New precursors in the chemistry of IVB transition metal alkoxides
II. Synthesis and molecular structure of $Zr_2Co_4(\mu_6\text{-}O)(\mu_2\text{-}OC_3H_7)_8(OC_3H_7)_2(\text{acetylacetone})_4$

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Abstract

The title compound crystallizes in the triclinic system (space group $P\bar{1}$) with parameters: $a=1206.9(2)$, $b=1304.7(3)$, $c=1335.0(3)$ pm, $\alpha=106.32(2)$, $\beta=113.74(1)$. $\gamma=102.66(1)°$. The crystal structure determination reveals discrete hexanuclear molecules. The $Zr_2Co_4O_{19}$ inorganic core adopts a cubic close packing of oxygens, the metal atoms occupying octahedral holes. A μ_6 oxygen atom is located at the center of the metal octahedron.

Introduction

For several years, metal alkoxides have been used as starting products in the synthesis of mixed metal oxides via a sol–gel processing [1–5]. Bimetallic alkoxides should be the best potential precursors as they already contain the two metals in the same molecule and they hydrolyze to hydrated oxides. However, the attempts to start from the alkoxides $M(Zr_2(OC_3H_7)_9)_n$, with M = Fe(III), Co(II), Cu(II) and $n=3$, 2, 2, respectively, failed to give homogeneous gels [6].

The best results were obtained by hydrolysis of a propanolic solution containing the zirconium n-propanolate and the acetylacetonate of the second metal. Homogeneous monolithic clear gels were obtained with VO(II), Co(II), Co(III), Cr(III), Fe(III) and Gd(III). This paper accounts for the reaction with Co(II) yielding the precursor $Zr_2Co_4(\mu_6\text{-}O)(\mu_2\text{-}OC_3H_7)_8(OC_3H_7)_2(acac)_4$.

Experimental

Synthesis

n-propanol was dried on sodium and distilled under dry nitrogen. The precursor solution was prepared under nitrogen.

A total of 2.11 g (0.0082 mol) of cobalt(II) acetylacetonate is suspended in 100 ml n-propanol. After the addition of 10.75 g (0.0328 mol) of zirconium n-propanolate, the mixture is stirred and refluxed for 24 h. The solution is concentrated under vacuum. When approximately two-thirds of the solvent volume is removed, the solution is allowed to cool down very gently. Violet–brown single crystals grow slowly; they are stable in dry air.

It is noteworthy that the complete removal of the solvent yields a purple–violet dry powder which is very sensitive to moisture.

Data collection and structure refinement

A single crystal (0.2×0.4×0.1 mm) was selected for the data collection on an Enraf-Nonius CAD4 diffractometer. The lattice parameters were least-squares refined using 25 *hkl* reflections in the range $3<\theta<26$ (Table 1) shows the crystallographic data and the informations concerning the data collection and the refinement procedure.

After some unsuccessful trials using direct methods, the positions of the three independent metal atoms were derived from a Patterson synthesis. The remaining atoms, except hydrogens, were located from successive difference Fourier maps. The last isotropic refinement gave a R value equal to 0.094. An empirical absorption correction (program DIFABS [7]) and the averaging of symmetry-related intensities reduced R to 0.076. After introduction in the refinement of the anisotropic thermal factors and the extinction coefficient and after including the calculated H positions in the structure factor calculation, the final R value was equal to 0.048.

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TABLE 1. Crystal data and structure refinement parameters

Formula	$Zr_2Co_4O_{19}C_{50}H_{98}$
Molecular weight	1437.5
Symmetry	triclinic
Space group	$P\bar{1}$
Cell parameters	
a (pm)	1206.9(2)
b (pm)	1304.7(3)
c (pm)	1335.0(3)
α (°)	106.32(2)
β (°)	113.74(1)
γ (°)	102.66(1)
Cell volume, V (pm^3)	1709.3×10^6
No. formula unit, Z	1
Specific weight, ρ (g/cm^3)	1.396
Linear absorption coefficient	12.951
Radiation	Mo Kα
Measurement temperature (°C)	20
Scan type	ω/θ
θ range (°)	3–26
Reflections measured	7013
Reflections refined ($I>3\sigma(I)$)	3219
Refined parameters	343
Secondary extinction coefficient	4.816×10^{-8}
Reliability indexes	
R	0.048
R_w	0.047

Description of the molecular structure

Final positional and displacement parameters are given in Table 2. Selected bond angles and distances are given in Tables 3 and 4.

Figure 1 shows the inorganic core of the molecule. In this small unit the oxygen atoms adopt a cubic close packing, the metal atoms occupying octahedral holes. Thus, the $Zr_2Co_4O_{19}$ core can be viewed as a part of a NaCl-type structure. Alternatively, as CoO crystallizes with a tetragonally-distorted NaCl structure, it could be said that the inorganic part of the molecule corresponds to a partial substitution of zirconium to cobalt in the CoO structure.

This arrangement results in a μ_6 octahedral coordination for the oxygen atom O10 located at the center of the molecule, which is also a center of symmetry. The coordination angles around the O10 atom correspond to an almost perfect octahedral geometry (Table 3). This octahedron is slightly flattened with a Zr–O distance (220.72(6) pm) shorter than the Co–O distances, 237.7(1) pm) and 236.3(2) pm for Co1 and Co2, respectively. This surrounding is extremely unusual in coordination chemistry. From our knowledge, it has already been described for molybdenum and tungsten polyanions. For example, the $(Mo_6O_{19})^{2-}$ anion with a μ_6 oxygen atom has been observed in several structures: $(Mo(S_2CNEt_2)_4)_2$ (Mo_6O_{19}), $(HN_3P_3(NMe_2)_6)_2$ (Mo_6O_{19}), $(C_{12}H_{24}O_6)_2$ (Mo_6O_{19}) K_2, H_2O, ... [8–10]. However, in these ionic structures, the molybdate anion is purely inorganic and not coordinated to the ligands. The only example of a coordination complex which shows this cage encapsulating a central μ_6-O has been observed for the $((\eta_5\text{-}C_5H_5)TiM_5O_{18})^{3-}$ anion (M = Mo, W) [11, 12]. More recently [13], a polyoxovanadate complex with a hexametallate core has been characterized.

The three crystallographically independent metal atoms are coordinated to six oxygen atoms of a slightly distorted octahedron (Tables 3 and 4). The zirconium atom is coordinated to five oxygen atoms from alkoxy groups, O10 achieving the octahedron.

TABLE 2. Final positional and displacement parameters (Å)

Atom	x	y	z	B (Å^2)
Zr1	0.17244(6)	0.15340(5)	0.06254(5)	4.76(2)
Co1	0.02756(9)	−0.09660(8)	−0.16276(8)	5.47(3)
Co2	0.13609(9)	−0.07300(8)	0.11978(8)	5.52(3)
O1	0.1866(4)	0.0468(4)	−0.0787(4)	5.6(1)
O2	0.1209(4)	0.2257(4)	0.1902(4)	5.6(1)
O3	0.2719(4)	0.0793(4)	0.1710(4)	5.9(1)
O4	−0.0919(4)	−0.0293(4)	−0.2608(3)	6.1(1)
O5	0.0444(4)	−0.1821(4)	−0.3043(4)	7.0(2)
O6	0.1567(4)	−0.1540(4)	−0.0255(4)	5.9(1)
O7	0.2511(5)	−0.1375(4)	0.2197(4)	7.1(2)
O8	0.0373(4)	0.1958(3)	−0.0574(4)	5.9(1)
O9	0.3230(4)	0.2893(4)	0.1192(4)	6.9(2)
O10	0.000	0.000	0.000	4.5(2)
C1	0.3801(9)	−0.2433(8)	0.2756(9)	11.4(3)
C2	0.3006(7)	−0.2033(6)	0.1851(7)	7.4(3)
C3	0.2948(7)	−0.2416(6)	0.0738(7)	7.2(2)
C4	0.2250(7)	−0.2167(6)	−0.0229(6)	6.7(2)
C5	0.2356(7)	−0.2660(7)	−0.1332(7)	8.4(3)
C6	−0.2120(9)	0.0063(8)	−0.4300(7)	9.5(3)
C7	−0.1274(7)	−0.0510(7)	−0.3719(6)	7.0(2)
C8	−0.0923(8)	−0.1245(8)	−0.4408(6)	8.4(3)
C9	−0.0132(7)	−0.1848(7)	−0.4064(6)	7.6(3)
C10	0.0049(9)	−0.263(1)	−0.5006(8)	10.9(4)
C11	0.3047(7)	0.0459(8)	−0.0799(7)	8.6(3)
C12	0.343(1)	0.110(1)	−0.1360(9)	17.4(5)
C13	0.280(1)	0.120(1)	−0.2304(9)	15.4(5)
C21	0.1405(8)	0.3431(7)	0.2457(7)	8.1(3)
C22	0.250(1)	0.4009(9)	0.370(1)	13.1(5)
C23	0.277(2)	0.515(2)	0.435(1)	23.4(9)
C31	0.3866(9)	0.1336(8)	0.2819(9)	10.8(4)
C32	0.499(1)	0.121(1)	0.280(1)	17.7(6)
C33	0.617(2)	0.164(1)	0.375(2)	22.5(9)
C81	0.0542(8)	0.2619(7)	−0.1224(8)	8.7(3)
C82	0.0447(9)	0.3709(8)	−0.0825(9)	10.3(4)
C83	0.051(1)	0.4370(7)	−0.1572(8)	12.5(4)
C91	0.431(1)	0.387(1)	0.161(1)	18.6(6)
C92	0.478(2)	0.456(1)	0.164(2)	27(1)
C93	0.607(1)	0.554(1)	0.222(1)	17.6(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

TABLE 3. Selected bond angles (°); numbers in parentheses are e.s.d.s. in the least significant digits

Co1–O10–Co1′	180	Zr1–O1–Co1	104.8(4)	O5–Co1–O10	178.0(1)
Co2–O10–Co2′	180	Zr1–O2–Co1′	105.1(4)	O4–Co1–O6	169.9(2)
Zr1–O10–Zr1′	180	Zr1–O3–Co2	104.4(4)	O1–Co1–O2	160.5(3)
Co1–O10–Co2	89.95(4)	Zr1–O8–Co2′	104.7(4)	O7–Co2–O10	179.1(1)
Co1–O10–Zr1	89.85(3)	Zr1–O9–C91	179.5(6)	O4–Co2–O6	170.3(2)
Co2–O10–Zr1	89.96(3)	Co1–O6–Co2	99.6(4)	O3–Co2–O8	161.2(2)
O1–Zr1–O2	166.7(2)	Co1–O4–Co2′	100.2(4)		
O10–Zr1–O9	179.2(2)	O3–Zr1–O8	167.3(2)		
Zr1–O1–C11	126.6(5)	Co1–O1–C11	121.6(5)	Zr1–O2–C21	127.6(4)
Co1–O2–C21	122.2(4)	Zr1–O3–C31	128.7(6)	Co2–O3–C31	122.9(6)
Co1–O4–C7	123.8(5)	Co2–O4–C7	136.0(5)	Co1–O5–C9	125.1(5)
Co1–O6–C4	137.4(5)	Co2–O6–C4	125.7(5)	Co2–O7–C2	125.7(5)
Zr1–O8–C81	130.0(4)	Zr1–O9–C91	179.5(6)		

Dihedral angles (°)	
Plane 1	Co1, Co2, O10, O4, O5, O6, O7
Plane 2	Zr1, Co1, O10, O1, O2, O5, O9
Plane 3	Zr1, Co2, O10, O3, O7, O8, O9
Plane 1/plane 2	89.90(5)
Plane 1/plane 3	90.57(6)
Plane 2/plane 3	89.86(6)

TABLE 4. Selected interatomic distances (pm); numbers in parentheses are e.s.d.s. in the least significant digits

Zr1–O10	220.72(6)	Co1–O1	198.9(4)	Co2–O3	200.2(4)
Co1–O10	237.7(1)	Co1–O2	199.6(5)	Co2–O4	230.6(5)
Co2–O10	236.3(2)	Co1–O4	206.0(5)	Co2–O6	207.2(5)
Zr1–O1	209.9(5)	Co1–O5	202.0(6)	Co2–O7	201.6(6)
Zr1–O2	209.5(5)	Co1–O6	230.0(5)	Co2–O8	200.6(4)
Zr1–O3	209.1(5)	O4–C7	128.8(9)	O5–C9	124(1)
Zr1–O8	207.8(5)	O6–C4	129(2)	O7–C2	124(1)
Zr1–O9	193.5(5)	C1–C2	151(1)	C2–C3	139(1)
		C3–C4	141(1)	C4–C5	150(1)
		C6–C7	150(1)	C7–C8	139(1)
		C8–C9	138(1)	C9–C10	151(1)

The cobalt atoms are coordinated to three oxygen atoms from acetylacetonato ligands, two other oxygen atoms from alkoxy groups and to the μ_6 atom.

The three planes defined by the metal atoms (plane 1: Co1 Co2 Co1′ Co2′; plane 2: Co1 Zr1 Co1′ Zr1′; plane 3: Co2 Zr1 Co2′ Zr1′) contain the oxygen atoms, the greatest deviation being observed for O1 (12.8(5) pm). These planes are almost strictly perpendicular to each other: 89.90(5)° between planes 1 and 2, 90.57(6)° for planes 1–3, 89.86(6)° for planes 2–3.

Figure 2 shows the entire molecule. The high symmetry of the M_6O_{19} core is lost because of the carbon atoms.

The two independent acetylacetonato groups have the same coordination scheme towards the cobalt atoms: O4-η_2; O5-η_1 (respectively O6-η_2; O7-η_1). The dicoordinated oxygen atoms have a highly asymmetric environment with a long metal–oxygen distance (mean value 230.5 pm). The carbon atoms lie slightly outside of the plane defined by Co1, Co2, O4, O5, O6 and O10, the greatest deviation being 25.9(12) pm. In the chelating rings, all the C–O and C–C distances are significantly shorter than the sum of the covalent radii; the mean values are 139.2 pm for the C–C bonds and 126.4 pm for the C–O single bonds. This shortening can be reasonably attributed to the establishment of a delocalized π-bonding system.

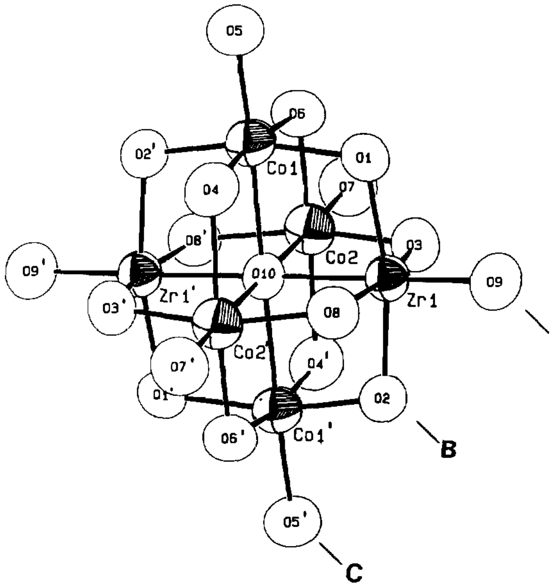

Fig. 1. Oxygen packing in the $Zr_2Co_4O_{19}$ core.

The alkoxy groups show two coordination schemes. Four groups are coordinated, through a μ_2-O, to

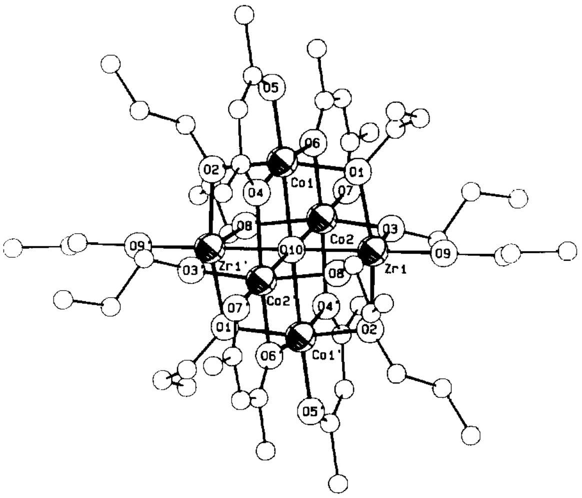

Fig. 2. ORTEP drawing of the hexanuclear molecule.

the zirconium atom and a cobalt atom. The last one is only bound to the zirconium atom. The mean value of the Zr–μ_2-O distance is 209 pm, a little shorter than the Co–μ_2-O distances (199 and 200 pm for Co1 and Co2, respectively). The mean value of the Co–O–Zr angles is equal to 104.7°, relatively close to the tetrahedral angle. So, the oxygen atoms O1, O2, O3 and O8 are sp^3 hybridized. On the contrary, the oxygen atom O9 corresponding to the fifth group is sp hybridized. Indeed, the Zr–O–C angle is equal to 179.5(6)°. This linear arrangement can be explained by the capability of oxygen to act as a π-donor towards d^0 metals [2]. This π-bonding is also responsible for the short Zr–O distance (193.5(5) pm). Such a geometry has already been observed in the structural chemistry of metal alkoxides: 167.6(5) and 178.9(4)° in $(Ta(OMe)_3(OC_6H_3\text{-}iPr_2)_2)_2$ for example [14].

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