energy dispersive spectrometer (EDS). Mass-spectra were recorded using a 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 a 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 the Moscow State

University, Russia and Mikrokemi AB, Uppsala, Sweden using the combustion technique.

Synthesis and isolation of the products obtained

Interaction of Co(acac)₂ with 2 eq. of Ti(OⁱPr)₄. Co(acac)₂ (0.379 g, 1.45 mmol) and Ti(OⁱPr)₄ (1.040 g, 3.36 mmol) were dissolved in 4 ml of hexane and refluxed for half an hour. The purple solution obtained was left to crystallize overnight at 4 °C. The precipitate, purple platelet crystals, was isolated by decantation and dried *in vacuo*. Yield 0.56 g (77%).

[Co₂Ti₂(acac)₂(OⁱPr)₁₀] **1**. IR/cm⁻¹: 1721w, 1592s, 1521s, 1329m, 1274m, 1163s, 1128s, 1014s, 956s, 850m, 831w, 769w, 687w, 657w, 619m, 545w, 462m. UV-Vis, λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 500 (86), 565 (117). MS, *m/z* [*I* (%), interpretation]: 305 [16.1, Ti(acac)₂(OⁱPr)⁺], 283 [1.8, Ti(OⁱPr)₃(OC₃H₆)⁺], 269 [49.5, Ti(OⁱPr)₃(OC₂H₄)⁺], 265 [19.3, Ti(acac)(OⁱPr)₂⁺], 263 [12.5, Ti(acac)₂(OH)⁺], 257 [100, Co(acac)₂⁺], 242 [100, Ti(OⁱPr)₃- (OH)⁺ and Co(acac)(CH₃COCHCO)⁺], 225 [15.7, Ti(OⁱPr)₃⁺], 181 [14.2, Ti(acac)(OH)₂⁺], 163 [13.1, TiO(acac)⁺], 158 [100, Co(acac)⁺], 143 [17.1, Co(CH₃COCHCO)⁺].

The supernatant was slowly evaporated *in vacuo*. The residue was found to contain both purple platelet crystals with Co : Ti = 1 : 1 and also prismatic colorless crystals containing only Ti as metal (by SEM-EDS). Investigation of single crystals of the latter showed unit cell parameters identical to those earlier described for Ti₂(OⁱPr)₆(acac)₂ [9] thus testifying the formation of the latter as byproduct.

Solvolysis of [Co₂Ti₂(acac)₂(OⁱPr)₁₀] (1) in ⁱPrOH. A portion of **1** (0.191 g, 0.19 mmol) was dissolved at room temperature in 2 ml ⁱPrOH giving a bluish violet solution which was left to crystallize at −30 °C for a week. The pink prismatic crystals obtained were isolated by decantation and dried *in vacuo*. Yield 0.028 g (46%).

[Co₂(acac)₄(ⁱPrOH)₂] **2**. IR/cm⁻¹: 3402s br, 1655m sharp, 1596s, 1521s, 1307w, 1259m, 1200m, 1160s, 1133s, 1018s, 950s, 931s, 855w, 812w, 768m, 665m, 621m, 570m, 463w, 420m. UV-Vis, λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 470 (74), 490 (76), 510 (72), 575 (54).

Interaction of Co(acac)₂ with 3 eq. of Ta(OⁱPr)₅. Co(acac)₂ (0.118 g, 0.46 mmol) and Ta(OⁱPr)₅ (0.652 g, 1.37 mmol) were dissolved in 2 ml of toluene and refluxed for half an hour. The purple solution obtained was left under a septum at −30 °C for two months. The slow diffusion of toluene through the septum led to the almost complete evaporation of the solution leaving a mixture of purple platelets and colorless blocks. The crystals were dried *in vacuo* and separated by hand under the microscope. No exact yield could be established, but an almost quantitative transformation could be observed.

[Co₂Ta₂(OⁱPr)₁₄] **3** *(purple platelets)*. IR/cm⁻¹: 1159s, 1128s, 1003s, 840m, 820m, 789sh, 575s, 462m, 423m. UV-Vis, λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 540 (67), 590 (61).

[Ta(acac)(OⁱPr)₄] *(colorless blocks)*. IR/cm⁻¹: 1595m, 1525m, 1459s, 1373s, 1330m, 1284w, 1159s, 1128s, 1003s, 980s, 952s, 863sh, 836m, 817s, 781sh, 727w, 692w, 657w, 571s, 458m, 419m. MS, *m/z* [*I* (%), interpretation]: 457 [92.1, Ta(OⁱPr)₃- (acac)⁺], 417 [28.0, Ta(OⁱPr)₄⁺], 355 [15.4, TaO(OⁱPr)(acac)⁺], 313 [43.6, TaO(OH)(acac)⁺], 249 [12.8, Ta(OH)₄⁺].

Interaction of Ni(acac)₂ with 4 eq. of Nb(OⁱPr)₅. Ni(acac)₂ (0.417 g, 1.63 mmol) and Nb(OⁱPr)₅ (2.679 g, 6.90 mmol) were dissolved in 5 ml of toluene and refluxed for half an hour. The resulting bluish violet solution was left to crystallize for 3 weeks at −30 °C. The needle-shaped bluish violet crystals obtained were separated by filtration and dried *in vacuo*. Yield 1.191 g (68%).

[NiNb₂(OⁱPr)₁₂] **4**. IR/cm⁻¹: 1161s, 1128s, 1003s, 843m, 816m, 754w, 583s, 462m, 431sh. UV-Vis, λ/nm (ε/dm³ mol⁻¹

cm⁻¹): 440 (285), 530 (154), 585 (136), 765 (49). MS, *m/z* [*I* (%), interpretation]: 329 [100, Nb(OⁱPr)₄⁺].

Interaction of Co(acac)₂ with 2 eq. of Al(OⁱPr)₃. Co(acac)₂ (0.287 g, 1.11 mmol) and Al(OⁱPr)₃ (0.445 g, 2.18 mmol) were dissolved in 2 ml of toluene and heated to reflux (with complete dissolution of the aluminium alkoxide). The pinkish purple solution obtained was left to crystallize overnight at −30 °C. No formation of the solid phase could be observed. It was then evaporated to dryness and the residue was redissolved in 2.5 ml hexane on heating. The resulting solution was left to crystallize overnight at +4 °C. The purple cubo-octahedral crystals were separated by decantation and dried *in vacuo*. Yield 0.314 g [38% based on Co(acac)₂].

Interaction of Mᴵᴵ(acac)₂ (Mᴵᴵ = Co, Ni, Mg) with 2 eq. of Al(OⁱPr)₃ and 2 eq. Hacac. In a typical procedure Mᴵᴵ(acac)₂ (~0.4 g) and Al(OⁱPr)₃ (~1.0 g), Mᴵᴵ : Al = 1 : 2, were dissolved in toluene, refluxed for 10 min, and then cooled to +4 °C in the refrigerator (2 h). 2 eq. of acetylacetone were then added drop-wise by syringe with vigorous stirring. The reaction mixture was slowly evaporated *in vacuo* leaving (by microscopic observation) exclusively the cubo-octahedral crystals of the corresponding [MᴵᴵAl₂(acac)₄(OⁱPr)₄].

[CoAl₂(acac)₄(OⁱPr)₄] **5**. IR/cm⁻¹: 1599s, 1404m, 1377s, 1358m, 1283m, 1182w, 1167w, 1132s, 1027m, 968s, 929m, 832m, 766m, 680w, 634m, 599w, 575w, 493s, 474s. UV-Vis, λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 500 (116), 550 (180). MS, *m/z* [*I* (%), interpretation]: 757 [2.0, Al₄(OⁱPr)₁₁⁺], 721 [0.8, Al₄(OH)(OⁱPr)₁₀⁺], 655 [3.9, Al₄O(OⁱPr)₉⁺], 553 [8.6, Al₃(OⁱPr)₈⁺], 257 [30.9, Co(acac)₂⁺], 242 [40.8, Al(acac)₂(OH)⁺], 229 [100, Al(acac)- (OⁱPr)(OC₂H₄)⁺], 225 [86.7, Al(acac)₂⁺], 171 [43.5, Al(acac)- (OC₂H₅)⁺], 158 [83.4, Co(acac)⁺], 141 [91.8, AlO(CH₃COCH- COCH₂)⁺], 127 [87.7, AlH(acac)⁺], 126 [40.1, Al(acac)⁺].

[NiAl₂(acac)₄(OⁱPr)₄] **6**. IR/cm⁻¹: 1599s, 1402m, 1380s, 1284m, 1185w, 1163w, 1134s, 1028m, 967s, 930m, 831m, 767m, 678w, 600w, 575w, 495s, 475s. UV-Vis, λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 410 (195), 530 (122), 580 (102), 750 (41). MS, *m/z* [*I* (%), interpretation]: 757 [36.1, Al₄(OⁱPr)₁₁⁺], 655 [48.8, Al₄O- (OⁱPr)₉⁺], 553 [75.2, Al₃(OⁱPr)₈⁺], 256 [23.1, Ni(acac)₂⁺], 242 [22.3, Al(acac)₂(OH)⁺], 229 [72.6, Al(acac)(OⁱPr)(OC₂H₄)⁺], 225 [61.0, Al(acac)₂⁺], 171 [30.4, Al(acac)(OC₂H₅)⁺], 157 [16.2, Ni(acac)⁺], 141 [44.5, AlO(CH₃COCHCOCH₂)⁺], 127 [27.7, AlH(acac)⁺], 126 [13.0, Al(acac)⁺].

[MgAl₂(acac)₄(OⁱPr)₄] **7**. IR/cm⁻¹: 1615sh, 1599s br, 1529s, 1288s, 1186w, 1159m, 1136s, 1023s, 976s, 933s, 828m, 770s, 676w, 657w, 622m, 591m, 575sh, 548w, 505s, 482s, 419m. ¹H NMR, ppm: 5.36 (singlet, 4H, C*H*, acac), 3.82 (septet, 4H, C*H*, ⁱPr), 1.94 (singlet, 12H, C*H₃*, acac), 1.86 (singlet, 12H, C*H₃*, acac), 1.28 (doublet, 6H, C*H₃*, ⁱPr), 1.26 (doublet, 6H, C*H₃*, ⁱPr), 1.11 (doublet, 6H, C*H₃*, ⁱPr), 1.09 (doublet, 6H, C*H₃*, ⁱPr).

Solvolysis of [NiAl₂(acac)₄(OⁱPr)₄] (6) in ⁱPrOH. A portion of **6** (0.091 g, 0.12 mmol) was dissolved in 1.0 ml toluene and then 1.0 ml of isopropanol was added to the solution obtained. The initially bluish violet solution changed color first to brown and then to greenish brown. It was then left to crystallize under a septum at −30 °C for one month in a freezer. A small crop of bright green prismatic crystals was collected and identified to be an isopropanol solvate of nickel acetylacetonate (compound **9**) by a single crystal X-ray study.

[Ni₂(acac)₄(ⁱPrOH)₂] **9**. 3460sh, 3281s br, 1599s, 1377s, 1315m, 1287m, 1256s, 1194m, 1163m, 1128s, 1019s, 945s, 926s, 859w, 832w, 817w, 774s, 762s, 676m br, 657sh, 614w, 579s, 486m, 416s. UV-Vis, λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 530 (10), 645 (18), 745 (12).

Solvolysis of [MgAl₂(acac)₄(OⁱPr)₄] (7) in toluene. A portion of **7** (0.814 g, 1.15 mmol) was dissolved in 2 ml toluene and refluxed for 1 h. It was then left to crystallize overnight at

Table 1 Crystal data and data collection details for compounds 1–9									
	1	2	3	4	5	6	7	8	9
Formula weight	1002.73	634.47	1306.96	953.56	745.66	745.44	711.04	935.64	634.03
Formula	$C_{40}H_{94}Co_2O_{14}Ti_2$	$C_{26}H_{44}Co_2O_{10}$	$C_{42}H_{98}Co_2O_{14}Ta_2$	$C_{36}H_{94}Nb_2NiO_{12}$	$C_{32}H_{56}Al_2CoO_{12}$	$C_{32}H_{56}Al_2NiO_{12}$	$C_{32}H_{56}Al_2MgO_{12}$	$C_{38}H_{70}Al_2O_{14}Zn_2$	$C_{26}H_{44}Ni_2O_{10}$
T/K	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	293(2)	295(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$	$C2/c$	$C2/c$	$Ccca$	$Ccca$	$C2/c$	$P2(1)/n$
a/Å	9.953(5)	9.4213(14)	9.586(6)	29.509(7)	17.451(9)	15.479(3)	15.4139(17)	17.044(3)	9.335(7)
b/Å	10.004(6)	8.4980(13)	10.551(6)	9.536(2)	15.407(9)	17.480(4)	17.417(2)	30.978(6)	8.508(6)
c/Å	15.639(10)	19.315(3)	15.938(10)	18.973(5)	14.656(8)	14.666(3)	14.6913(16)	11.788(2)	19.213(13)
α/°	83.275(9)	90	83.624(15)	90	90	90	90	90	90
β/°	79.323(15)	97.481(3)	78.361(13)	107.790(4)	90.288(17)	90	90	118.10(3)	97.51(2)
γ/°	64.758(9)	90	68.940(14)	90	90	90	90	90	90
V/Å³	1382.8(15)	1533.3(4)	1472.0(16)	5083(2)	3941(4)	3968.2(14)	3944.2(8)	5490.4(19)	1513(1)
Z	1	2	1	4	4	4	4	4	2
μ/mm⁻¹	0.919	1.131	4.308	0.857	1.257	0.587	0.144	0.955	1.277
R1	0.0554	0.0544	0.0827	0.0675	0.0482	0.0546	0.0420	0.0758	0.0607
wR2	0.1358	0.1175	0.1671	0.1712	0.1121	0.1496	0.1178	0.2372	0.1208
No. of independent reflections	1634 [R(int) = 0.1283]	3723 [R(int) = 0.0659]	2667 [R(int) = 0.1055]	2303 [R(int) = 0.0543]	1826 [R(int) = 0.1268]	1378 [R(int) = 0.0337]	925 [R(int) = 0.0442]	2545 [R(int) = 0.0627]	1263 [R(int) = 0.1163]
No. of observed reflections	928 [I > 2σ(I)]	1798[I > 2σ(I)]	1194[I > 2σ(I)]	1427[I > 2σ(I)]	1108[I > 2σ(I)]	1020[I > 2σ(I)]	685[I > 2σ(I)]	1696[I > 2σ(I)]	647[I > 2σ(I)]

−30 °C. The needle-shaped crystals formed were separated by decantation and dried *in vacuo*, and the volume of the parent solution was reduced then to about 1 ml and it was again left to crystallize overnight. The crop of needle-shaped crystals formed was again separated by decantation, dried *in vacuo* and joined with the product obtained on the first crystallization. This product was identified to be Al(acac)₃[10] by its IR, ¹H NMR spectra and the single crystal parameters determined for four randomly chosen crystals. Yield 0.467 g (94%).

Interaction of Zn(acac)₂ with 2 eq. of Al(O^iPr)₃ and 2 eq. Hacac. Zn(acac)₂ (0.332 g, 1.26 mmol) and Al(O^iPr)₃ (0.514 g, 2.52 mmol) were dissolved in 3 ml of toluene and warmed to reflux (with complete dissolution of the aluminium alkoxide). The colorless solution thus obtained was cooled to +4 °C in the refrigerator (2 h) and then acetylacetone (0.25 ml, ≈2.5 mmol) was added dropwise by syringe with vigorous stirring. No visible changes occurred with the solution. The solution was diluted with 1.5 ml of hexane and left overnight at −30 °C for crystallization. The thin platelet crystals formed were separated by filtration and dried *in vacuo*. Yield 0.338 g (73%).

[Zn₂Al₂(acac)₄(O^iPr)₆] **8**. IR/cm⁻¹: 1614sh, 1603s, 1529s, 1288m, 1190m, 1167s, 1136s, 1085w, 1027s, 1011sh, 972s, 933s, 828m, 770s, 731m, 700w, 684w, 657w, 630m, 583s, 490s, 478s, 435w, 416w. ¹H NMR, ppm: 5.36 (singlet, 4H, C*H*, acac), 4.21 (septet, 2H, C*H*, ^iPr), 3.92 (septet, 4H, C*H*, ^iPr), 1.95 (singlet, 12H, C*H₃*, acac), 1.89 (singlet, 12H, C*H₃*, acac), 1.31 (doublet, 12H, C*H₃*, ^iPr), 1.24 (12H, C*H₃*, ^iPr), 1.12 (doublet, 6H, C*H₃*, ^iPr), 1.04 (doublet, 6H, C*H₃*, ^iPr).

Preparative sublimation of [CoAl₂(acac)₄(O^iPr)₄] (5). A portion of **5** (0.116 g) was placed in a 150 mm long Schlenk tube, 12 mm in diameter, and heated slowly to 160 °C with the help of a poly(ethyleneglycol) bath on continuous evacuation to 10⁻² mmHg (35 mm of the total length of the tube were placed into the liquid). The pinkish violet sample melted at 116–118 °C and the drops of light pinkish liquid started to condense on the part of the tube not dipped into the bath. On subsequent heating to 140–150 °C in the upper part of the condensate there was observed the formation of round aggregates of platelet crystals. The residue on the bottom had darkened and solidified and the experiment was stopped. The determination of the unit cell parameters for the platelet crystals that were colorless under the microscope showed them to be Al(acac)₃. The liquid condensate did not solidify at the room temperature for several hours and in ~24 h became a glassy solid. Its IR spectrum did not differ significantly from that of **5** in the position of the bands, but the band corresponding to the presence of acetylacetonate ligands (1599 cm⁻¹) was at a noticeably higher relative intensity, indicating the higher content of this ligand in the product of sublimation.

Crystallography

The data collection for all the single crystals of compounds studied was carried out at 22 °C (for details see Table 1). All the structures were solved by direct methods. The coordinates of the metal atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. The structures were refined by least-squares first in isotropic and then in anisotropic approximations [except for: two pairs of methyl groups, defined by the methyne atoms C(30) and C(40) which were disordered because of the thermal motion in **1**; the structure of **3**, where the rotational disorder and a too low data-to-parameter ratio precluded the anisotropic refinement of the carbon atoms and compound **4**, where the orientational disorder precluded the successful carrying out of this step for the carbon atoms, due to the proximity of positions with partial population and a too low data-to-parameter ratio. The population of the alternative positions in **4** was

refined independently on the supposition of the total population being unity. No anisotropic refinement has been made for the central two bridging alkoxide groups, disordered between two symmetrically dependent positions. The population of ½ for each orientation was in this case imposed by the symmetry operation. The disorder of the carbon atoms precluded the possibility to calculate geometrically the hydrogen atom positions in this structure]. The coordinates of the hydrogen atoms were calculated geometrically and were included into the final refinement in isotropic approximation for all the compounds (except for **4**). All calculations were performed using the SHELXTL-NT program package[11] on an IBM PC.

CCDC reference numbers 168879 and 168880 for compounds **1** and **2** and 189538–189544 for compounds **3–9**, respectively.
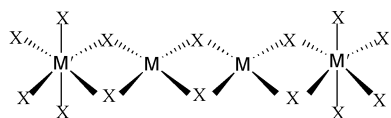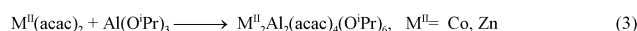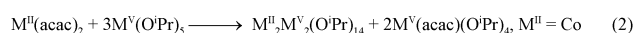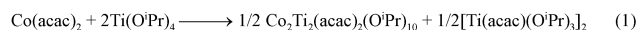
See http://www.rsc.org/suppdata/dt/b2/b206662a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Reaction pathways

Heterometallic species with M : M′ = 1 : 1. The data on the molecular structures of the heterometallic complexes of divalent metals in combination with the early transition metals, such as titanium(IV), zirconium(IV), niobium(V), tantalum(V) and molybdenum(VI) derivatives of primary alcohols indicated that the complexes of 1 : 1 composition most often displayed structures belonging to the so called titanium methoxide, $Ti_4(OMe)_{16}$,[12] or simply M_4X_{16}-type, where four edge-sharing octahedra are combined in a fragment of a CdI_2-type layer, the metal atoms being arranged in a planar rhombus.[13,14] Formation of the heteroleptic β-diketonato-alkoxide heterometallic species of this type has been observed on reactions of $Co(acac)_2$ with $Zr(O^nPr)_4$ giving $Co_2Zr_2(acac)_2$-$(O^nPr)_{10}$,[15] $Ba(thd)_2$ with $Ti(OEt)_4$ giving $Ba_2Ti_2(thd)_4(OEt)_8$-$(EtOH)_2$,[16] and also $M^{II}(acac)_2$ (M^{II} = Co, Ni, Mg, Zn) with niobium and tantalum methoxides giving $M^{II}M_2^V(acac)_2$-$(OMe)_{12}$,[5] and Co and Ni acetylacetonates with $MoO(OMe)_4$ giving $M_2^{II}Mo_2O_2(acac)_2(OMe)_{10}$.[17] It was interesting to investigate whether the interaction of divalent metal acetylacetonates with metal alkoxides—derivatives of secondary alcohols, like isopropanol—follows the same pattern.

The large size of the isopropoxo-ligand was intended to enforce a 1 : 2 stoichiometry on the reaction according to eqn. (1) (Scheme 1) opening up the possibility for the partial

$$Co(acac)_2 + 2Ti(O^iPr)_4 \longrightarrow 1/2\ Co_2Ti_2(acac)_2(O^iPr)_{10} + 1/2[Ti(acac)(O^iPr)_3]_2 \quad (1)$$

$$M^{II}(acac)_2 + 3M^V(O^iPr)_5 \longrightarrow M^{II}M_2^V(O^iPr)_{14} + 2M^V(acac)(O^iPr)_4,\ M^{II} = Co \quad (2)$$

$$M^{II}(acac)_2 + Al(O^iPr)_3 \longrightarrow M^{II}_2Al_2(acac)_4(O^iPr)_6,\quad M^{II} = Co,\ Zn \quad (3)$$
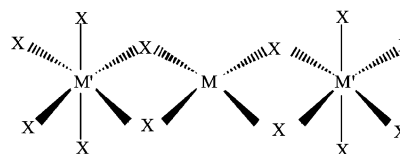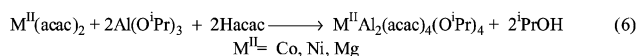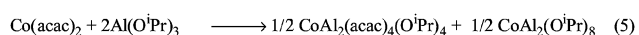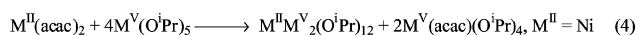

Scheme 1

removal of bidentate acetylacetonate ligands to permit the reduction of the total number of donor atoms [in analogy with the reaction pathway observed for the interaction of $M^{II}(acac)_2$ with $M^V(OMe)_5$].[5] We expected in this case the formation of an analog of the $Co_2Zr_2(acac)_2(O^nPr)_{10}$[15] compound, where the M_4X_{16}-type structure is conserved, but the number of donor atoms is reduced due to pentacoordination of the cobalt atoms. The investigation of the nature of the reaction products confirmed that the reaction followed eqn. (1), but the molecular structure of the heterometallic species obtained turned out to belong to a different, linear chain-structure type: $M_2M'_2X_{14}$.

This result appeared reasonable, taking into account that a considerable number of heterometallic isopropoxides, for example $BaNb_2(O^iPr)_{12}(^iPrOH)_2$ or $LaNb_2(O^iPr)_{13}$,[8] display chain-like molecular structures.

Obtaining heterometallic species with a chain-like molecular structure opens up the prospect for the preparation of derivatives of early transition metals other than titanium with the same type of molecular structure using the interaction of acetylacetonates with their isopropoxides. It was then evident that the structure of the $M_2M_2'X_{14}$-type should be a homoleptic alkoxide complex for M = M^{II}, and M′ = M^V ($14 = 2 \times 2 + 5 \times 2$, *i.e.* number of donor atoms is equal to the sum of the formal charges—no bidentate ligands necessary). At the same time, for the methoxide derivatives, it has been found that the action of $M^V(OR)_5$ results in removal of an acac-ligand in the form of $M^V(acac)(OR)_4$. This opened up the possibility to approach the $M_2M_2'(O^iPr)_{14}$ type complexes using eqn. (2), Scheme 1 (reactant ratio—$M^{II} : M^V = 1 : 3$), which was realized for the cobalt–tantalum derivative.

An analogous calculation showed that the $M_2M_2'X_{14}$ composition for the derivatives of the divalent metals and aluminium [$14 = 2 \times 2 \times 2$(from acac) + 2×3(from O^iPr)] can be achieved by reaction of their acetylacetonates and aluminium isopropoxide in a 1 : 1 ratio, see eqn. (3), Scheme 1 ‡

Heterometallic species with M : M′ = 1 : 2. The species of the $M_2M_2'X_{14}$-type were built up of two tetrahedral blocks for the divalent metal atoms at the center and two octahedral blocks at the periphery. The question raised at this point was: Why not the linear chain structure with only one tetrahedral unit in the center for the titanium derivative and can such a structure be obtained for the niobium and tantalum derivatives? We applied then one more equivalent of $3M^V(OiPr)_5$ [reactant ratio 1 : 4, eqn. (4), Scheme 2], which permitted us to obtain a nickel–

$$M^{II}(acac)_2 + 4M^V(O^iPr)_5 \longrightarrow M^{II}M_2^V(O^iPr)_{12} + 2M^V(acac)(O^iPr)_4,\ M^{II} = Ni \quad (4)$$

$$Co(acac)_2 + 2Al(O^iPr)_3 \longrightarrow 1/2\ CoAl_2(acac)_4(O^iPr)_4 + 1/2\ CoAl_2(O^iPr)_8 \quad (5)$$

$$M^{II}(acac)_2 + 2Al(O^iPr)_3 + 2Hacac \longrightarrow M^{II}Al_2(acac)_4(O^iPr)_4 + 2^iPrOH \quad (6)$$
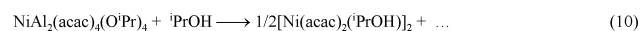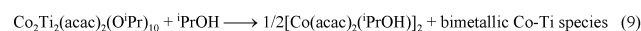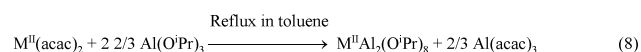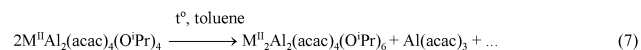$$M^{II} = Co,\ Ni,\ Mg$$

Scheme 2

niobium derivative with the molecular structure of the $MM_2'X_{12}$-type. The formation of a representative of this structure type did not occur in the case of titanium isopropoxide supposedly due to its relative weakness as a Lewis acid, a stronger donor unit consisting of two tetrahedra being necessary in this case. It should be mentioned that the same reason lies supposedly behind the inability of titanium isopropoxide to affect the poorly soluble magnesium acetylacetonate (remaining unchanged in its presence even on prolonged reflux).

The success achieved in the preparation of the $[NiNb_2(O^iPr)_{12}]$ (**4**) has drawn our attention to the synthesis of the bimetallic derivatives of divalent metals and aluminium, being of interest in connection with the preparation of spinel coatings.[18] We have first simply analyzed the interaction of the cobalt acetylacetonate and aluminium alkoxide in a 1 : 2 ratio and have found that this reaction is associated with the ligand

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‡ The synthesis and structural investigation of $Co_2Al_2(acac)_4(O^iPr)_6$ has been carried out and reported by our group[19] since the submission of this paper for publication.

redistribution according to eqn. (5), Scheme 2. It was then clear that the system, even in this case, had a trend towards formation of the complexes of the $MM_2'X_{12}$ structure type, but needed additional donor atoms to be provided. The latter was achieved by the addition of two equivalents of acetylacetone per divalent metal derivative and gave the quantitative yields of the corresponding acetylacetonato-alkoxides [eqn. (6), Scheme 2] except for zinc, where only the tetranuclear $[Zn_2Al_2(acac)_4(O^iPr)_6]$ (**8**) could be isolated. The observed trend to formation of a $M_2M'_2X_{14}$ type structure can in this case be explained by much smaller difference in Lewis acidity and basicity between zinc and aluminium compounds compared to those of the compounds of the other divalent metals used.

Solvolysis of isopropoxo-acetylacetonate complexes. *Solvolysis by alcohol.* An attempt at recrystallization of compound **1** from ^iPrOH was found to produce cobalt acetylacetonate solvate with isopropanol, $[Co(acac)_2(^iPrOH)]_2$, **2**, as the only crystalline isolable product, thus confirming the earlier general observation that polar, protic solvents such as alcohols often destroy the heterometallic alkoxide complexes derived from two metals which have only a small difference in Lewis acid–base properties.[5] The same kind decomposition could even be observed for the acetylacetonato-isopropoxoaluminates in the presence of the parent alcohol [eqns. (9) and (10), Scheme 3].

$$2M^{II}Al_2(acac)_4(O^iPr)_4 \xrightarrow{t^o, \text{ toluene}} M^{II}_2Al_2(acac)_4(O^iPr)_6 + Al(acac)_3 + ... \quad (7)$$

$$M^{II}(acac)_2 + 2\,2/3\,Al(O^iPr)_3 \xrightarrow{\text{Reflux in toluene}} M^{II}Al_2(O^iPr)_8 + 2/3\,Al(acac)_3 \quad (8)$$

$$Co_2Ti_2(acac)_2(O^iPr)_{10} + {}^iPrOH \longrightarrow 1/2[Co(acac)_2(^iPrOH)]_2 + \text{bimetallic Co-Ti species} \quad (9)$$

$$NiAl_2(acac)_4(O^iPr)_4 + {}^iPrOH \longrightarrow 1/2[Ni(acac)_2(^iPrOH)]_2 + ... \quad (10)$$

Scheme 3

The UV-Vis spectral study of the solutions of **6** in the toluene : isopropanol (1 : 1) mixture has shown very distinct and easily observable color changes from bluish violet to brownish green and then bright green, corresponding to the coordination changes for nickel atoms from tetrahedral to octahedral. The isolation of the nickel acetylacetonate solvate from this mixture indicates that the solvolysis occurs with complete decomposition of the heterometallic species. The isopropanol solvates of cobalt and nickel acetylacetonates were found to be the only isolable crystalline products on reaction of the corresponding $M(acac)_2$ with metal isopropoxides in the presence of ^iPrOH.

The decomposition of heterometallic species on addition of Lewis bases was earlier observed for the alkoxide β-diketonates both for the late transition metals in combination with niobium and tantalum[5] and for yttrium–barium and barium–copper derivatives.[20]

Solution thermolysis of acetylacetonato-isopropoxoaluminates in inert solvents. ^{1}H NMR study of the transformation of the $[MgAl_2(acac)_4(O^iPr)_4]$ (**7**) solution in an inert solvent on heating has shown very clearly its rather quick decomposition at 50 °C with formation of $Al(acac)_3$ and a new complex with the 2 : 1 intensity ratio for the alkoxide functions, corresponding supposedly to the formation of a magnesium analog of complex **8** [eqn. (7), Scheme 3]. Complex **8** itself turned out to be much more stable, but also decomposed slowly with the formation of $Al(acac)_3$. These data indicated that heating of the solutions should be avoided in the application of compounds **5**–**7** for the preparation of spinel materials. At the same time, the quite low solubility of the aluminium acetylacetonate in toluene compared to that of the bimetallic isopropoxides of the divalent metals (which is practically unlimited), permits the supposition that the isopropoxoaluminate derivatives may be obtained by the reaction of metal acetylacetonates with aluminium isopropoxide on prolonged reflux. This supposition is indirectly

confirmed by the possibility of almost quantitative separation of $Al(acac)_3$ from the products of the prolonged reflux of **5** in toluene.

Behavior of the acetylacetonato-isopropoxides of divalent metals on evaporation

Being interested in the possibility to purify the samples of alkoxide acetylacetonates by sublimation described in the literature[6] for **6**, we have studied the electron ionization mass-spectra of compounds **1**, **5** and **6**, hoping to find the heterometallic species to be present in the gas phase. Unfortunately, the mass-spectra have provided proof for decomposition of the complexes, the fragments corresponding to fragmentation of the homometallic acetylacetonates of the divalent metals being the only species containing these metal atoms. Another factor indicating the decomposition on evaporation, and not under ionization by the electron beam in the gas phase, was the total ratio of intensities of the peaks containing the divalent metal atoms and those containing aluminium: in all the cases it was lower than 1 : 3, while a ratio of 1 : 2 would be required if the evaporation occurred without decomposition. The preparative study of the sublimation of **5** revealed the formation of crystalline $Al(acac)_3$ as one of the major products of this process, confirming the results of the mass-spectral studies. No fragments at all containing the late transition metal atom were found in the mass-spectrum of the homoleptic alkoxide compound **4**, indicating the decomposition to be the major process under thermal treatment *in vacuo* even in this case. This permits us to conclude that the alkoxide complexes of late transition metals in general cannot be purified by sublimation in contradiction to the data presented in ref. 6.

Crystal and molecular structures

The centrosymmetric linear molecular structure of compound **1** (see Fig. 1 and Table TS2, ESI) contains in its center a pair of
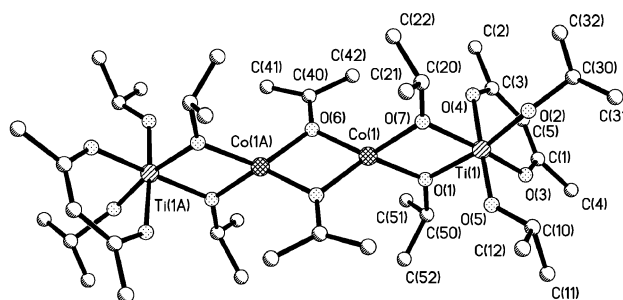

Fig. 1 Molecular structure of $[Co_2Ti_2(acac)_2(O^iPr)_{10}]$ (**1**).

$Co(O^iPr)_4$ tetrahedra sharing a common edge. Two $Ti(O^iPr)_4$-(acac) octahedra are attached to the opposite (OR)$_2$-edges of this pair, all alkoxide groups at the cobalt atoms being thus bridging ones. The tetrahedral arrangement of ligands around the Co atoms is slightly distorted: the bridges between two cobalt atoms are practically symmetric [Co(1)–O(6) 1.923(9), Co(1)–O(6)#1 1.933(9) Å], while the bridges between the cobalt and titanium atoms differ more from each other in length and are both longer than the Co–O(R)–Co ones [Co(1)–O(7) 1.946(10), Co(1)–O(1) 1.959(10) Å]. The tetrahedral arrangement around the cobalt is rather strongly linearly distorted with only 77.7(4)–80.0(4)° angles between the neighboring oxygen atoms. All the observed Co–O distances are very close to the Co–μ-OPr bond lengths earlier discovered in $Zr_2Co_4(\mu_6$-O)-$(\mu$-$OC_3H_7)_8(OC_3H_7)_2(acac)_4$[3] and $Zr_3Fe(\mu_4$-O)$(\mu$-$OC_3H_7)_6$-$(OC_3H_7)_4(acac)_3$[4] [1.930(6), 1.935(5) Å]. The octahedral arrangement for the titanium atoms is rather severely distorted: the Ti–O distances for the terminal alkoxide ligands are much shorter [Ti(1)–O(5) 1.773(9), Ti(1)–O(2) 1.773(11) Å] than both

the Ti–μ-OR ones [Ti(1)–O(7) 1.945(10), Ti(1)–O(1) 2.012(9) Å] and those to the oxygen atoms of acetylacetonate ligand [Ti(1)–O(3) 2.024(11), Ti(1)–O(4) 2.088(10) Å]. The observed Ti–O bond lengths are, in fact, practically coinciding with those in the structure of $Ti_2(acac)_2(\mu-O^iPr)_2(O^iPr)_2$, also containing the $Ti(O^iPr)_4(acac)$ fragments with analogous structural functions.[9]

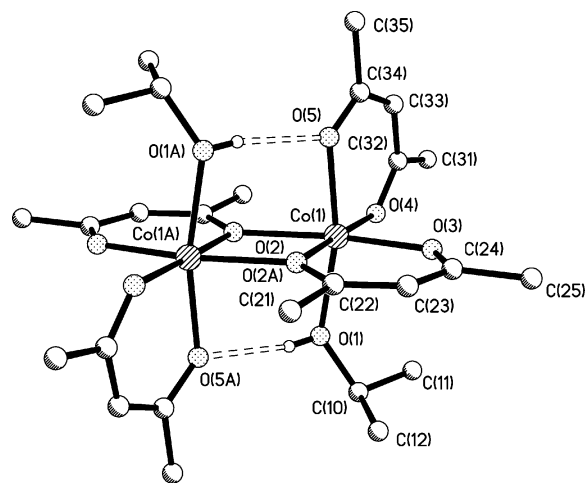The centrosymmetric molecular structures of the structurally analogous compounds **2** and **9** (see Fig. 2 and Tables TS3 and

Fig. 2 Molecular structure of $[Co_2(acac)_4(^iPrOH)_2]$ (**2**).

TS9 respectively) contain two $[M^{II}(\mu,\eta^2-acac)(acac)(^iPrOH)]$ [M^{II} = Co (**2**), Ni (**9**)] octahedra, sharing a common edge (both M^{II}-atoms and the μ,η^2-acac-groups lying in the equatorial plane). The found M^{II}–O bond lengths fall into the usually observed ranges for the ligands involved.[3–5]

The centrosymmetric molecular structure of compound **3** (Fig. 3, Table TS4) is surprisingly close in appearance to that of
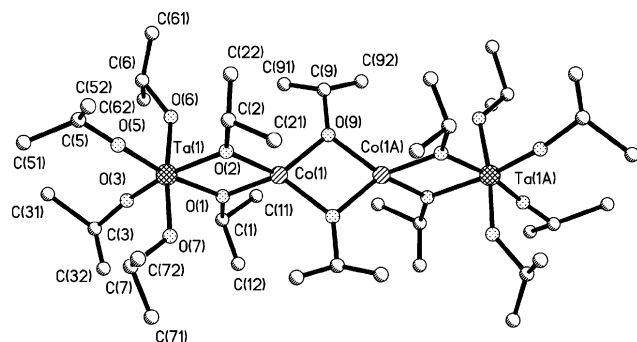
Fig. 3 Molecular structure of $[Co_2Ta_2(O^iPr)_{14}]$ (**3**).

compound **1**: the cobalt atoms are tetrahedrally coordinated, the two tetrahedra sharing a common edge with each other and the opposite edges with two $Ta(O^iPr)_6$-octahedra (the difference with **1** given by the presence of two isopropoxide ligands instead of an acetylacetonate one). The same kind of distortion of the $Co(O^iPr)_4$-tetrahedra occurs with a bit more asymmetric and shorter bridges between the Co-atoms [Co(1)–O(6A) 1.911(19), Co(1)–O(6) 1.943(17) Å] and in contrast more symmetric and a bit longer bridges between the cobalt and the tantalum atoms [Co(1)–O(1) 1.946(17) and Co(1)–O(2) 1.95(2) Å]. The tantalum–oxygen bond lengths are noticeably longer for the bridging ligands [1.95(2)–1.97(2) Å], compared to the terminal ones and fall into the range usually observed for the tantalum isopropoxides.[7]

The centrosymmetric crystal structure of compound **4** (Fig. 4, Table TS5) originates from the combination of two non-centrosymmetric $NiNb_2(O^iPr)_{12}$-molecules with the common nickel and niobium atoms and the two arrangements of the alkoxide ligands (with equal probability) turned nearly exactly 90° with

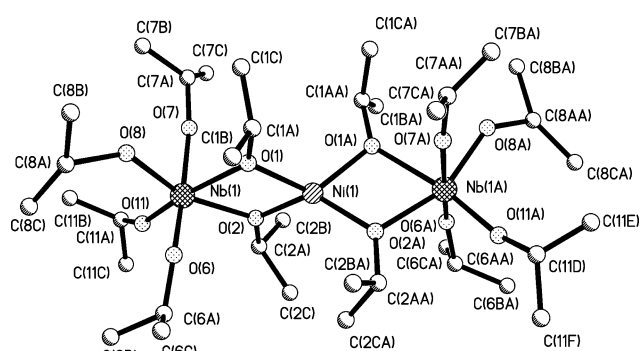**Fig. 4** Molecular structure of $[NiNb_2(O^iPr)_{12}]$ (**4**).

respect to one another. The $Ni(O^iPr)_4$-tetrahedra are rather strongly linearly distorted with only a 78.6(6)–78.8(6)° angle between the two pairs of neighboring oxygen atoms. The nickel–oxygen bond lengths [1.889(15)–1.947(13) Å] are very close to those observed for the analogous cobalt-containing tetrahedra in **1** and **3**. The bond lengths and angles inside the $Nb(O^iPr)_6$-octahedra fall into the ranges observed usually for the niobium isopropoxides.[8]

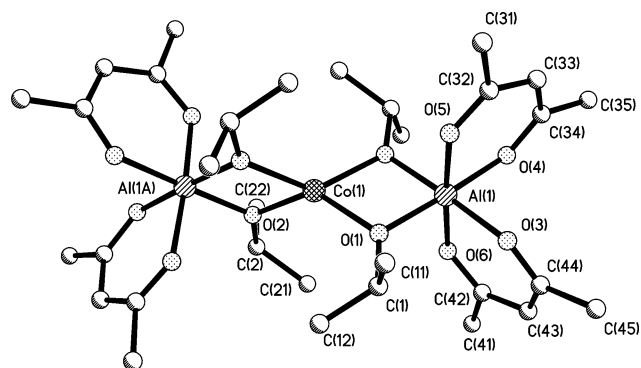The centrosymmetric crystal structure of compound **5** (Fig. 5,

Fig. 5 Molecular structure of $[CoAl_2(acac)_4(O^iPr)_4]$ (**5**).

Table TS6) is built up of the non-centrosymmetric $CoAl_2(acac)_4$-$(O^iPr)_4$ molecules containing a linearly distorted $Co(O^iPr)_4$ tetrahedron in the center and two symmetrically identical $Al(acac)_2(O^iPr)_2$ octahedra turned 90° with respect to one another. The bond lengths and angles inside the cobalt-based tetrahedra are very close to those in **1** and **3** described above. The aluminium-based octahedra are rather symmetric with the almost orthogonal arrangement of the metal–oxygen bonds and bond lengths and angles very close to those observed in the related homometallic complex $Al_2(O^iPr)_2(Et_2acac)_4$.[10]

The centrosymmetric crystal structure of the compound **7** (Fig. 6, Table TS7, compound **6** has an analogous structure, but the details of its structural study will be reported separately together with spinel thin film elaboration and characteriz-
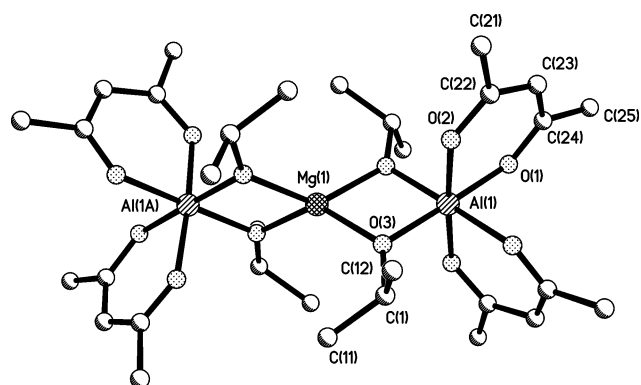
Fig. 6 Molecular structure of $[MgAl_2(acac)_4(O^iPr)_4]$ (**7**).

ation)[21] is built up of the non-centrosymmetric MgAl$_2$(acac)$_4$-(O^{i}Pr)$_4$ molecules closely analogous those of compound **5**. The only difference lies in the slightly higher symmetry realized for this molecule, so that there is present only one symmetrically independent magnesium–oxygen bond Mg(1)–O(3) 1.935(2) Å, and only one symmetrically independent acetyacetonate ligand with almost symmetric attachment to the aluminium atom [Al(1)–O(1) 1.996(3) and Al(1)–O(2) 1.900(3) Å].

The centrosymmetric molecular structure of compound **8** (Fig. 7, Table TS8) is in its turn an analog of the structures of **1**
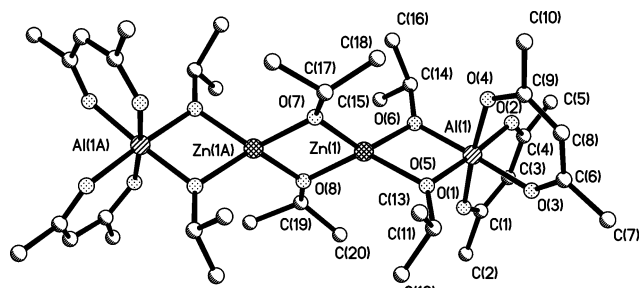

Fig. 7 Molecular structure of [Zn$_2$Al$_2$(acac)$_4$(O^{i}Pr)$_6$] (**8**).

and **3**. Its central part is composed of two edge-sharing linearly distorted Zn(O^{i}Pr)$_4$-tetrahedra and the peripheral ones—by the Al(acac)$_2$(O^{i}Pr)$_2$ octahedra. The Zn–O bond lengths are quite logically slightly longer than the Co–O and Ni–O ones [1.946(5)–1.960(6) Å] and in good agreement with those observed in the structures of Zn(μ-OCEt$_3$)$_2$[N(SiMe$_3$)$_2$]$_2$[22] and I$_2$Zn$_2$Ta$_4$O$_4$(O^{i}Pr)$_{14}$.[23] The geometry of the aluminium-based fragment is identical to those described above for compounds **5** and **7**.

Conclusions

The data presented in this work together with analysis of data in the literature permit the formulation of a number of general considerations concerning the formation and stability of the heterometallic alkoxide complexes: (1) The formation of the heterometallic alkoxide complexes appears, in the majority of cases, to be a thermodynamically controlled process, resulting in formation of species displaying molecular structures belonging to a relatively small number of structural types as has already been suggested in refs. 13 and 24. This opens up the prospect of relatively simple design for novel alkoxide complexes *via* choice of ligands with the proper number of donor atoms (and proper steric requirements) to fit a chosen model. Detailed explanation of this *Molecular Structure Design Concept* is provided in ref. 25. (2) Application of solvents able to act as Lewis bases should be avoided in the synthesis and the heterometallic precursors should have similar Lewis acidities. (3) The lability of the heterometallic alkoxide complexes (especially the heteroleptic ones), which is rather high in general, can easily lead to different reaction products at different temperatures, because of the easy redistribution of ligands in these species in solution. (4) Sublimation or distillation of the heterometallic compounds leads very often to their decomposition due to very strong differences in volatility for the possible homometallic products. Data on the possibility of distillation for the heterometallic derivatives of the late transition metals published so far[6] were found to be erroneous.

References

1 J. H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts and Applications*, J. Wiley and Sons, New York, 1983; B. Jongsomjit, J. Panpranot and J. G. Goodwin, *J. Catal.*, 2001, **204**, 98–109.
2 D. C. Bradley, R. C. Mehrotra and P. D. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978.
3 R. Schmid, A. Mosset and J. Galy, *Inorg. Chim. Acta*, 1991, **179**, 167.
4 R. Schmid, H. Ahamdane and A. Mosset, *Inorg. Chim. Acta*, 1991, **190**, 237.
5 P. Werndrup and V. G. Kessler, *J. Chem. Soc., Dalton Trans.*, 2001, 574.
6 R.C. Mehrotra, *Coord. Chem.*, 1981, **21**, 113 (IUPAC).
7 N. Y. Turova, A. V. Korolev, D. E. Tchebukov, A. I. Belokon, A. I. Yanovsky and Y. T. Struchkov, *Polyhedron*, 1996, **15**, 3869.
8 E. P. Turevskaya, N. Y. Turova, A. V. Korolev, A. I. Yanovsky and Y. T. Struchkov, *Polyhedron*, 1995, **14**, 1531.
9 R. J. Errington, J. Ridland, W. Clegg, R. A. Coxall and J. M. Sherwood, *Polyhedron*, 1998, **17**, 659.
10 J. H. Wengrovius, M. F. Garbauskas, E. A. Williams, R. C. Going, P. E. Donahue and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 982.
11 SHELXTL 5.3 Reference Manual, Bruker AXS, Madison, WI, 1997.
12 K. Watenpaugh and C. N. Coughlan, *Chem. Commun.*, 1967, 76.
13 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
14 N. Ya. Turova, E. P. Turevskaya, V. G. Kessler and A. I. Yanovskaya, *The Chemistry of Metal Alkoxides*, Kluwer Academic Publishers, London, 2002.
15 R. Schmid, A. Mosset and J. Galy, *Acta Crystallogr., Sect. C*, 1991, **47**, 750.
16 V. G. Kessler, L. G. Hubert-Pfalzgraf, S. Daniele and A. Glaizes, *Chem. Mater.*, 1994, **6**, 2336.
17 V. G. Kessler, G. A. Seisenabeva and P. Werndrup, *9th Nordic Symposium on Coordination Chemistry*, June 14–16, 2002, Umeå, Sweden, P19.
18 M. Veith, *J. Chem. Soc., Dalton Trans.*, 2002, 2405.
19 E. Suslova, G. A. Seisenbaeva and V. G. Kessler, *Inorg. Chem. Commun.*, 2002, **5**, 946.
20 F. Labrize, L. G. Hubert-Pfalzgraf, J. Vaissermann and C. B. Knobler, *Polyhedron*, 1996, **15**, 577.
21 S. Parola, V. G. Kessler, to be published.
22 S. C. Goel, M. Y. Chiang and W. E. Buhro, *Inorg. Chem.*, 1990, **29**, 4646.
23 S. Boulmaaz, L. G. Hubert-Pfalzgraf, S. Halut and J.-C. Daran, *J. Chem. Soc., Chem. Commun.*, 1994, 601.
24 V. G. Kessler, L. G. Hubert-Pfalzgraf, S. Halut and J.-C. Daran, *J. Chem. Soc., Chem. Commun.*, 1994, 705.
25 V. G. Kessler, *Chem. Commun.*, 2003, DOI: 10.1039/b209168m.