DALTON
FULL PAPER

Interaction of $Co(acac)_2$ and $Ta(OMe)_5$: isolation and single crystal study of the products. $M^{II}_2M^{V}_2(acac)_2(OMe)_{12}$, M^{II} = Co, Ni, Zn or Mg and M^{V} = Ta or Nb: A new class of heterometallic heteroleptic alkoxide complexes

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The interaction of $Co(acac)_2$ and $Ta(OMe)_5$ in dry toluene led to formation of crystalline $[Co_2Ta_2(acac)_2(OMe)_{12}]$ **1** and $[Ta(acac)(OMe)_4]$ **2** complexes. If the starting material is not completely water-free the products obtained are $[Co_4(acac)_6(OMe)_2(MeOH)_2]$ **3** and $Co(acac)_2{\cdot}2MeOH$ **4** due to hydrolysis of $Ta(OMe)_5$ producing free methanol and thus altering the reaction pathway. The interaction of $M^{II}(acac)_2$, M^{II} = Co, Ni, Zn or Mg, and $M^{V}(OMe)_5$, M^{V} = Ta or Nb, in dry toluene was found generally to provide $M^{II}_2M^{V}_2(acac)_2(OMe)_{12}$ **5**–**8**, a new class of heterometallic heteroleptic alkoxide complexes. The crystal structures of **1**–**8** have been determined.

Introduction

Heterometallic alkoxide complexes of late and heavy transition metals are of interest as precursors of materials for catalysis. Catalytic processes could include oil cracking and transformation of methanol into formaldehyde.[1] The approaches to heterometallic compounds are restricted because alkoxides of late transition metals are insoluble and non-reactive.[2] An interesting way to heterometallic complexes is the reaction between a metal alkoxide and β-diketonate complex of another metal atom. Very little is known about the interactions of late transition metal β-diketonates and metal alkoxides. Two of the three heterometallic species structurally characterised so far, $Zr_2Co_4(\mu_6\text{-}O)(\mu\text{-}OC_3H_7)_8(OC_3H_7)_2(acac)_4$[3] and $Zr_3Fe(\mu_4\text{-}O)(\mu\text{-}OC_3H_7)_6(OC_3H_7)_4(acac)_3$,[4] were found to be oxo complexes. It appeared attractive to investigate in detail the interaction of late transition metal β-diketonates and tantalum or niobium alkoxide. We report here the isolation and complete characterisation of the products of these reactions and their application for preparation of a new class of heterometallic heteroleptic alkoxide complexes, $M^{II}_2M^{V}_2(acac)_2(OMe)_{12}$.

Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk techniques or a glove box. Methanol (Merck, p.a.) was purified by destillation over $Mg(OMe)_2$ and toluene (Merck, p.a.) by distillation over $LiAlH_4$. The metal ratio in the bimetallic complex 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). IR spectra of Nujol mulls were registered with a Perkin-Elmer FT-IR spectrometer 1720 X, ^1H NMR spectra for solutions in anhydrous $CDCl_3$ with a Varian 400 MHz spectrometer.

Synthesis and isolation of the products obtained

Water-free $Co(acac)_2$ was obtained by sublimation of $Co(acac)_2{\cdot}xH_2O$ (Aldrich Chemical Company Inc.) at 110–145 °C and 1 mmHg, waterfree $Ni(acac)_2$ by sublimation of $Ni(acac)_2{\cdot}xH_2O$ (Aldrich) at 145–165 °C and 1 mmHg and water-free $Zn(acac)_2$ by refluxing $Zn(acac)_2{\cdot}xH_2O$ (Aldrich) with dry toluene and 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. $Ta(OMe)_5$ and $Nb(OMe)_5$ were prepared by anodic oxidation of the metal in methanol and purified according to conventional techniques.[5,6]

$[Co_2Ta_2(acac)_2(OMe)_{12}]$ 1. Water-free $Co(acac)_2$ (0.921 mmol, 0.237 g) and $Ta(OMe)_5$ (2.66 mmol, 0.894 g) (molar ratio Co : Ta = 1 : 2.9) were dissolved in 2.5 ml toluene in an inert atmosphere. The solution was heated to 60 °C and then slowly cooled to +4 °C. Purple prismatic crystals of $Co_2Ta_2(acac)_2(OMe)_{12}$ **1** precipitated in almost quantitative yield. The solvent was removed by decantation and the crystals were dried *in vacuo* at room temperature. Found: C 24.93, H 4.53. Calculated for $C_{11}H_{25}CoO_8Ta$: C 25.16, H 4.80%. IR, $\tilde{\nu}/cm^{-1}$: 3087sh, 3063sh, 3028m, 2822m, 2356w br, 1605s, 1520s, 1496s, 1457s, 1379s, 1112s, 1082m, 1030s, 921w, 894w, 765w, 728s, 694s, 503m br, 464s and 417m br. UV-Vis: ε at 555 nm 58.1 M^{-1} cm^{-1}. Co : Ta ratio 1 : 1, within the experimental error of SEM-EDS.

$[Ta(acac)(OMe)_4]$ 2. $Ta(acac)(OMe)_4$ **2** precipitated at −20 °C as clear pink crystals from the decantated solvent from the synthesis of compound **1** with a yield of approximately 30%. Found: C 25.9, H 4.45. Calculated for $C_9H_{19}O_6Ta$: C 26.74, H 4.74%. IR, $\tilde{\nu}/cm^{-1}$: 1594s, 1525s, 1150br, 1108m, 1075sh, 1022m, 927m, 807m, 764m, 658m, 546s, 500br, 476sh and 419m. mp 85.3 °C (84.3–86.8 °C) by use of an Electrothermal IA9100 instrument.

$[Co_4(acac)_6(OMe)_2(MeOH)_2]$ 3 and $Co(acac)_2{\cdot}2MeOH$ 4. $Co(acac)_2$ (1.93 mmol, 0.496 g) (used as provided from the manufacturer) and $Ta(OMe)_5$ (1.90 mmol, 0.638 g) (molar ratio Co : Ta = 1 : 1.7) were dissolved in 3 ml toluene. $Co_4(acac)_6(OMe)_2(MeOH)_2$ **3** and $Co(acac)_2{\cdot}2MeOH$ **4** precipitated at +4 °C in minor yields as the only products. No precipitated product containing tantalum was found. Found: C 43.56, H 6.67. Calculated for $C_{12}H_{22}CoO_6$ **4**: C 44.87, H 6.90%. IR, $\tilde{\nu}/cm^{-1}$: 3170m br, 3086sh, 3027m, 2989sh, 1604s, 1520s, 1496s, 1477sh, 1408 s br, 1363m, 1256m, 1195w, 1123w, 1082w, 1043w,

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1016m, 924m, 768m, 729s, 695s, 659w, 562m, 464m and 419m. UV-Vis: ε at 495 nm 35.7 M^{-1} cm^{-1}.

$Co(acac)_2 \cdot 2MeOH$ 4. $Co(acac)_2$ (0.749 mmol, 0.195 g) and dry methanol (3.00 mmol, 0.12 ml) were dissolved in 2.5 ml toluene and refluxed for 30 minutes. $Co(acac)_2 \cdot 2MeOH$ **4** precipitated at +4 °C in almost a quantitative yield. The solvent was removed by decantation and the crystals were dried *in vacuo* at room temperature.

$[Co_2Nb_2(acac)_2(OMe)_{12}]$ 5. Water-free $Co(acac)_2$ (0.582 mmol, 0.150 g) and $Nb(OMe)_5$ (2.04 mmol, 0.560 g) (molar ratio Co : Nb = 1 : 3.5) were dissolved in 2.5 ml toluene in an inert atmosphere. The synthesis was carried out according to that of compound **1**. Purple flat crystalline needles of $Co_2Nb_2(acac)_2(OMe)_{12}$ **5** were obtained. IR, $\tilde{\nu}/cm^{-1}$: 2729s, 2669br, 2355br, 1935m, 1604s, 1593s, 1496s, 1466s, 1454s, 1374s, 1306m, 1256s, 1195sh, 1156sh, 1114m, 1052s, 1005s, 917s, 893s, 763s, 728s, 695s, 651s, 555sh, 527m, 465s and 409 m.

$Ni_2Ta_2(acac)_2(OMe)_{12}$] 6. Water-free $Ni(acac)_2$ (1.68 mmol, 0.432 g) and $Ta(OMe)_5$ (4.71 mmol, 1.58 g) (molar ratio Ni : Ta = 1 : 2.8) were dissolved in 4.0 ml toluene in an inert atmosphere. The synthesis was carried out accordingly to that of compound **1**. Dark green prismatic crystals of $Ni_2Ta_2(acac)_2(OMe)_{12}$ **6** were obtained. IR, $\tilde{\nu}/cm^{-1}$: 2726s, 2682sh, 2355m, 1595m, 1519s, 1454s, 1374s, 1262s, 1197m, 1155sh, 1126m sh, 1055m, 1014m sh, 919s, 763s, 654s, 574s, 491m sh, 471m sh and 421m.

$[Zn_2Ta_2(acac)_2(OMe)_{12}]$ 7. Water-free $Zn(acac)_2$ (0.937 mmol, 0.247 g) and $Ta(OMe)_5$ (2.21 mmol, 0.743 g) (molar ratio Zn : Ta = 1 : 2.4) were dissolved in 2.0 ml toluene in an inert atmosphere. The synthesis was carried out according to that of compound **1**. Colourless clear prismatic crystals of $Zn_2Ta_2(acac)_2(OMe)_{12}$ **7** were obtained. IR, $\tilde{\nu}/cm^{-1}$: 2348s, 2032sh, 1731m, 1643m br, 1567m br, 1530w, 1514w, 1462s, 1377s, 1286m br, 1121m, 1018m, 723m, 437m and 407m br. ^1H NMR ($CDCl_3$): δ 5.300 (1 H, acac CH), 4.199 (3 H, μ_3-OMe), 4.153 (6 H, μ-OMe), 4.120 (9 H, terminal OMe) and 1.950 (6 H, acac Me).

$[Mg_2Ta_2(acac)_2(OMe)_{12}]$ 8. Water-free $Mg(acac)_2$ (1.70 mmol, 0.379 g) and $Ta(OMe)_5$ (4.17 mmol, 1.40 g) (molar ratio Mg : Ta = 1 : 2.4) were dissolved in 4.0 ml toluene in an inert atmosphere. The synthesis was carried out according to that of compound **1**. Colourless clear crystalline needles of $Mg_2Ta_2(acac)_2(OMe)_{12}$ **8** were obtained. IR, $\tilde{\nu}/cm^{-1}$: 2758sh, 2361m, 2377m, 1734s, 1613s, 1557s, 1516s, 1474s, 1400s, 1359s, 1330m sh, 1259s, 1188s, 1129s, 1061s, 1008s, 916s, 763s, 728m sh, 692m sh, 654m, 547s, 497s, 473s and 441s. ^1H NMR ($CDCl_3$): δ 5.250 (1 H, acac CH), 4.275 (9 H, (μ_3- and μ-OMe), 3.828 (9 H, (terminal OMe) and 1.857 (6 H, acac Me).

X-Ray crystallography

The crystal data and the experimental conditions for compounds **1**–**8** are shown in Table 1. The compounds studied are all sensitive to the ambient atmosphere and were therefore placed in glass capillaries, sealed under vacuum, for data collection. The data were collected using a SMART CCD 1K diffractometer. All calculations were performed using the SHELXTL program package[7] Version 5.3 on an IBM PC. The structures were solved by standard direct methods; the coordinates of the cobalt and tantalum atoms taken from the initial solutions and the other non-hydrogen atoms located in subsequent Fourier syntheses. The structures were refined by full matrix least squares in an isotropic and anisotropic approximation. The positions of the hydrogen atoms were calculated geometrically and included in the final cycles of the refinement in isotropic approximation.

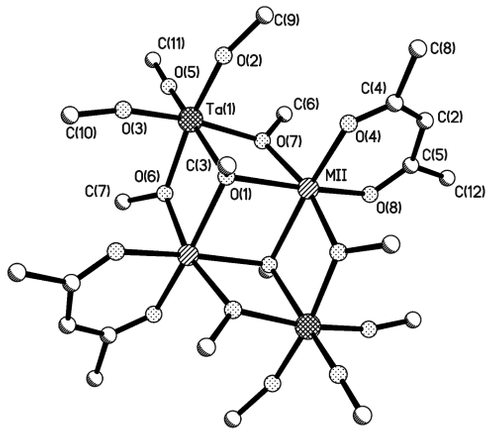

Fig. 1 Molecular structure of $M^{II}{}_2Ta_2(acac)_2(OMe)_{12}$, M^{II} = Co **1**, Ni **6** or Zn **7**.

CCDC reference number 186/2319.

See http://www.rsc.org/suppdata/dt/b0/b008526j/ for crystallographic files in .cif format.

Results and discussion

Molecular and crystal structures

The structure of complex **1**, Fig. 1, is built up by centrosymmetric $Co_2Ta_2(acac)_2(OMe)_{12}$ molecules that belong to the very widespread $Ti_4(OMe)_{16}$ structural type:[8] four edge-sharing octahedra are situated in the same plane, two methoxide groups triply bridging and four doubly bridging. Each cobalt atom is connected to both triply and doubly bridging oxygens and the acetylacetonate ligand is terminal and attached to the cobalt atom in an η^2 manner. The observed Co–O distances, Table 2, are in agreement with those found in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$.[9] The Co–($\mu_3$-O) distances (2.178(10) and 2.188(10) Å) in **1** are slightly longer than the same kind of distances (2.04–2.14 Å) in the complex determined by Bertrand *et al.*[9] The Co–(acac O) distances (2.011(11) and 2.025(10) Å) are in between those (2.00 and 2.05 Å) of the mentioned cobalt complex. The O–Co–O angle in the acetylacetonate ring is 90.3(4)° in **1** and 89.8° in the earlier described cobalt complex which indicates the same type of coordination. The coordination sphere of the tantalum atom is an octahedron composed of one triply bridging, two doubly bridging and three terminal methoxide ligands. The Ta–O distances, Table 2, fall into the range usually observed.[10] The Ta–O (OMe) distances (1.864(10)–1.877(12) Å) **1** are close in length to the same kind of distances in $[Ta_2O(OPr^i)_8] \cdot Pr^iOH$.[10] Distortion of the octahedron of the tantalum atom occurs due to a smaller *trans*-O–Ta–O axial angle (169.0(4)°) in **1** than the expected 180°. This also occurs in the cobalt octahedron, with an axial *trans*-O–Co–O angle of 167.4(4)°. Complexes **5**–**8** are isostructural and **6** and **7** even isomorphous with **1**, the only differences being the nature of the metal atoms involved. The observed Co–O, Nb–O, Ni–O, Zn–O, Mg–O, and Ta–O distances, Tables 6, 7, 8, and 9, fall into the ranges usually observed.[11,12] In $[Co_2Nb_2(acac)_2(OMe)_{12}]$ **5**, Fig. 2, the Co–(μ_3-O) bond distances are the same (2.166(3) Å compared to 2.18 Å) as in **1**. The Co–(acac O) bond lengths are 2.031(4) Å in **5** and 2.011(11)–2.025(10) Å in **1**. The bond angle in the acetylacetonate ring is the same, 90.1(2)°, and the axial O–Co–O angle is the same too, 167.38(16)°, indicating the same type of distortion of the cobalt atom in both complexes. The Nb–(μ-O) bond distances (2.033(4) Å) are shorter than the same kind of bonds in $[Nb(\mu\text{-}OCH_2SiMe_3)(OCH_2SiMe_3)_4]_2$ (2.13 and 2.17 Å, respectively) but the Nb–O (OMe) bonds (1.860(4)–1.873(6) Å) are slightly shorter than the same kind of bonds (1.90–1.92 Å) in the complex determined by Goel *et al.*[11] The axial O–Nb–O angle is

Table 1 Crystal data and details of the diffraction experiments for compounds **1**–**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Chemical formula	$C_{22}H_{50}Co_2O_{16}Ta_2$	$C_9H_{19}O_6Ta$	$C_{34}H_{56}Co_4O_{16}$	$C_{12}H_{22}CoO_6$	$C_{22}H_{50}Co_2Nb_2O_{16}$	$C_{22}H_{50}Ni_2O_{16}Ta_2$	$C_{22}H_{50}O_{16}Ta_2Zn_2$	$C_{22}H_{50}Mg_2O_{16}Ta_2$
Formula weight	1050.38	404.19	956.51	321.23	874.30	1049.94	1063.26	981.14
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	*Pbca*	$P\bar{1}$	$P\bar{1}$	$C2/m$	$P2_1/c$	$P2_1/c$	$C2/m$
μ/mm^{-1}	7.008	8.278	1.449	1.096	1.604	7.239	7.427	6.214
a/Å	11.946(3)	7.4134(8)	10.6192(16)	5.228(3)	12.455(7)	11.875(3)	11.9609(14)	12.462(2)
b/Å	14.175(4)	14.5311(15)	11.9216(18)	8.553(6)	20.295(12)	14.158(3)	14.1848(17)	20.282(4)
c/Å	12.044(3)	24.678(3)	18.284(3)	9.744(7)	8.740(5)	11.925(3)	12.0136(14)	8.7636(17)
α/°			72.429(3)	108.127(12)				
β/°	117.787(5)		89.482(3)	90.263(12)	126.266(9)	117.538(4)	117.844(2)	126.209(3)
γ/°			83.716(3)	105.385(13)				
V/Å^3	1804.3(9)	2658.5(5)	2192.7(6)	397.4(5)	1781.2(18)	1777.8(6)	1802.2(4)	1787.3(6)
T/K	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
Z	4	8	2	1	2	2	2	2
Number of independent reflections	3152 [R(int) = 0.0708]	7091 [R(int) = 0.0399]	5750 [R(int) = 0.0751]	2022 [R(int) = 0.0528]	4568 [R(int) = 0.0528]	3061 [R(int) = 0.0454]	10983 [R(int) = 0.0411]	5615 [R(int) = 0.0822]
Number of observed reflections	1483 [$I > 2\sigma(I)$]	2845 [$I > 2\sigma(I)$]	2688 [$I > 2\sigma(I)$]	1558 [$I > 2\sigma(I)$]	1558 [$I > 2\sigma(I)$]	2001 [$I > 2\sigma(I)$]	4294 [$I > 2\sigma(I)$]	2207 [$I > 2\sigma(I)$]
R	0.0617	0.0411	0.0693	0.0522	0.0492	0.0865	0.0854	0.0718
$wR2$	0.1505	0.0940	0.1566	0.1490	0.1237	0.1872	0.1784	0.1849

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Ta(1)–O(5)	1.864(10)	Co(2)–O(4)	2.011(11)
Ta(1)–O(2)	1.874(11)	Co(2)–O(8)	2.025(10)
Ta(1)–O(3)	1.877(12)	Co(2)–O(7)	2.067(10)
Ta(1)–O(7)	2.035(10)	Co(2)–O(6)#1	2.085(10)
Ta(1)–O(6)	2.036(11)	Co(2)–O(1)	2.178(10)
Ta(1)–O(1)	2.111(9)	Co(2)–O(1)#1	2.188(10)
O(5)–Ta(1)–O(2)	96.7(6)	O(4)–Co(2)–O(8)	90.3(4)
O(5)–Ta(1)–O(3)	98.3(5)	O(4)–Co(2)–O(7)	96.4(4)
O(2)–Ta(1)–O(3)	91.8(5)	O(8)–Co(2)–O(7)	94.1(4)
O(5)–Ta(1)–O(7)	92.2(5)	O(4)–Co(2)–O(6)#1	94.1(4)
O(2)–Ta(1)–O(7)	90.3(4)	O(8)–Co(2)–O(6)#1	96.0(4)
O(3)–Ta(1)–O(7)	169.0(4)	O(7)–Co(2)–O(6)#1	165.4(4)
O(5)–Ta(1)–O(6)	92.5(5)	O(4)–Co(2)–O(1)	95.1(4)
O(2)–Ta(1)–O(6)	170.0(4)	O(8)–Co(2)–O(1)	167.4(4)
O(3)–Ta(1)–O(6)	90.7(5)	O(7)–Co(2)–O(1)	74.0(4)
O(7)–Ta(1)–O(6)	85.4(4)	O(6)#1–Co(2)–O(1)	94.9(4)
O(5)–Ta(1)–O(1)	164.9(5)	O(4)–Co(2)–O(1)#1	167.9(4)
O(2)–Ta(1)–O(1)	93.0(4)	O(8)–Co(2)–O(1)#1	94.8(4)
O(3)–Ta(1)–O(1)	93.0(4)	O(7)–Co(2)–O(1)#1	94.1(4)
O(7)–Ta(1)–O(1)	76.1(4)	O(6)#1–Co(2)–O(1)#1	74.5(4)
O(6)–Ta(1)–O(1)	77.2(4)	O(1)–Co(2)–O(1)#1	82.1(4)

Symmetry transformation used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$.

170.30(16)° compared to 169.0(4)° for the O–Ta–O angle in **1** indicating the same kind of distortion in both complexes. The Ni–(μ_3-O) bond distances in $[Ni_2Ta_2(acac)_2(OMe)_{12}]$ **6**, Fig. 1, are 2.123(17) Å, slightly longer than the same kind of bonds in $[Ni_4(OMe)_4(dbm)_4(MeOH)_4]$ (2.046–2.065 Å) (Hdbm = dibenzoylmethane).[12] The Ni–(acac O) bond distances in **6** are 1.97(2)–1.99(2) Å compared to 1.97–2.04 Å of Ni–(dbm O) bonds. The O–Ni–O angle in the acetylacetonate ring is 92.0(9)° and the axial O–Ni–O angle is 168.1(8)° indicating the same kind of distortion of the coordination sphere of nickel in **6** as for the cobalt atom in **1**. In $[Zn_2Ta_2(acac)_2(OMe)_{12}]$ **1**, Fig. 1, the Zn–(μ_3-O) bond distances are 2.196(11) Å and the Ta-(μ_3-O) bond distances 2.081(10) Å. The Zn-(μ-O) bond distances are 2.065(12)–2.080(11) Å, close to those of the same kind involving cobalt in **1** and the Zn–(acac O) bonds are 2.020(14) and 2.035(14) Å, respectively, *i.e.* practically equal in length to the bonds in **1**. The O–Zn–O angle of the acetylacetonate ring is 91.7(6)° and the axial O–Zn–O angles 163.8(5)–166.3(5)° indicating the same kind of distortion of the metal atom in **7** as in **1**, **5** and **6**. The Mg–(μ_3-O) bond lengths in $[Mg_2Ta_2(acac)_2(OMe)_{12}]$ **8**, Fig. 2, are 2.148(10) Å and the Mg–(μ-O) distances are 2.076(9) Å. The O–Mg–O angle in the acetylacetonate ring is 89.4(6)° and the axial O–Mg–O angles are 165.3(6)–167.0(5)°, all indicating the same kind of distortion of the coordination sphere as in **5**.

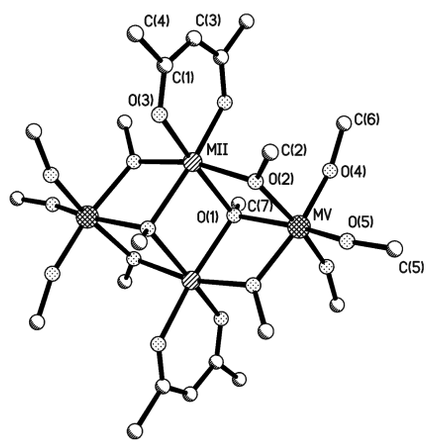

Fig. 2 Molecular structure of $M^{II}_2M^{V}_2(acac)_2(OMe)_{12}$, M^{II} = Co **5** or Mg **8** and M^{V} = Nb **5** or Ta **8**.

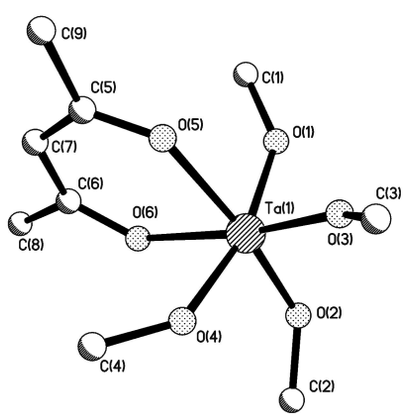

Fig. 3 Molecular structure of [Ta(acac)(OMe)$_4$] **2**.

The crystal structure of compound **2**, Fig. 3, is in agreement with a very recently published observation [13] built up by monomeric octahedral Ta(acac)(OMe)$_4$ molecules situated in general

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Ta(1)–O(3)	1.868(6)	Ta(1)–O(1)	1.908(6)
Ta(1)–O(2)	1.887(5)	Ta(1)–O(5)	2.101(5)
Ta(1)–O(4)	1.902(6)	Ta(1)–O(6)	2.115(5)
O(3)–Ta(1)–O(2)	99.7(3)	O(4)–Ta(1)–O(5)	84.0(2)
O(3)–Ta(1)–O(4)	93.9(3)	O(1)–Ta(1)–O(5)	85.1(2)
O(2)–Ta(1)–O(4)	93.8(2)	O(3)–Ta(1)–O(6)	169.3(2)
O(3)–Ta(1)–O(1)	95.5(3)	O(2)–Ta(1)–O(6)	90.9(2)
O(2)–Ta(1)–O(1)	95.5(2)	O(4)–Ta(1)–O(6)	84.0(2)
O(4)–Ta(1)–O(1)	165.5(2)	O(1)–Ta(1)–O(6)	84.8(2)
O(3)–Ta(1)–O(5)	89.4(2)	O(5)–Ta(1)–O(6)	80.0(2)
O(2)–Ta(1)–O(5)	170.7(2)		

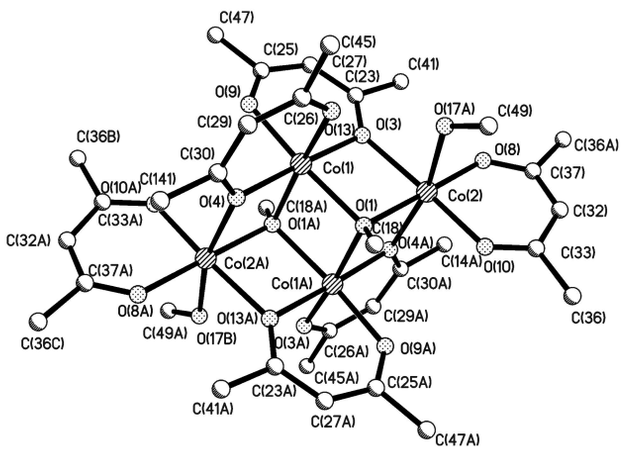

Fig. 4 Molecular structure of $[Co_4(acac)_6(OMe)_2(MeOH)_2]$ **3**.

positions. The present experiment has however provided data characterised by noticeably lower standard deviation values. The structure investigation was completed before we received the reference. Bond distances and angles (Table 3) are in good agreement with those reported recently.[13] The distortion of the tantalum octahedron is the same in both determinations of the complex, the *trans*-O–Ta–O angle (for the apical OR groups) being only 165.5(2)–170.7(2)° instead of the expected 180°.

Complex **3**, Fig. 4, is structurally built up by centrosymmetric $Co_4(acac)_6(OMe)_2(MeOH)_2$ molecules that also belong to the $Ti_4(OMe)_{16}$ structural type.[8] This type is very common for tetramers and even for late transition metal β-diketonate tetramers[14] but has not been reported earlier for cobalt derivatives. Each cobalt atom in **3** is connected to both triply and doubly bridging oxygens and the acetylacetonate ligands are of two different types: two of the cobalt atoms have a terminal acetylacetonate ligand which is attached in an η^2 manner and the other two have two acetylacetonate ligands attached with the oxygen bridging in a μ-η^2 manner and the other oxygen bonded to the cobalt atom in an ordinary η^2 manner. Bond distances and angles are in agreement with the distances found in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$,[9] Table 4. The Co–($\mu_3$-O) distances (2.035(5)–2.099(5) Å) are in the same range (2.04–2.11 Å) as in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$ and the Co–(μ-O) bonds (2.080(5)–2.242(6) Å) derived from one of the oxygens in the four acetylacetonate rings are longer when the cobalt atoms attach also to a terminal η^2-acetylacetonate ring as Co2 and Co3 do. These Co–(μ-O) bonds are 0.04 to 0.16 Å longer than those derived from the two cobalt atoms with no terminal rings attached. The Co–O bond distances in the two acetylacetonate rings attached only to one cobalt atom (1.990(5)–2.022(6) Å) in **3** are close to the same kind of bonds in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$ (2.00–2.05 Å). The two Co–O bonds from the two methanols are 2.194(7) and 2.205(7) Å, respectively, in agreement with those in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$ (2.15 and 2.20 Å, respectively).[9] The acetylacetonate rings do not influence the octahedral coordination of the cobalt atoms because the O–Co–O angles in the rings are all 90 ± 2°. However the μ_3-oxygens do disturb the coordination spheres of the cobalt atoms because the angles between these oxygen atoms and Co1 and Co4 are 82.2(2) and 83.5(2)°, respectively.

Table 4 Selected bond lengths (Å) and angles (°) for compound **3**

Co(1)–O(9)	2.008(6)	Co(2)–O(8)	1.990(6)
Co(1)–O(13)	2.051(6)	Co(2)–O(10)	2.012(6)
Co(1)–O(1)#1	2.069(5)	Co(2)–O(1)	2.035(5)
Co(1)–O(4)	2.080(5)	Co(2)–O(3)	2.156(6)
Co(1)–O(3)	2.090(5)	Co(2)–O(17A)	2.194(7)
Co(1)–O(1)	2.099(5)	Co(2)–O(4)#1	2.242(6)
O(9)–Co(1)–O(13)	92.1(3)	O(8)–Co(2)–O(10)	88.9(3)
O(9)–Co(1)–O(1)#1	95.6(2)	O(8)–Co(2)–O(1)	178.2(3)
O(13)–Co(1)–O(1)#1	169.1(2)	O(10)–Co(2)–O(1)	92.4(2)
O(9)–Co(1)–O(4)	91.1(2)	O(8)–Co(2)–O(3)	97.8(2)
O(13)–Co(1)–O(4)	90.0(2)	O(10)–Co(2)–O(3)	171.8(2)
O(1)#1–Co(1)–O(4)	82.2(2)	O(1)–Co(2)–O(3)	80.9(2)
O(9)–Co(1)–O(3)	90.5(2)	O(8)–Co(2)–O(17A)	91.2(3)
O(13)–Co(1)–O(3)	91.1(2)	O(10)–Co(2)–O(17A)	94.0(3)
O(1)#1–Co(1)–O(3)	96.4(2)	O(1)–Co(2)–O(17A)	90.0(2)
O(4)–Co(1)–O(3)	178.0(2)	O(3)–Co(2)–O(17A)	81.3(2)
O(9)–Co(1)–O(1)	170.9(2)	O(8)–Co(2)–O(4)#1	99.5(3)
O(13)–Co(1)–O(1)	91.3(2)	O(10)–Co(2)–O(4)#1	95.0(3)
O(1)#1–Co(1)–O(1)	82.2(2)	O(1)–Co(2)–O(4)#1	79.1(2)
O(4)–Co(1)–O(1)	97.3(2)	O(3)–Co(2)–O(4)#1	88.5(2)
O(3)–Co(1)–O(1)	81.0(2)	O(17A)–Co(2)–O(4)#1	166.1(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+1$.

Table 5 Selected bond lengths (Å) and angles (°) for compound **4**

Co(1)–O(1)	2.013(3)	Co(1)–O(3)	2.147(4)
Co(1)–O(2)	2.036(3)		
O(1)–Co(1)–O(1)#1	180.000(1)	O(1)#1–Co(1)–O(3)#1	92.13(14)
O(1)–Co(1)–O(2)	90.47(13)	O(2)–Co(1)–O(3)#1	89.41(15)
O(1)#1–Co(1)–O(2)	89.53(13)	O(1)–Co(1)–O(3)	92.13(14)
O(2)–Co(1)–O(2)#1	180.0(2)	O(2)–Co(1)–O(3)	90.59(15)
O(1)–Co(1)–O(3)#1	87.87(14)	O(3)#1–Co(1)–O(3)	180.0(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

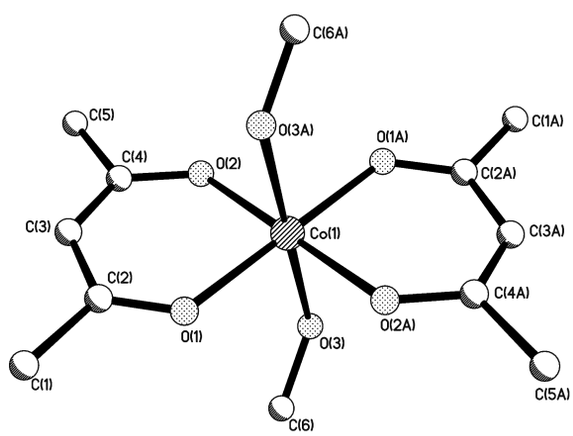

Fig. 5 Molecular structure of $Co(acac)_2 \cdot 2MeOH$ **4**.

The structure of complex **4**, Fig. 5, is built up by octahedral centrosymmetric $Co(acac)_2 \cdot 2MeOH$ molecules. The cobalt atom is connected to the oxygens of both acetylacetonate ligands in an η^2 manner. Bond distances and angles, Table 5, fall into the range usually observed for Co–O.[9] The Co–(acac O) bonds are 2.013(3) and 2.036(3) Å, respectively, the same length as in **3** and in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$ (2.00–2.05 Å).[9] The two Co–O bonds derived from the methanol are 2.147(4) Å, in the same range as in **3** and in $[Co_4(acac)_4(OMe)_4(MeOH)_4]$ (2.15 and 2.20 Å, respectively). The O–Co–O angle of the acetylacetonate ring is 90.47(13)° and the angles between one oxygen

Table 6 Selected bond lengths (Å) and angles (°) for compound **5**

Nb(1)–O(4)	1.860(4)	Co(2)–O(3)	2.031(4)
Nb(1)–O(5)	1.873(6)	Co(2)–O(2)	2.083(4)
Nb(1)–O(2)	2.033(4)	Co(2)–O(1)	2.166(3)
Nb(1)–O(1)	2.114(5)		
O(4)#1–Nb(1)–O(4)	92.4(3)	O(3)–Co(2)–O(3)#2	90.1(2)
O(4)–Nb(1)–O(5)	97.75(19)	O(3)–Co(2)–O(2)#2	96.02(15)
O(4)–Nb(1)–O(2)#1	170.30(16)	O(3)–Co(2)–O(2)	93.61(15)
O(4)–Nb(1)–O(2)	90.22(19)	O(2)#2–Co(2)–O(2)	166.3(2)
O(5)–Nb(1)–O(2)	91.15(18)	O(3)–Co(2)–O(1)	167.38(16)
O(2)#1–Nb(1)–O(2)	85.7(2)	O(3)#2–Co(2)–O(1)	95.03(15)
O(4)–Nb(1)–O(1)	93.92(16)	O(2)#2–Co(2)–O(1)	95.15(16)
O(5)–Nb(1)–O(1)	163.1(2)	O(2)–Co(2)–O(1)	74.41(15)
O(2)–Nb(1)–O(1)	76.58(13)	O(1)–Co(2)–O(1)#3	82.35(18)

Symmetry transformations used to generate equivalent atoms: #1 x, $-y$, z; #2 $-x$, y, $-z+2$; #3 $-x$, $-y$, $z+2$.

Table 7 Selected bond lengths (Å) and angles (°) for compound **6**

Ta(1)–O(5)	1.72(3)	Ni(2)–O(7)	1.97(2)
Ta(1)–O(3)	1.83(2)	Ni(2)–O(8)	1.99(2)
Ta(1)–O(2)	1.89(2)	Ni(2)–O(6)#1	2.041(17)
Ta(1)–O(4)	2.03(2)	Ni(2)–O(4)	2.053(16)
Ta(1)–O(6)	2.05(2)	Ni(2)–O(1)	2.123(17)
Ta(1)–O(1)	2.092(15)	Ni(2)–O(1)#1	2.159(16)
O(5)–Ta(1)–O(3)	96.2(10)	O(7)–Ni(2)–O(8)	92.0(9)
O(5)–Ta(1)–O(2)	95.9(9)	O(7)–Ni(2)–O(6)#1	94.3(9)
O(3)–Ta(1)–O(2)	91.6(10)	O(8)–Ni(2)–O(6)#1	93.4(8)
O(5)–Ta(1)–O(4)	92.8(9)	O(7)–Ni(2)–O(4)	93.9(8)
O(3)–Ta(1)–O(4)	170.4(8)	O(8)–Ni(2)–O(4)	94.4(8)
O(2)–Ta(1)–O(4)	90.8(9)	O(6)#1–Ni(2)–O(4)	168.5(7)
O(5)–Ta(1)–O(6)	92.2(8)	O(7)–Ni(2)–O(1)	93.7(8)
O(3)–Ta(1)–O(6)	89.6(9)	O(8)–Ni(2)–O(1)	167.9(8)
O(2)–Ta(1)–O(6)	171.7(8)	O(6)#1–Ni(2)–O(1)	96.7(7)
O(4)–Ta(1)–O(6)	86.7(7)	O(4)–Ni(2)–O(1)	74.6(7)
O(5)–Ta(1)–O(1)	164.1(8)	O(7)–Ni(2)–O(1)#1	168.1(8)
O(3)–Ta(1)–O(1)	94.7(8)	O(8)–Ni(2)–O(1)#1	93.6(8)
O(2)–Ta(1)–O(1)	95.5(8)	O(6)#1–Ni(2)–O(1)#1	75.0(7)
O(4)–Ta(1)–O(1)	75.8(6)	O(4)–Ni(2)–O(1)#1	96.1(7)
O(6)–Ta(1)–O(1)	76.2(6)	O(1)–Ni(2)–O(1)#1	82.8(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$.

in methanol and an oxygen in the ring are between 87.87(14) and 92.13(14)° indicating an almost perfect octahedral coordination of the cobalt atom.

Reaction pathways

Interaction of tantalum methoxide with water-free cobalt acetylacetonate. The chemical composition of the structurally characterised products permits one to conclude that the reaction proceeds according to eqn. (1). The first step in this process

$$Co(acac)_2 + 2\ Ta(OMe)_5 \longrightarrow \tfrac{1}{2}[CoTa(acac)(OMe)_6]_2 + [Ta(acac)(OMe)_4] \quad (1)$$

might be complex formation between $Co(acac)_2$ and $Ta(OMe)_5$ which then leads to transfer of one acetylacetonate ligand from cobalt to tantalum resulting in formation of unreactive [Ta(acac)(OMe)$_4$] **2**. The unstable $[Co(acac)(OMe)]^{\#}$ intermediate further reacts with $Ta(OMe)_5$ forming $[Co_2Ta_2(acac)_2(OMe)_{12}]$ **1**, Scheme 1. We have not observed the formation of any oxo

$$Ta_2(OMe)_{10} \rightleftharpoons 2\ Ta(OMe)_5 \quad (1a)$$

$$[Co(acac)_2]_4 \rightleftharpoons 4\ Co(acac)_2 \quad (1b)$$

$$Co(acac)_2 + Ta(OMe)_5 \longrightarrow [CoTa(acac)_2(OMe)_5]^{\#} \quad (1c)$$

$$[CoTa(acac)_2(OMe)_5]^{\#} \longrightarrow [Co(acac)(OMe)]^{\#} + [Ta(acac)(OMe)_4]\ \mathbf{2} \quad (1d)$$

$$[Co(acac)(OMe)]^{\#} + Ta(OMe)_5 \longrightarrow \tfrac{1}{2}[CoTa(acac)(OMe)_6]_2\ \mathbf{1} \quad (1e)$$

Scheme 1 Proposed reaction pathway for the process in eqn. (1).

Table 8 Selected bond lengths (Å) and angles (°) for compound **7**

Ta(1)–O(5)	1.788(18)	Zn(1)–O(8)	2.020(14)
Ta(1)–O(3)	1.884(15)	Zn(1)–O(4)	2.035(14)
Ta(1)–O(2)	1.883(15)	Zn(1)–O(6)#1	2.065(12)
Ta(1)–O(7)	2.031(12)	Zn(1)–O(7)	2.080(11)
Ta(1)–O(6)	2.065(13)	Zn(1)–O(1)	2.196(11)
Ta(1)–O(1)	2.081(10)	Zn(1)–O(1)#1	2.271(11)
O(5)–Ta(1)–O(3)	98.8(7)	O(8)–Zn(1)–O(4)	91.7(6)
O(5)–Ta(1)–O(2)	97.3(7)	O(8)–Zn(1)–O(6)#1	96.3(6)
O(3)–Ta(1)–O(2)	90.4(7)	O(4)–Zn(1)–O(6)#1	93.9(6)
O(5)–Ta(1)–O(7)	91.7(6)	O(8)–Zn(1)–O(7)	94.3(5)
O(3)–Ta(1)–O(7)	169.1(5)	O(4)–Zn(1)–O(7)	98.1(5)
O(2)–Ta(1)–O(7)	91.3(6)	O(6)#1–Zn(1)–O(7)	163.8(5)
O(5)–Ta(1)–O(6)	91.0(6)	O(8)–Zn(1)–O(1)	165.9(5)
O(3)–Ta(1)–O(6)	91.3(7)	O(4)–Zn(1)–O(1)	95.0(5)
O(2)–Ta(1)–O(6)	171.2(6)	O(6)#1–Zn(1)–O(1)	95.7(5)
O(7)–Ta(1)–O(6)	85.5(5)	O(7)–Zn(1)–O(1)	72.5(4)
O(5)–Ta(1)–O(1)	163.5(6)	O(8)–Zn(1)–O(1)#1	94.0(5)
O(3)–Ta(1)–O(1)	93.2(5)	O(4)–Zn(1)–O(1)#1	166.3(5)
O(2)–Ta(1)–O(1)	94.0(6)	O(6)#1–Zn(1)–O(1)#1	73.2(4)
O(7)–Ta(1)–O(1)	75.9(4)	O(7)–Zn(1)–O(1)#1	93.9(4)
O(6)–Ta(1)–O(1)	77.3(4)	O(1)–Zn(1)–O(1)#1	82.3(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$.

Table 9 Selected bond lengths (Å) and angles (°) for compound **8**

Ta(1)–O(4)	1.855(11)	Mg(2)–O(3)	2.017(11)
Ta(1)–O(5)	1.861(12)	Mg(2)–O(2)	2.076(9)
Ta(1)–O(2)	2.023(10)	Mg(2)–O(1)	2.148(10)
Ta(1)–O(1)	2.116(12)		
O(4)#1–Ta(1)–O(4)	91.5(8)	O(3)–Mg(2)–O(3)#3	89.4(6)
O(4)–Ta(1)–O(5)	99.1(5)	O(3)–Mg(2)–O(2)	93.3(4)
O(4)–Ta(1)–O(2)#1	168.9(4)	O(3)#3–Mg(2)–O(2)	97.1(4)
O(5)–Ta(1)–O(2)#1	91.2(5)	O(2)#3–Mg(2)–O(2)	165.3(6)
O(4)–Ta(1)–O(2)	90.9(5)	O(3)–Mg(2)–O(1)	167.0(5)
O(5)–Ta(1)–O(2)	91.2(5)	O(3)#3–Mg(2)–O(1)	95.9(4)
O(2)#1–Ta(1)–O(2)	84.7(6)	O(2)#3–Mg(2)–O(1)	94.4(4)
O(4)–Ta(1)–O(1)	93.0(4)	O(2)–Mg(2)–O(1)	74.3(4)
O(5)–Ta(1)–O(1)	162.7(6)	O(2)–Mg(2)–O(1)#2	94.4(4)
O(2)–Ta(1)–O(1)	76.1(4)	O(1)–Mg(2)–O(1)#2	81.4(6)

Symmetry transformations used to generate equivalent atoms: #1 x, $-y$, z; #2 $-x$, $-y$, $-z+2$; #3 $-x$, y, $-z+2$.

complexes in this reaction. The earlier reported[3,4] isolation of oxo complexes in reactions of cobalt acetylacetonate and iron acetylacetonate with zirconium isopropoxide resulted most probably from desolvation of $Zr(OPr^i)_4(Pr^iOH)$ in toluene on heating of zirconium alkoxides as reported by Turova *et al.*[5]

Interaction of tantalum methoxide with commercial cobalt acetylacetonate. Our observations indicated clearly that commercial cobalt acetylacetonate is contaminated with water. The latter causes hydrolysis of tantalum methoxide and leads to release of free methanol. The formation of compound **4** in quantitative yield could also be observed in separate experiments on reaction of water-free cobalt acetylacetonate with methanol in toluene, eqn. (2). The formation of a

$$Co(acac)_2 + 2\ MeOH \longrightarrow Co(acac)_2{\cdot}2MeOH \quad (2)$$

methoxoacetylacetonate solvate with methanol, compound **3**, results apparently from the combination of reactions (1c) and (2), *i.e.* alkoxylation and solvation with methanol, eqn. (3).

$$2\ [Co(acac)(OMe)]^{\#} + 2\ Co(acac)_2 + 2\ MeOH \longrightarrow [Co_4(acac)_6(OMe)_2(MeOH)_2] \quad (3)$$

Reaction (1) can be rewritten in a more general form with metal β-diketonates of cobalt, nickel, or zinc and metal

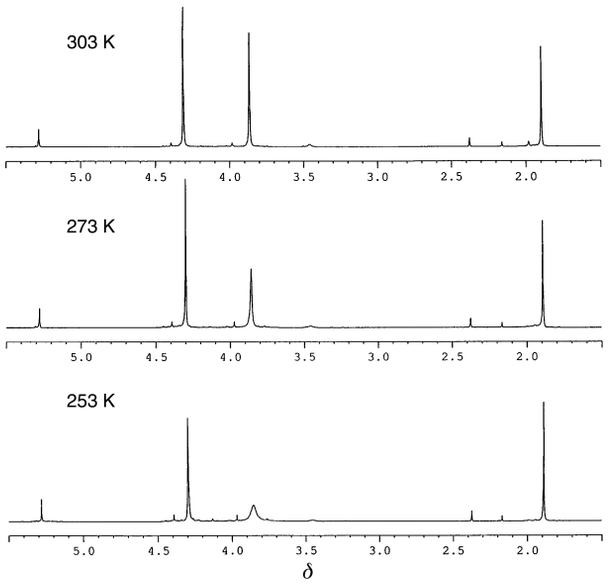

Fig. 6 Variable temperature ^{1}H NMR spectra of $[Mg_2Ta_2(acac)_2(OMe)_{12}]$ **8**.

methoxides of tantalum or niobium. This then produces $M^{II}_2M^{V}_2(acac)_2(OMe)_{12}$ which are isostructural with **1**. Experiments with $Cu(acac)_2$ and $Pd(acac)_2$ in the same manner as with the above mentioned metal β-diketonates did not produce a mixed metal complex. We believe this is because of the preferred square planar coordination of copper and palladium atoms. The metal atoms that do produce the mixed metal complexes prefer octahedral coordination which they easily achieve in the reaction with the metal alkoxide.

The ^{1}H NMR spectrum of compound **7** demonstrated that the heterometallic complexes appear to preserve their molecular structure in solution: three different signals corresponding to three different alkoxide functions (μ_3-OR, μ-OR, and terminal OR) could clearly be observed and show the appropriate relation (μ_3-OR : μ-OR : terminal OR = 1 : 2 : 3) on integration. The ^{1}H NMR spectrum of **8** is different in the sense that there is no splitting into different μ_3-OCH_3 and μ-OCH_3 peaks. The mainly ionic bonding of magnesium to the μ_3-O and μ-O results in equivalent chemical shifts for them. Another reason for the equivalent chemical shifts in this case can be a quick exchange in the complex facilitated by the ionic nature of the bonds. This latter supposition appears to be confirmed by the data of a variable temperature experiment (Fig. 6) with the peak corresponding to the signal from bridging OCH_3 groups becoming noticeably broadened on cooling (freezing of the exchange).

The stability of the heterometallic species to solvolysis with methanol was tested by addition of several drops of the latter to a toluene solution of **8**. This resulted in nearly quantitative precipitation of $[Mg_4(acac)_4(OMe)_4(MeOH)_4]$ crystals thus indicating the complete destruction of **8** in this reaction.

Conclusion

For the preparation of heterometallic alkoxide complexes it appears in this case to be crucial to avoid the presence of external Lewis bases (such as donor solvents), for example methanol, since the desired reactions appear always to occur *via* Lewis acid–base interaction.

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