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Synthesis, X-ray single crystal and magnetic study of new heteroleptic late transition metal alkoxides with tetranuclear square planar metal core, $Co_4Cl_2(OC_2H_4OEt)_6$, $Co_4(OMe)_2(acac)_6(MeOH)_2$ and $Zn_4(OMe)_2(acac)_6(C_7H_8)$

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Abstract

Interaction of 4 equiv. $CoCl_2$ with 6 equiv. of $NaOC_2H_4OEt$ in toluene/HOC_2H_4OEt medium provided $Co_4Cl_2(OC_2H_4OEt)_6$ (**1**) with practically quantitative yield. Reaction of $Co(acac)_2$ with $Ti(OMe)_4$ in 1:1 ratio in toluene gave $Co_4(OMe)_2(acac)_6(MeOH)_2$ (**2**) with moderate yields. The same reaction for $Zn(acac)_2$ resulted in formation of $Zn_4(OMe)_2(acac)_6(C_7H_8)$ (**3**). The structures of **1**–**3** contain planar tetranuclear cores of $M_4(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_4$ type ($[Ti(OMe)_4]_4$ type structure), where the metal atoms are pentacoordinated in **1**, hexacoordinated in **2**, and both penta- and hexacoordinated in **3**. The magnetic measurements have revealed competing ferromagnetic and antiferromagnetic interactions between the **4** Co(II) atoms in **1**, but only ferromagnetic in **2**.

Keywords: Antiferromagnetic interaction; Alkoxide; Late transition metal; X-ray; Molecular structure

1. Introduction

Oligo- and polynuclear complexes of late transition metals, particularly carboxylates and β-diketonates, have recently, attracted attention of researchers as prospective molecular magnetic materials [1]. Alkoxide groups have been recognized as extremely attractive bridging ligands in such aggregates and a number of molecular magnets—derivatives of Co(II) with methoxide bridges, such as $Co_4(OMe)_4(acac)_4(MeOH)_4$ [2], and di-2-pyridylketone bridges in the gem-diol form such as $[Co_4(N_3)_2(O_2CPh)_2\{(py)_2C(OH)O\}_4]2DMF$ [3], $[Co_4(N_3)_2(N_3)_2\{(py)_2C(OH)O\}_2\{(py)_2C(OMe)O\}_2]2H_2O$ [4], and $[Co_4(N_3)_2(H_2O)_2\{(py)_2C(OH)O\}_2\{(py)_2C(OMe)O\}_2](BF_4)_2\cdot 4H_2O$ [5], have been obtained and structurally characterized. The magnetic behavior of all these complexes could be explained using the concept of ferromagnetic coupling on both intramolecular and intermolecular level. In the present contribution we report the synthesis, structural characterization and magnetic properties of two new heteroleptic Co(II) alkoxides, $Co_4Cl_2(OC_2H_4OEt)_6$ (**1**) and $Co_4(OMe)_2(acac)_6(MeOH)_2$ (**2**), and also the synthesis and structural characterization of a zinc analog of the latter, $Zn_4(OMe)_2(acac)_6(C_7H_8)$ (**3**).

2. Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk techniques or a glove box. Waterfree $CoCl_2$ was purchased from Aldrich Chemical Company Inc. and used without further purification. Waterfree $Co(acac)_2$ was obtained by sublimation of the commercial anhydrous $Co(acac)_2$ (Aldrich Chemical Company Inc.) at 110–145 °C and 1 mmHg. Waterfree $Zn(acac)_2$ was obtained by refluxing $Zn(acac)_2\cdot xH_2O$ (Aldrich Chemical Company Inc.) with dry toluene with

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subsequent evaporation, repeated twice. $Ti(OMe)_4$ was obtained by dissolution of about 2.0 g of $Ti(O^iPr)_4$ in 30 ml MeOH and 30 ml toluene with subsequent evaporation to dryness. This operation was repeated trice leaving a light yellow glassy solid. Toluene (Merck, PA) was purified by distillation over $LiAlH_4$. UV–Vis spectra were registered for 0.025–0.05 M solutions in toluene using an Hitachi U-2001 spectrophotometer. IR spectra of nujol mulls were registered with a Perkin–Elmer FT-IR spectrometer 1720X. ^1H NMR spectra were recorded for the $CDCl_3$ solutions on a Bruker 400 MHz spectrometer at 300 K. Satisfactory results of microanalysis (C, H) were obtained for all the reported compounds by Mikrokemi AB, Uppsala, Sweden using the combustion technique.

The AC magnetic susceptibility on polycrystalline samples of **1** and **2** were measured (at 500 Hz, 125 A m^{-1} and at 500 Hz, 500 A m^{-1}) in the temperature range 12–320 K using a Lake Shore Inc. AC Susceptometer, Model 7130, equipped with a helium cryostat. Diamagnetic corrections of raw data were made using Pascal's constants [6,7].

2.1. $Co_4Cl_2(OC_2H_4OEt)_6$ (**1**)

Sodium metal (1.325 g, 57.6 mmol) was dissolved in the mixture of 2-ethoxyethanol (10.4 ml) and toluene (50 ml). $CoCl_2$ (5.001 g, 38.5 mmol) was added to the obtained clear solution with vigorous stirring. The dark greyish blue mixture thus formed was subjected to reflux for 40 min, left to precipitate for 30 min at room temperature and then the dark blue solvent was separated from the greyish precipitate by decantation and left for crystallization overnight at $-30\,^\circ C$. Dark blue crystals formed were separated from the weakly colored violet solution by decantation and dried in vacuo. Yield: 11.621 g (96%). IR (cm^{-1}): 1482 s, 1412 m, 1346 s, 1295 w, 1264 w, 1241 m, 1163 sh, 1124 s, 1101 s, 1070 s, 933 s, 910 s, 844 sh, 828 s, 801 w, 610 s, 598 s, 478 s, 427 m, 380 s. UV–Vis, λ, nm ε): 632(113), 614(118), 589(120), 524(93).

2.2. $Co_4(OMe)_2(acac)_6(MeOH)_2$ (**2**)

$Co(acac)_2$ (0.179 g, 0.7 mmol) and $Ti(OMe)_4$ (0.150 g, 0.9 mmol) were dissolved by refluxing in 3 ml toluene and the pinkish violet solution was left for crystallization overnight at $-30\,^\circ C$. The pinkish violet precipitate was separated by decantation and dried in vacuo. Yield: 0.071 g (42%). IR (cm^{-1}): 1604 s, 1520 s, 1496 s, 1477 sh, 1408 s br, 1363 m, 1256 m, 1195 w, 1123 w, 1082 w, 1043 w, 1016 m, 924 m, 768 m, 729 s, 695 s, 659 w, 562 m, 464 m, 419 m. UV–Vis, λ, nm ε): 500 (38).

2.3. $Zn_4(OMe)_2(acac)_6(C_7H_8)$(**3**)

$Zn(acac)_2$ (0.321 g, 1.2 mmol) and $Ti(OMe)_4$ (0.210 g, 1.2 mmol) were dissolved by refluxing in 4 ml toluene and the colorless solution was left for crystallization overnight at $-30\,^\circ C$. The colorless precipitate was separated by decantation from the light yellow solution and dried in vacuo. Yield: 0.11 g (40%). IR (cm^{-1}): 1603 s br, 1377 s br, 1256 s, 1194 w, 1144 sh, 1093 s br, 1042 s, 1015 s, 925 s, 793 w, 782 w, 770 m, 696 w, 667 w, 649 w, 630 m, 564 s, 552 sh, 439 m, 408 m. ^1H NMR, ppm: 7.25–7.15 (phenyl-C*H* toluene, 5H), 5.39 (singlet, C*H* acac, 6H), 3.54 (singlet, CH_3 OMe, 6H), 2.34 (singlet, CH_3 toluene, 3H), 1.99 (singlet, CH_3 acac, 36H).

2.4. Crystallography

For details of data collection and refinement experiments see Table 1. The air sensitive crystals of **1**–**3** were chosen under nitrogen and vacuum-sealed into Lindeman tubes. All structures were solved by standard direct methods, the majority of non-hydrogen atoms being located already from the initial solution. The missing non-hydrogen atoms were then found in subsequent difference Fourier syntheses. All non-hydrogen atoms (except for the disordered carbon atoms of the clathrate toluene molecule in **3** refined only isotropically) were refined in isotropic and then anisotropic approximations. Hydrogen atom positions (except for the OH-proton in **2**, located in the difference Fourier syntheses and refined isotropically) were calculated geometrically and included into the final refinement in isotropic approximation riding on the correspondent carbon atoms with $U = 1.2U_{iso}$ for the methyne- and methylene-, and $U = 1.5U_{iso}$ for methyl groups, respectively.

3. Results and discussion

3.1. Synthetic approaches and molecular structures

Continuing the systematic search for the alkoxide precursors of late transition metal based oxide materials, we investigated the possibility to obtain cobalt(II) alkoxy-alkoxides using the metathesis of cobalt(II) chloride with alkali alkoxy-alkoxides:

$$CoCl_2(s) + 2NaOC_2H_4OR \xrightarrow{Toluene/HOC_2H_4OR} Co(OC_2H_4OR)_2 + 2NaCl, \quad R = Me,\ Et$$

These reactions tended to lead to viscous dark blue solutions extraordinarily sensitive to the ambient atmosphere due, supposedly, to easily occurring oxidation of Co(II) to Co(III), which was indicated by formation of a voluminous precipitate possessing the greenish brown color characteristic of Co(II)–Co(III) mixed-valence

Table 1
Crystal data and the diffraction experiments details for compounds **1**–**3**

	1	**2**	**3**
Chemical formula	$C_{24}H_{54}Cl_2Co_4O_{12}$	$C_{34}H_{56}Co_4O_{16}$	$C_{32}H_{48}O_{14}Zn_4$
Formula weight	841.29	956.51	918.18
Temperature (K)	295(2)	295(2)	295(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	9.2988(11)	10.387(3)	9.8561(13)
b (Å)	19.048(2)	20.246(4)	10.5271(15)
c (Å)	10.9380(13)	11.005	11.4424(16)
α (°)	90	90	93.946(2)
β (°)	111.393(2)	111.053(15)	100.463(3)
γ (°)	90	90	103.504(2)
V (Å^3)	1803.9(4)	2159.7(9)	1127.5(3)
Z	2	2	1
μ (mm^{-1})	2.006	1.573	2.155
Number of independent reflections	4187 [$R_{int} = 0.0502$]	3768 [$R_{int} = 0.0740$]	3864 [$R_{int} = 0.0315$]
Number of observed reflections	2291 [$I > 2\sigma(I)$]	1827 [$I > 2\sigma(I)$]	2046[$I > 2\sigma(I)$]
R_1	0.0513	0.0586	0.0564
wR_2	0.1216	0.1017	0.1332

derivatives [8]. In the case of R = Et in one of the syntheses we have observed also the formation of a small crop of bluish violet prismatic single crystals. X-ray single crystal study showed them to be an alkoxide chloride—compound **1**. Carrying out the metathesis reaction with the proper stoichiometry offered **1** in practically quantitative yield:

$$4CoCl_2(s) + 6NaOC_2H_4OEt \xrightarrow{Toluene/HOC_2H_4OEt} Co_4Cl_2(OC_2H_4OEt)_6(\mathbf{1}) + 2NaCl$$

Compound **1** is poorly soluble in any organic solvent at room temperature, but dissolves readily on heating in the parent alcohol, toluene or mixtures of these two.

The molecular structure of **1** belongs to the $[Ti(OMe)_4]_4$ structure type [9], based on the $M_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4$-core. The specific feature of **1** is that all the four metal atoms in it are pentacoordinated (see Fig. 1, Table 2). The coordination around the Co atoms is distorted tetragonal pyramidal with the bond lengths dependent clearly on the structural function of the oxygen atoms: the shortest ones are those to the μ_2-O atoms of the alkoxide bridges (1.871(3)–2.019(3) Å), those to the μ_3-O atoms of the alkoxide bridges are noticeably longer (2.098(3)–2.206(3) Å) and the longest in average (2.173(3)–2.281(4) Å) are the bonds to the ether functions of the alkoxy-alkoxide groups. The Co(2)–Cl(1) bond length 2.6938(18) Å is ca. 0.5 Å longer than the Co–O bonds due to the bigger radius of the chloride ligand. It is also important to note the remarkably short Co(1)–Co(1A) bond length of 2.7238(12) Å, indicating the possibility of metal–metal bonding interactions (alternatively—the antiferromagnetic spin coupling) in this structure. The other Co–Co distance (Co(1)–Co(2) 3.235(1) Å) is very close to those commonly observed in the oligonuclear complexes of Co(II) [2–5].

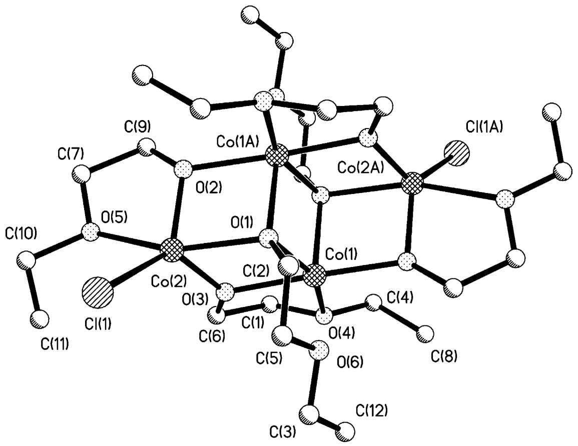

Fig. 1. Molecular structure of $Co_4Cl_2(OC_2H_4OEt)_6$ (**1**).

It appeared interesting to compare the structure and properties of **1** with those of compound **2**, discovered earlier as the product of the interaction of $Co(acac)_2$ with $Ta(OMe)_5$ in the presence of traces of MeOH [10]:

$$4Co(acac)_2 + 2Ta(OMe)_5 + 4MeOH \xrightarrow{Toluene} Co_4(OMe)_2(acac)_6(MeOH)_2 + 2Ta(OMe)_4(acac)$$

The triclinic modification of **2**, described in literature was obtained at +4 °C. The yield of **2** in the reaction above was very low and we considered an alternative approach with a medium introducing small amounts of MeOH in this reaction. The interaction of $Co(acac)_2$ with the glassy product of the $Ti(OMe)_4$ preparation (via the alcohol interchange reaction) permitted the increase of yields to moderate ones (about 40%). The

Table 2
Selected bond distances (Å) and angles (°) in the structure of **1**

Bond lengths			
Co(1)–O(3)	1.975(4)	Co(2)–O(2)	1.871(3)
Co(1)–O(2)#1	2.019(3)	Co(2)–O(3)	1.904(4)
Co(1)–O(1)	2.098(3)	Co(2)–O(1)	2.105(3)
Co(1)–O(4)	2.173(3)	Co(2)–O(5)	2.281(4)
Co(1)–O(1)#1	2.206(3)	Co(2)–Cl(1)	2.6938(18)
Co(1)–Co(1)#1	2.7238(12)		
Bond angles			
O(3)–Co(1)–O(2)#1	173.96(15)	O(2)–Co(2)–O(3)	97.37(16)
O(3)–Co(1)–O(1)	71.90(13)	O(2)–Co(2)–O(1)	84.34(13)
O(2)#1–Co(1)–O(1)	114.07(13)	O(3)–Co(2)–O(1)	73.11(13)
O(3)–Co(1)–O(4)	87.36(14)	O(2)–Co(2)–O(5)	73.23(14)
O(2)#1–Co(1)–O(4)	86.64(14)	O(3)–Co(2)–O(5)	99.02(15)
O(1)–Co(1)–O(4)	159.19(13)	O(1)–Co(2)–O(5)	155.23(14)
O(3)–Co(1)–O(1)#1	99.79(14)	O(2)–Co(2)–Cl(1)	129.99(11)
O(2)#1–Co(1)–O(1)#1	78.44(13)	O(3)–Co(2)–Cl(1)	132.54(13)
O(1)–Co(1)–O(1)#1	101.53(12)	O(1)–Co(2)–Cl(1)	104.75(10)
O(4)–Co(1)–O(1)#1	79.90(12)	O(5)–Co(2)–Cl(1)	97.80(11)

Table 3
Selected bond distances (Å) and angles (°) in the structure of **2**

Bond lengths			
Co(1)–O(5)	2.020(4)	Co(2)–O(7)	2.000(4)
Co(1)–O(4)	2.054(4)	Co(2)–O(6)	2.012(4)
Co(1)–O(2)	2.081(4)	Co(2)–O(1)	2.037(3)
Co(1)–O(1)#1	2.084(3)	Co(2)–O(3)#1	2.157(4)
Co(1)–O(3)	2.084(3)	Co(2)–O(8)	2.202(5)
Co(1)–O(1)	2.091(3)	Co(2)–O(2)	2.242(4)
Bond angles			
O(5)–Co(1)–O(4)	91.74(16)	O(7)–Co(2)–O(6)	88.85(18)
O(5)–Co(1)–O(2)	89.30(15)	O(7)–Co(2)–O(1)	179.01(17)
O(4)–Co(1)–O(2)	89.75(15)	O(6)–Co(2)–O(1)	90.40(16)
O(5)–Co(1)–O(1)#1	171.45(14)	O(7)–Co(2)–O(3)#1	100.93(16)
O(4)–Co(1)–O(1)#1	89.14(15)	O(6)–Co(2)–O(3)#1	168.67(16)
O(2)–Co(1)–O(1)#1	99.21(14)	O(1)–Co(2)–O(3)#1	79.88(13)
O(5)–Co(1)–O(3)	90.92(15)	O(7)–Co(2)–O(8)	88.78(18)
O(4)–Co(1)–O(3)	93.47(15)	O(6)–Co(2)–O(8)	94.44(18)
O(2)–Co(1)–O(3)	176.76(15)		

IR spectrum of the $Ti(OMe)_4$ prepared by this route contains always a broad band at 3460 cm^{-1} indicating presence of residual MeOH that cannot be removed completely even by a prolonged drying in vacuum at room temperature. The data of elementary microanalysis permit to formulate the reactant thus obtained as $Ti(OMe)_4 \cdot x MeOH$, where $x \simeq 0.15–0.20$. **2** crystallized from the reaction mixture as a new monoclinic modification at −30 °C that remained, however, stable indefinitely at room temperature. It has rather high solubility in toluene at room temperature and can be recrystallized from it. Its dissolution in MeOH leads to crystallization of $Co(acac)_2(MeOH)_2$, described earlier by us [10].

The molecular structure of **2** (Fig. 2, Table 3) also belongs to the $[Ti(OMe)_4]_4$ structure type, but all cobalt atoms in it are octahedrally coordinated. The bond length distribution is much less pronounced in **2** compared to **1** (two groups can be distinguished, where the first one with shorter distances of 2.000(4)–2.091(3) includes both the bonds to terminal O-atoms of the acac-ligands and to the μ_3-O atoms of the alkoxide bridges and the second one with longer ones, 2.157(4)–2.242(4) Å, —those to the bridging μ_2-O atoms of the acac-ligands and to the terminal O-atoms of the solvating MeOH molecules). The O–Co–O bond angles are fairly close to either 90° or 180°, manifesting that only minor distortion of the octahedra takes place in this case. The Co–Co distances in the structure of **2** are close to each other (3.139(1) and 3.212(1) Å) and to those commonly observed [2–5].

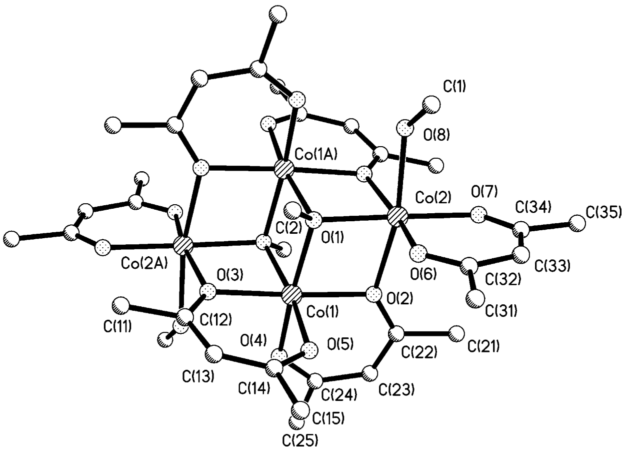

Fig. 2. Molecular structure of $Co_4(OMe)_2(acac)_6(MeOH)_2$ (**2**).

We attempted also in this work the preparation of a non-magnetic analog of **2** in order to try to follow its molecular structure in solution using the NMR technique. The reaction of $Zn(acac)_2$ with the glassy $Ti(OMe)_4$ provided **3** with moderate yields. **3** is readily soluble in toluene at room temperature. Its molecular structure (Fig. 3, Table 4) is close to that of **2**, with the only difference being the absence of the solvating alcohol molecules, which results in distorted trigonal bipyramidal coordination for half of the zinc atoms (Zn(2) having an octahedron with a missing vertex). The distribution in the bond lengths is analogous to that observed in **2** with the only exception that the bonds to the μ_3-O atoms of the alkoxide bridges are rather asymmetric in this case (1.980(4), 2.065(4) and 2.178(4) Å), indicating more covalent character of bonding in case of the zinc derivative. The ^1H NMR spectrum indicated the presence of only one type of alkoxide and acetylacetonate ligands in the structure of **3** in solution, permitting to suppose that its molecule is preserved on dissolution but undergoes a quick exchange of the acac-ligands, facilitated obviously by the presence of structurally unsaturated pentacoordinated zinc atoms.

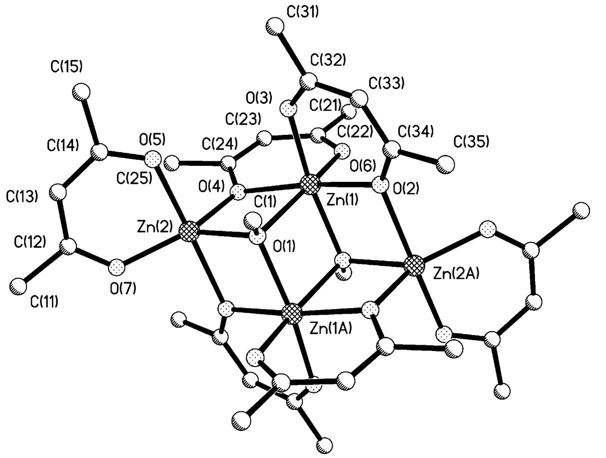

Fig. 3. Molecular structure of $Zn_4(OMe)_2(acac)_6(C_7H_8)$ (**3**).

Table 4
Selected bond distances (Å) and angles (°) in the structure of **3**

Bond lengths			
Zn(1)–O(3)	2.019(5)	Zn(2)–O(7)	1.944(5)
Zn(1)–O(6)	2.058(5)	Zn(2)–O(1)	1.980(4)
Zn(1)–O(1)#1	2.065(4)	Zn(2)–O(4)	2.018(5)
Zn(1)–O(2)	2.086(5)	Zn(2)–O(5)	2.035(5)
Zn(1)–O(4)	2.126(4)	Zn(2)–O(2)#1	2.204(5)
Zn(1)–O(1)	2.178(4)	Zn(2)–Zn(1)	3.1187(12)
Bond angles			
O(3)–Zn(1)–O(6)	93.8(2)	O(7)–Zn(2)–O(1)	136.9(2)
O(3)–Zn(1)–O(1)#1	166.98(19)	O(7)–Zn(2)–O(4)	135.0(2)
O(6)–Zn(1)–O(1)#1	92.23(19)	O(1)–Zn(2)–O(4)	86.05(18)
O(3)–Zn(1)–O(2)	87.31(19)	O(7)–Zn(2)–O(5)	91.3(2)
O(6)–Zn(1)–O(2)	102.27(19)	O(1)–Zn(2)–O(5)	98.7(2)
O(1)#1–Zn(1)–O(2)	80.13(18)	O(4)–Zn(2)–O(5)	94.8(2)
O(3)–Zn(1)–O(4)	94.2(2)	O(7)–Zn(2)–O(2)#1	87.7(2)
O(6)–Zn(1)–O(4)	85.93(19)	O(1)–Zn(2)–O(2)#1	79.18(17)
O(1)#1–Zn(1)–O(4)	97.71(18)	O(4)–Zn(2)–O(2)#1	88.81(19)
O(2)–Zn(1)–O(4)	171.55(18)	O(5)–Zn(2)–O(2)#1	175.7(2)

3.2. Magnetic properties

The $\chi_M T$ versus T curves of **1** and **2** are shown in Fig. 4. The molar magnetic susceptibility, χ_M is given per tetranuclear unit. For **1**, a minimum in the $\chi_M T$ curve is observed at 32 K. Below this temperature $\chi_M T$ increases monotonically down to 12 K. Above $T = 200$ K, $\chi_M T$ flattens out at a value of 10.8 cm^3 K mol^{-1}. The observed value is significantly higher than the spin-only value 7.50 cm^3 K mol^{-1} expected for a completely uncoupled $Co(II)_4$ cluster with the assumptions of $S = 3/2$ and a g value of 2 for high spin Co^{2+}. Looking at the molecular structure of **1**, it is possible to interpret these results as the result of competing antiferromagnetic and ferromagnetic exchange interactions. In the molecule, the Co–O–Co angles range between 78.5° and 113°. The larger angles would allow for antiferromagnetic exchange pathways and the angle Co(1)–O(1)–Co(2) (90.5°) would be consistent with a ferromagnetic exchange pathway.

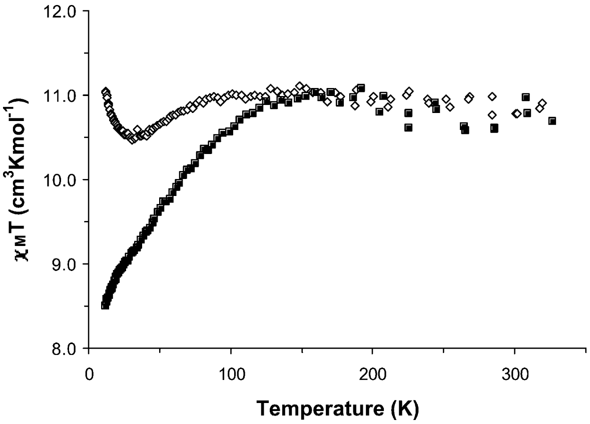

Fig. 4. Experimental $\chi_M T$ versus T for $Co_4Cl_2(OC_2H_4OEt)_6$ (**1**) (open squares) and $Co_4(OMe)_2(acac)_6(MeOH)_2$ (**2**) (filled squares).

For **2** $\chi_M T$ reaches approximately the same value (10.8 cm^3 K mol^{-1}) as for **1** in the high temperature limit and decreases continuously as the temperature is decreased down to 12 K. Clearly, **2** shows a different magnetic behavior compared to **1**. This $\chi_M T$ versus T curve is a typical indication of antiferromagnetic interactions between the Co atoms. Although **2** exhibits the same $Co_4(\mu_2\text{-}O)_4(\mu_3\text{-}O)_2$ core structure as **1**, the two complexes differ in their values of the Co–O–Co angles. For **2**, they range between 95.9° and 102.2°, these values also support a model where intramolecular antiferromagnetic couplings dominate in the temperature region investigated.

The disagreement between the measured data and the simple spin-only model is what can be expected for systems such as **1** and **2**. Moreover, the actual g values have not been measured and are probably underestimated [11,12]. These susceptibility measurements are not sufficient in order to make a more thorough analysis of the spin behavior in these complicated tetranuclear Co_4 systems. They have, however, showed that, two systems with the same core topology, but with different coordination environments can exhibit different magnetic behavior.

It is interesting to note, that from alkoxide chemistry the well known, $M_4(\mu_2\text{-}O)_4(\mu_3\text{-}O)_2$ structure unit ($Ti_4(OMe)_{16}$ [9]) is also well represented among the Co_4 complexes exhibiting ferromagnetic behavior. Some of these tetramers are based on the ligands di-2-pyridyl ketone and azide anions and the core is described as a double cubane with two missing metal atom vertices. Two of the bridging ligand atoms connecting the rhombic Co_4 unit are nitrogen instead of oxygen atoms. Examples with this specific core geometry and composition are the compounds $[Co_4(N_3)_2(O_2CPh)_2\{(py)_2C(OH)O\}_4]2DMF$ [3], $[Co_4(N_3)_2(N_3)_2\{(py)_2C(OH)O\}_2\{(py)_2C\ (OMe)O\}_2]2H_2O$ [4] and $[Co_4(N_3)_2(H_2O)_2$-

$\{(py)_2C(OH)O\}_2\{(py)_2C(OMe)O\}_2](BF_4)_2 \cdot 4H_2O$ [5]. As pointed out previously it is not possible to analyze polynuclear Co complexes with effective Hamiltonians based on pairwise spin only interactions [5]. Hence, the variable temperature magnetic susceptibility behavior of these complexes was only analyzed in a qualitative way. The magnetic susceptibility measurements on complexes **1** and **2** give the same $\chi_M T$ value (10.8 cm^3 K mol^{-1}) at room temperature as that found for the DMF derivative above [3]. However, while **1** exhibits a possible mixture of ferromagnetic and antiferromagnetic behavior the DMF derivative is purely ferromagnetic. Although the compounds have the same core topology this work shows that the nature of the ligands and the specific coordination geometry around each cobalt center play a decisive role in the magnetic properties of these tetranuclear complexes.

4. Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition numbers 201520–201522 for **1**–**3**, respectively.

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