New precursors in the chemistry of IVB transition metal alkoxides V. Synthesis and molecular structure of $Zr_3Fe(\mu_4\text{-}O)(\mu_2\text{-}OC_3H_7)_6(OC_3H_7)_4(acac)_3$

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Abstract

The reaction of iron(III) acetylacetonate with zirconium(IV) n-propanolate in n-propanol leads to a tetranuclear species $Zr_3FeO(OC_3H_7)_{10}(acac)_3$. This compound crystallizes in the triclinic system (space group $P\bar{1}$): $a = 12.426(2)$, $b = 12.977(2)$, $c = 20.129(4)$ Å, $\alpha = 91.55(1)$, $\beta = 97.90(1)$, $\gamma = 100.53(1)°$. The structure consists of discrete tetranuclear molecules. The metal atoms design an almost perfect tetrahedron around a four-fold coordinated oxygen atom. The zirconium atoms are in a seven-fold coordination and the iron atom in a five-fold coordination.

Introduction

The use of sol–gel technology to produce advanced materials from chemical precursors is a rapidly growing field. There are two important processes, namely the alkoxide and the colloidal methods. Alkoxides are generally considered as the most suitable precursors. Therefore, their synthesis, properties and structures have stimulated a great deal of interest [1, 2].

However, structural data on homometallic or heterometallic alkoxides as well as oxoalkoxides are still scarce. The early stages of the hydrolysis/condensation process have been characterized only through a few X-ray studies of intermediate compounds. In order to understand the mechanisms involved in the first steps of the process, the structural characterization of the different species appears to be essential. We recently reported such studies in the chemistry of titanium alkoxides [3] and the zirconium–cobalt system [4, 5]. This paper presents the reaction of zirconium alkoxide with iron acetylacetonate yielding a new precursor.

Experimental

Synthesis

Anhydrous iron(III) acetylacetonate (0.0102 mol) was dissolved in 100 ml n-propanol (dried on sodium and distilled under nitrogen). After the addition of 0.0306 mol of zirconium n-propanolate (molar ratio Fe/Zr = 1/3), the mixture was stirred and refluxed for 24 h. The resulting solution was concentrated under vacuum until one third of the solvent volume was removed and then cooled down rapidly in a refrigerator under nitrogen. Millimetric yellow single crystals grew after one week; they are very unstable against moisture. The same compound crystallizes if the molar ratio Fe/Zr is lowered from 1/3 to 1/6, but, if this ratio is equal to 1/1, iron acetylacetonate recrystallizes from the solution.

Microanalysis could not be done as only a small quantity of crystalline solid was obtained, but powder X-ray diffraction proved that the bulk consists of a pure phase identical to the analyzed single crystal.

Data collection and structure refinement

A single crystal (0.15 × 0.10 × 0.18 mm) was selected and encapsulated in a Lindemann tube for the data collection on an Enraf Nonius CAD4 diffractometer. The lattice parameters were least-squares refined using 25 *hkl* reflections in the range $3 < \theta < 22°$. Table 1 gives the crystallographic data and information concerning the data collection and the refinement procedure.

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TABLE 1. Crystal data and structure refinement parameters

Formula	$Zr_3FeO_{11}C_{45}H_{94}$
Molecular weight	1140.7
Symmetry	triclinic
Space group	$P\bar{1}$
Cell parameters	
a (Å)	12.426(2)
b (Å)	12.977(2)
c (Å)	20.129(4)
α (°)	91.55(1)
β (°)	97.90(1)
γ (°)	100.53(1)
Cell volume, V (Å^3)	3156.4
No. formula units, Z	2
Specific weight, ρ (g cm^{-3})	1.200
Linear absorption coefficient	6.84
Radiation	Mo Kα
Measurement temperature (°C)	20
Scan type	ω/θ
θ range (°)	3–22
Reflections measured	8551
Reflection refined, $I > 3\sigma(I)$	5087
Refined parameters	535
Reliability index, R	0.073

The positions of the four metal atoms were derived from the Patterson function. The remaining atoms, except hydrogens, were located from successive difference Fourier maps. An empirical absorption correction (program DIFABS [6]) was applied. Four alkoxo groups show large thermal motion, probably due to disorder; they were refined isotropically with geometrical constraints. All other atoms were refined with anisotropic thermal factors. The final R value was equal to 0.073.

Discussion

Final position and equivalent isotropic thermal parameters are given in Table 2. Selected bond angles and interatomic distances appear in Table 3.

The structure consists of discrete tetranuclear molecules [$Zr_3FeO(OC_3H_7)_{10}(acac)_3$], the structure of which is shown in Fig. 1. The metal atoms are located at the vertices of a slightly flattened tetrahedron, the center of which is occupied by a four-fold oxygen atom (Fig. 2).

Surrounding the zirconium is a monocapped octahedron involving the μ_4-oxygen, two oxygen atoms from a chelating acetylacetonato group, three oxygen atoms from μ_2-propoxo bridges and a seventh oxygen atom from a terminal propoxo group. In the three polyhedrons, the capping atom is the μ_4-oxygen atom. As already observed in other similar structures [4, 5, 7], the Zr–OPr^n distances are considerably shorter

TABLE 2. Final least-squares atomic parameters with e.s.d.s. for $Zr_3FeO(OC_3H_7)_{10}(acac)_3$

Atom	x/a	y/b	z/c	U_{eq} (Å^2)[a]
Zr1	0.0688(1)	0.1471(1)	0.18706(7)	0.066(2)
Zr2	0.2572(1)	−0.0212(1)	0.23760(7)	0.070(2)
Zr3	0.3045(2)	0.2403(1)	0.30872(8)	0.083(2)
Fe	0.3268(2)	0.1899(2)	0.1497(1)	0.074(3)
O1	0.2324(8)	0.1351(6)	0.2259(4)	0.06(1)
O2	0.3527(8)	0.0454(7)	0.1578(5)	0.08(1)
O3	0.1795(8)	0.2081(7)	0.1130(4)	0.07(1)
O4	0.0928(8)	−0.0170(7)	0.1857(5)	0.07(1)
O5	0.1487(9)	0.2782(7)	0.2593(5)	0.08(1)
O6	−0.0325(8)	0.0807(7)	0.0949(5)	0.07(1)
O7	−0.023(1)	0.2666(8)	0.1534(6)	0.09(1)
O8	0.3602(9)	0.0882(8)	0.3143(5)	0.08(1)
O9	−0.036(1)	0.1099(8)	0.2471(6)	0.10(2)
O10	0.3903(9)	0.2887(9)	0.2237(5)	0.09(1)
O11	0.403(1)	0.2352(9)	0.0841(5)	0.10(1)
O12	0.1936(9)	−0.0940(8)	0.3078(5)	0.09(1)
O13	0.2203(8)	−0.1607(8)	0.1701(5)	0.08(1)
O14	0.326(1)	0.409(1)	0.3336(6)	0.12(2)
O15	0.399(1)	−0.096(1)	0.2614(6)	0.10(2)
O16	0.239(1)	0.2119(9)	0.3890(5)	0.10(2)
O17	0.467(1)	0.284(1)	0.3669(6)	0.12(2)
C21	0.429(1)	0.004(1)	0.1226(8)	0.08(2)
C22	0.547(1)	0.043(1)	0.1558(9)	0.09(2)
C23	0.624(2)	−0.012(2)	0.119(1)	0.12(3)
C31	0.153(1)	0.254(1)	0.0506(7)	0.08(2)
C32	0.179(2)	0.373(1)	0.0628(9)	0.10(2)
C33	0.146(2)	0.422(1)	−0.004(1)	0.13(3)
C41	0.005(1)	−0.107(1)	0.160(1)	0.09(3)
C42	−0.056(2)	−0.148(2)	0.211(2)	0.18(5)
C43	−0.155(2)	−0.239(2)	0.183(1)	0.14(4)
C51	0.092(2)	0.354(1)	0.285(1)	0.10(3)
C52	0.115(2)	0.457(1)	0.248(1)	0.12(3)
C53	0.054(2)	0.537(2)	0.279(1)	0.15(5)
C61	−0.114(1)	0.101(1)	0.0531(8)	0.08(2)
C62	−0.160(1)	0.027(1)	−0.0052(8)	0.10(2)
C63	−0.159(2)	0.192(2)	0.0609(9)	0.10(2)
C64	−0.109(2)	0.271(1)	0.112(1)	0.09(3)
C65	−0.160(2)	0.370(1)	0.120(1)	0.12(3)
C81	0.424(1)	0.055(2)	0.3754(8)	0.09(3)
C82	0.545(1)	0.065(2)	0.3674(9)	0.11(3)
C83	0.601(2)	0.027(2)	0.434(1)	0.14(4)
C91	−0.147(1)	0.115(5)	0.254(2)	0.14(3)*
C92	−0.158(3)	0.124(3)	0.328(2)	0.14(2)*
C93	−0.055(5)	0.097(5)	0.368(1)	0.14(4)*
C101	0.5016(9)	0.342(1)	0.225(1)	0.14(1)*
C102	0.504(2)	0.452(1)	0.203(2)	0.14(1)*
C103	0.625(2)	0.509(2)	0.211(2)	0.14(1)*
C111	0.463(2)	0.233(1)	0.029(1)	0.14(1)*
C112	0.470(3)	0.335(2)	−0.007(1)	0.14(2)*
C113	0.557(3)	0.341(2)	−0.053(2)	0.14(2)*
C121	0.174(3)	−0.169(1)	0.357(1)	0.14(1)*
C122	0.134(3)	−0.121(2)	0.416(1)	0.14(2)*
C123	0.098(5)	−0.208(3)	0.462(2)	0.14(3)*
C151	0.419(2)	−0.186(2)	0.250(1)	0.11(3)
C152	0.529(2)	−0.212(2)	0.285(1)	0.12(4)
C153	0.350(2)	−0.268(2)	0.207(1)	0.12(3)
C154	0.250(2)	−0.253(2)	0.167(1)	0.10(3)
C155	0.181(2)	−0.334(1)	0.119(1)	0.11(3)
C161	0.206(3)	0.202(3)	0.453(1)	0.16(6)
C162	0.263(3)	0.261(3)	0.503(1)	0.18(7)
C163	0.236(3)	0.261(3)	0.572(2)	0.23(7)
C171	0.527(2)	0.366(3)	0.403(1)	0.14(5)
C172	0.638(2)	0.355(3)	0.436(1)	0.17(5)
C173	0.487(4)	0.462(3)	0.406(2)	0.15(6)
C174	0.386(3)	0.479(2)	0.373(1)	0.13(4)
C175	0.353(3)	0.585(2)	0.380(1)	0.16(5)

[a] Atoms labelled with an asterisk were refined isotropically with geometrical constraints.

TABLE 3. Selected interatomic distances and bond angles

Distances (Å)			
M–M		Zr–μ_2OPr^n	
Zr1–Zr2	3.553(2)	Zr1–O3	2.232(9)Å
Zr2–Zr3	3.553(2)	Zr1–O4	2.193(9)
Zr3–Zr1	3.551(2)	Zr1–O5	2.197(8)
Fe–Zr1	3.347(3)	Zr2–O2	2.227(10)
Fe–Zr2	3.347(3)	Zr2–O4	2.178(9)
Fe–Zr3	3.310(3)	Zr2–O8	2.172(9)
		Zr3–O5	2.197(10)
		Zr3–O8	2.207(11)
M–μ_4O		Zr3–O10	2.187(10)
Zr1–O1	2.106(9)		
Zr2–O1	2.123(8)		
Zr3–O1	2.111(7)	Fe–μ_2OPr^n	
Fe–O1	2.124(9)		
		Fe–O3	1.933(9)
		Fe–O2	1.962(10)
Zr–O(acac)		Fe–O10	1.925(9)
Zr1–O6	2.154(8)		
Zr1–O7	2.158(11)	M–OPr^n	
Zr2–O13	2.168(10)		
Zr2–O15	2.168(13)	Zr1–O9	1.903(12)
Zr3–O14	2.195(12)	Zr2–O12	1.905(10)
Zr3–O17	2.172(12)	Zr3–O16	1.924(11)
		Fe–O11	1.776(11)
Angles (°)			
μ_4–oxo		μ_2–propoxo	
Zr1–O1–Zr3	114.7(4)	Fe–O2–Zr2	105.9(5)
Zr1–O1–Zr2	114.3(3)	Fe–O3–Zr1	106.7(4)
Zr3–O1–Zr1	114.5(4)	Zr1–O4–Zr2	108.7(3)
Fe–O1–Zr2	104.6(3)	Zr1–O5–Zr3	107.8(4)
Fe–O1–Zr2	104.0(4)	Zr2–O8–Zr3	108.8(4)
Fe–O1–Zr3	104.8(3)	Fe–O10–Zr3	107.1(4)
Terminal group		Fe–O2–C21	123.2(8)
		Zr2–O2–C21	130.6(8)
Zr1–O9–C91	173(2)	Fe–O3–C31	124.0(9)
Zr2–O12–C121	159.6(1.4)	Zr1–O3–C31	129.3(9)
Zr3–O16–C161	171.0(1.3)	Fe–O10–C101	117.9(1.2)
Fe–O11–C111	163.7(1.7)	Zr3–O10–C101	127.9(1.2)

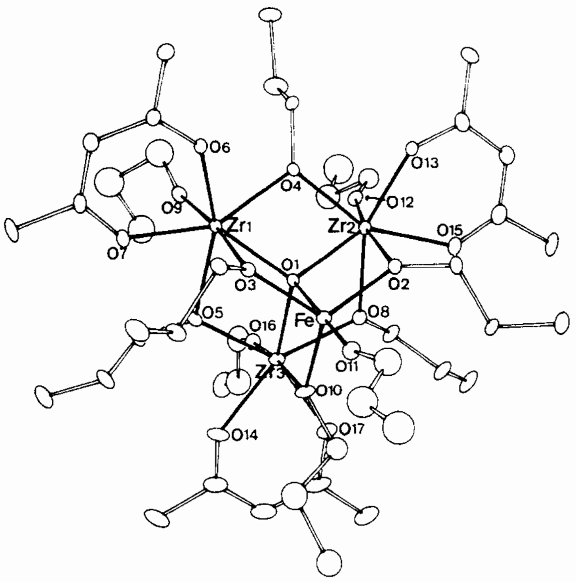

Fig. 1. ORTEP view of tetranuclear molecule.

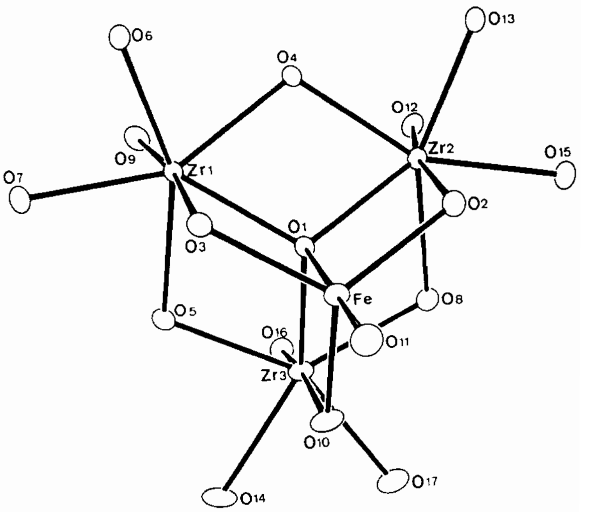

Fig. 2. Metal–oxygen arrangement in the Zr$_3$FeO$_{17}$ core.

for a terminal group (mean value 1.94 Å) than for a μ_2 bridging group (mean value 2.20 Å).

The iron environment is trigonal bipyramidal involving three oxygen atoms from μ_2-propoxo bridges in the equatorial plane, the μ_4-oxygen atom and a fifth oxygen from a terminal propoxo group occupying the axial positions. The polyhedron is heavily distorted, the μ_2-oxygen atoms being repelled in the direction opposite to the terminal group. The mean value of O1–Fe–μ_2O is 77.5° whereas the corresponding value for O11–Fe–μ_2O is 102.5°. The interatomic distance between the iron atom and the oxygen of the terminal propoxo group (1.776(11) Å) is remarkably shorter than the Fe–μ_2O distances (mean value 1.94 Å). This bond can probably be regarded as having some multiple-bond character. Such a distance has already been observed in a number of Fe(III)–oxo compounds containing Fe–O–Fe bridges [8].

The propoxo groups show two different coordination schemes. Six groups are dicoordinated either towards two zirconium atoms or to a zirconium and the iron atoms. In the latter case, the coordination is asymmetrical with mean values equal to 121.7° for Fe–O–C angles and 129.3° for Zr–O–C angles. The last four groups are terminal groups and show a quasi-linear M–O–C geometry explained by the capability of oxygen to act as a π-donor towards d^0 metals [9].

It is noteworthy that this 'Zr_3Fe' molecule has the same geometry as another tetranuclear cluster recently described [7]: $Zr_4(\mu_4\text{-}O)(\mu_2\text{-}OC_3H_7)_6(OC_3H_7)_4(acac)_4$. Both molecules have the same basic tetrahedral architecture, a $[Zr(acac)]^{3+}$ unit being replaced by the Fe^{3+} ion. This remarkable similarity poses the question of the mechanism of formation. For the 'Zr_4' molecule, a three-step mechanism is proposed. The complexation of the initial solvated dimeric structure leads to a first species $[Zr_2(\mu_2\text{-}OC_3H_7)_2(OC_3H_7)_4(acac)_2]$ and is followed by a partial hydrolysis replacing a $\mu_2\text{-}OPr^n$ group by a $\mu_2\text{-}OH$ group: $[Zr_2(\mu_2\text{-}OC_3H_7)(\mu_2\text{-}OH)(OC_3H_7)_4(acac)_2]$. The third step consists of a condensation reaction between the above-mentioned species. This mechanism is essentially based on the dimeric nature, in solution and in the solid state, of the zirconium n-propanolate and the differentiation between alkoxo groups upon hydrolysis.

For the 'Zr_3Fe' molecule, the odd number of zirconium atoms imposes the cleavage of the initial dimeric species. It must be noticed that the acetylacetonato groups, initially coordinated to the iron atom, chelate the zirconium atoms in the reaction product. So, the first step should be the dissociation of the $Fe(acac)_3$ complex, followed by the complexation of the dimeric zirconium alkoxide. In the second step, the dimeric molecule must be cleaved. A possible intermediate species in the reaction could be an oxo-centered trinuclear unit with a tetrahedral $\mu_3\text{-}O$. Such species are very stable and, in zirconium chemistry, this geometry has already been observed for $[Zr_3(\mu_3O)(\mu_2\text{-}OH)_3(\mu_2\text{-}C_6H_5COO)_3(n^5\text{-}C_5H_5)_3]^+$ [10]. Thus, in our case, the final product could form through the reaction of $[Zr_3(\mu_3\text{-}O)(\mu_2\text{-}OR)_3(OR)_3(acac)_3]^+$ with a tetrahedral $[Fe(OR)_4]^-$ unit, similar to the one observed in $[Fe(\mu_2\text{-}OCH^tBu)_2(OCH^tBu)]Li(^tBu_2HCOH)$ [11]. Such a mechanism could explain the asymmetrical coordination of the four-fold oxygen atom (114.5° for Zr–O–Zr angles and 104.5° for Fe–O–Zr angles) and also the distortion of the iron surroundings. Indeed, this environment can alternatively be regarded as a (4+1) coordination because O2, O3, O10 and O11 atoms design a distorted tetrahedron: the mean value of O–Fe–O angles, except O1, is 109°.

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