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New Precursors in the Chemistry of IVB Transition Metal Alkoxides. III. Synthesis and Structure of Zr₂Co₂(μ₃-OC₃H₇)₂(μ₂-OC₃H₇)₄(OC₃H₇)₄(acetylacetonate)₂

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Abstract. Bis(acetylacetonato)-bis(μ₃-propanolato)-1:2:4κO;2:3:4κO'-tetrakis(μ₂-propanolato)-1:2κO;-1:4-κO;2:3κO;3:4κO-tetrakis(propanolato)-2κ²O,-4κ²O-dicobaltdizirconium, Zr₂Co₂(OC₃H₇)₁₀-(O₂C₅H₈)₂, *M_r* = 1091.43, monoclinic, *P*2₁/*n*, *a* = 12.753 (3), *b* = 16.500 (3), *c* = 13.485 (2) Å, β = 99.27 (2)°, *V* = 2800.6 Å³, *Z* = 2, *D_x* = 1.29 Mg m⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 4.88 mm⁻¹, *F*(000) = 1124, room temperature, *R* = 0.057 for 2798 independent [*I* > 3σ(*I*)] reflections. The centrosymmetric molecule is tetranuclear. The Zr atom has a very distorted octahedral environment and the Co atom a distorted trigonal bipyramidal surrounding. The alkoxy groups show three different coordination schemes.

Introduction. The hydrolysis of bimetallic alkoxides allows the synthesis of very homogeneous mixed metal oxides *via* the sol-gel process (Dislich, 1988). However, these starting products are frequently extremely unstable. Recent studies (Schmid, Mosset & Galy, 1990) from this laboratory show that they can be stabilized by a chelating ligand such as acetylacetonate (Hacac).

The reaction of zirconium *n*-propanolate on cobalt(II) acetylacetonate yields a new hexanuclear precursor: Zr₂Co₄(μ₆-O)(μ₂-OC₃H₇)₈(OC₃H₇)₂-(acac)₄ (Schmid, Mosset & Galy, 1991). We report now the X-ray structure of the second product in this reaction: Zr₂Co₂(μ₃-OC₃H₇)₂(μ₂-OC₃H₇)₄(OC₃H₇)₄-(acac)₂.

Experimental. 0.0082 mol of cobalt(II) acetylacetonate is suspended in 100 ml *n*-propanol, dried on

sodium and distilled under dry nitrogen. After the addition of 0.0328 mol of zirconium *n*-propanolate, the solution is stirred and refluxed for 24 h under nitrogen. This solution is then concentrated until one third of the solvent is removed and rapidly cooled in the refrigerator. Violet single crystals grow slowly; 0.25 × 0.35 × 0.15 mm; Enraf-Nonius CAD-4 diffractometer; graphite-monochromatized Mo *Kα* radiation; 25 reflections (8 < θ < 15°) for refined unit-cell parameters; θ/2θ scan mode; scan width 1.2°; independent reflections with 3 < θ < 19°; range of *hkl*: 0 < *h* < 11, 0 < *k* < 15, -12 < *l* < 12; no intensity deterioration of the three standard reflections; *Lp* corrections, no absorption correction; 2798 independent reflections with *I* > 3σ(*I*); metal positions from Patterson function, other non-H atoms from difference-Fourier syntheses; anisotropic full-matrix least-squares refinement on *F*; 262 refined parameters; unit weights; *R* = 0.057; *wR* = 0.055; (Δ/σ)_{max} = 0.1; final Δρ values < 0.6 e Å⁻³. Calculations performed with *SHELX76* (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149–150).

Discussion. Final atomic coordinates for the non-H atoms are listed in Table 1* and selected bond distances and angles in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53643 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic parameters for the non-H atoms, with e.s.d.'s in parentheses

	x	y	z	$U_{eq}(\text{\AA}^2)$
Zr	0.00595 (7)	0.10799 (6)	0.02751 (6)	0.088 (1)
Co	0.17656 (9)	0.01506 (9)	-0.10386 (9)	0.095 (2)
O(2)	0.1644 (4)	0.0978 (4)	-0.0052 (4)	0.100 (8)
O(3)	-0.1544 (4)	0.0915 (4)	0.0512 (4)	0.094 (7)
O(1)	-0.0140 (4)	0.0155 (4)	-0.0946 (4)	0.087 (7)
O(4)	0.0568 (5)	0.1609 (5)	0.1522 (5)	0.12 (1)
O(5)	-0.0346 (5)	0.1978 (4)	-0.0619 (5)	0.116 (9)
O(6)	0.3348 (5)	0.0159 (5)	-0.1020 (5)	0.12 (1)
O(7)	0.1503 (5)	0.0275 (5)	-0.2476 (5)	0.114 (9)
C(1)	0.2582 (9)	0.1432 (9)	0.040 (1)	0.13 (2)
C(2)	0.331 (3)	0.255 (2)	0.011 (3)	0.35 (8)
C(3)	0.262 (2)	0.213 (1)	-0.032 (3)	0.21 (5)
C(4)	-0.2417 (8)	0.1495 (7)	0.0323 (9)	0.12 (1)
C(5)	-0.249 (1)	0.1892 (9)	0.141 (1)	0.16 (3)
C(6)	-0.336 (2)	0.238 (1)	0.134 (2)	0.25 (4)
C(7)	-0.0684 (7)	0.0344 (7)	-0.1966 (6)	0.10 (1)
C(8)	-0.1861 (7)	0.0359 (7)	-0.1977 (7)	0.12 (1)
C(9)	-0.2429 (9)	0.0533 (8)	-0.3100 (8)	0.14 (2)
C(10)	0.102 (2)	0.211 (2)	0.231 (2)	0.23 (5)
C(11)	0.061 (3)	0.242 (2)	0.296 (2)	0.26 (7)
C(12)	0.022 (2)	0.175 (2)	0.342 (2)	0.29 (6)
C(13)	-0.061 (1)	0.257 (1)	-0.140 (1)	0.17 (2)
C(14)	-0.062 (2)	0.335 (2)	-0.107 (2)	0.25 (5)
C(15)	-0.020 (2)	0.371 (2)	-0.034 (2)	0.27 (5)
C(16)	0.380 (1)	0.0192 (8)	-0.182 (1)	0.13 (2)
C(17)	0.5019 (8)	0.015 (1)	-0.155 (1)	0.16 (3)
C(18)	0.325 (1)	0.0243 (9)	-0.278 (1)	0.14 (2)
C(19)	0.219 (1)	0.0279 (8)	-0.3075 (9)	0.13 (2)
C(20)	0.174 (1)	0.0296 (9)	-0.4178 (8)	0.16 (2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(U_1^2 U_2^2 U_3^2)^{1/3}$, where U_1 , U_2 and U_3 are root-mean-square amplitudes of the vibrational tensor.

Table 2. Selected bond distances (Å) and angles (°)

Zr—O(4)	1.913 (7)	Zr—Co	3.372 (3)
Zr—O(5)	1.928 (7)	Zr—Co	3.386 (3)
Zr—O(3)	2.138 (5)	Zr—Zr	3.638 (2)
Zr—O(2)	2.144 (5)	O(2)—C(1)	1.460 (9)
Zr—O(1)	2.225 (6)	O(3)—C(4)	1.458 (8)
Zr—O(1)	2.229 (5)	O(1)—C(7)	1.472 (8)
Co—O(7)	1.924 (6)	O(4)—C(10)	1.397 (7)
Co—O(2)	1.930 (6)	O(5)—C(13)	1.438 (9)
Co—O(3)	1.935 (5)	O(6)—C(16)	1.306 (9)
Co—O(6)	2.014 (6)	O(7)—C(19)	1.282 (8)
Co—O(1)	2.454 (5)		
O(4)—Zr—O(5)	102.5 (2)	O(2)—Co—O(1)	76.8 (2)
O(4)—Zr—O(3)	97.1 (2)	O(3)—Co—O(6)	101.9 (3)
O(4)—Zr—O(2)	91.1 (2)	O(3)—Co—O(1)	77.3 (3)
O(4)—Zr—O(1)	94.3 (2)	O(6)—Co—O(1)	176.3 (2)
O(4)—Zr—O(1)	160.7 (3)	C(1)—O(2)—Co	120.1 (5)
O(5)—Zr—O(3)	91.4 (3)	C(1)—O(2)—Zr	127.5 (6)
O(5)—Zr—O(2)	95.6 (2)	Co—O(2)—Zr	112.3 (2)
O(5)—Zr—O(1)	161.5 (3)	C(4)—O(3)—Co	120.5 (5)
O(5)—Zr—O(1)	94.4 (3)	C(4)—O(3)—Zr	127.8 (4)
O(3)—Zr—O(2)	167.8 (2)	Co—O(3)—Zr	111.7 (3)
O(3)—Zr—O(1)	78.8 (3)	C(7)—O(1)—Zr	123.9 (5)
O(3)—Zr—O(1)	91.4 (2)	C(7)—O(1)—Zr	121.8 (4)
O(2)—Zr—O(1)	91.6 (3)	C(7)—O(1)—Co	105.9 (6)
O(2)—Zr—O(1)	78.1 (2)	Zr—O(1)—Zr	109.5 (2)
O(1)—Zr—O(1)	70.5 (3)	Zr—O(1)—Co	92.1 (3)
O(7)—Co—O(2)	126.8 (3)	Zr—O(1)—Co	92.5 (3)
O(7)—Co—O(3)	117.0 (3)	C(10)—O(4)—Zr	168.3 (5)
O(7)—Co—O(6)	91.3 (2)	C(13)—O(5)—Zr	171.6 (5)
O(7)—Co—O(1)	92.2 (2)	C(16)—O(6)—Co	124.3 (6)
O(2)—Co—O(3)	110.9 (3)	C(19)—O(7)—Co	127.6 (6)
O(2)—Co—O(6)	100.2 (3)		

The structure consists of discrete tetranuclear molecules situated on a centre of symmetry (Fig. 1). The inorganic core of this molecule can be viewed as two planes Zr—O(2)—Co—O(3)—Zr—O(1), folded

along Co—O(1), connected through the Zr—Zr' axis.

Surrounding the zirconium is a very distorted octahedron involving six O atoms from six alkoxy groups. The main distortion comes from the coordination to the μ_3 O atoms with a narrow O(1)—Zr—O(1)' angle, 70.5 (3)°, and a remarkably short O(1)—O(1)' distance, 2.569 (9) Å.

The cobalt environment is trigonal bipyramidal involving three O atoms from three alkoxy groups and the two O atoms of a chelating acetylacetonato group. The polyhedron is distorted, the O(2) and O(3) atoms being repelled in the direction opposite to the chelate ring. The Co—O(1) bond is very weak: 2.454 (5) Å compared to the mean value of the four other Co—O distances (1.95 Å).

The acetylacetonato group shows a slightly asymmetric dicoordination towards the Co atom. The ring is perfectly planar, the greatest deviation being 0.007 (6) Å for C(16). C(17) lies in this plane but C(20) is displaced by 0.075 (8) Å.

The alkoxy groups show three different coordination schemes. Two groups are coordinated, through a μ_3 -O, to a Co and two Zr atoms. Four groups are dicoordinated to a Co atom and a Zr atom and four groups are only monocoordinated towards the Zr atoms. The Zr—O distances are significantly different according to the coordination mode. The mean values are: 1.92, 2.14 and 2.23 Å respectively for a mono-, di- or tricoordinated group.

The O atoms of the monocoordinated groups, O(4) and O(5), are *sp* hybridized. Indeed, the Zr—O—C angle is equal to 168.3 (5) and 171.6 (5)°, respectively. This linear agreement can be explained by the ability of oxygen to act as a π donor towards

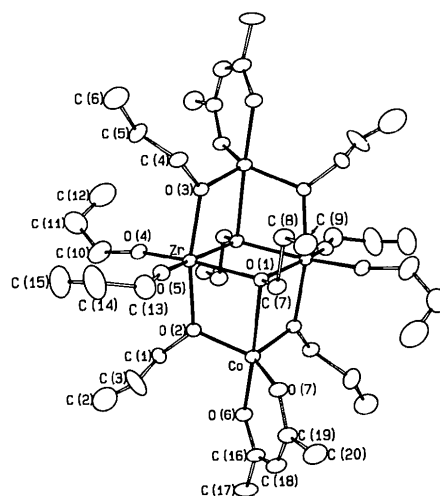


Fig. 1. ORTEP (Johnson, 1965) drawing of the tetranuclear molecule.

*d*⁰ metals (Hubert-Pfalzgraf, 1987). Such a geometry has already been observed in the hexanuclear complex synthesized through the same reaction [Zr—O—C = 179.5 (6)°] (Schmid, Mosset & Galy, 1991).

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Quasi-One-Dimensional Structure of *cis*-Dichlorobis(2,6-dimethylphenyl isocyanide)-palladium(II), [Pd{2,6-(CH₃)₂C₆H₃NC}₂Cl₂]

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Abstract. C₁₈H₁₈Cl₂N₂Pd, *M_r* = 439.66, triclinic, *P* $\bar{1}$, *a* = 8.2168 (9), *b* = 10.4799 (7), *c* = 10.8272 (12) Å, α = 85.966 (7), β = 80.018 (10), γ = 86.929 (7)°, *V* = 915.14 (16) Å³, *Z* = 2, *D_x* = 1.596 Mg m⁻³, μ = 1.29 mm⁻¹, λ (Mo *K* α) = 0.70930 Å, *F*(000) = 439.95, *T* = 293 K. The structure was refined to *R* = 0.034, *wR* = 0.030 for 2100 observed reflections. The Pd atom has a square-planar coordination with the two Cl atoms and the two isocyanide groups in *cis* configurations. The dihedral angles between the xylenyl isocyanide planes and the Pd coordination plane are 20.9 (1) and 46.6 (1)°. The compound forms a quasi linear chain with Pd···Pd separations of 4.186 (2) and 4.061 (2) Å, and a Pd···Pd···Pd angle of 170.17 (2)°.

Introduction. [Pd{2,6-(CH₃)₂C₆H₃NC}₂Cl₂] (1) can be obtained from direct reaction between xylenyl isocyanide and palladium(II) dichloride in aqueous solutions or from photochemical decomposition of hexakis(xylenyl isocyanide)dipalladium(I) hexafluorophosphate, dichlorotetrakis(xylenyl isocyanide)-dipalladium(I) hexafluorophosphate or dichlorotetrakis(xylenyl isocyanide)dipalladium(I) in chloroform solutions (Yamamoto & Yamazaki, 1985). (1) is of some interest in catalysis; the related *cis*-dichlorobis(phenyl isocyanide)palladium(II) compound (2) is found to be an efficient catalyst in hydroformylation reactions (Mondal, Banerjee &

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Sen, 1980). The presence of methyl groups at the *ortho* positions in (1) should induce important intramolecular steric hindrance and should influence molecular structure, crystal packing and reactivity. In the course of our work, we have noticed that (1) crystallizes from acetonitrile or chloroform/ether solutions forming long needles from which suitable single crystals were available for X-ray diffraction analysis. After solving the X-ray single-crystal diffraction data, we find that contrary to most analogous non-planar compounds (*cis*-PdCl₂L₂; L = bulky ligand), a quasi-one dimensional (1D) structure is found despite the distorted structure of (1). We are currently investigating the design of new 1D compounds using mono- and diisocyanide ligands with Pd^{II}, Ag^I and Au^I metals. This work describes the crystal and molecular structures of (1).

Experimental. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Mo *K* α radiation; lattice parameters determined from 24 reflections (40 ≤ 2 θ ≤ 45°); 2 θ / ω technique; three standard reflections monitored every 60 min without significant deviation. Crystal: 0.20 × 0.20 × 0.20 mm; −8 ≤ *h* ≤ 8, 0 ≤ *k* ≤ 10, −11 ≤ *l* ≤ 11; 2364 unique measured reflections; *R*_{int} = 0.016, 2100 observed with *I*_{net} ≥ 2.5 σ *I*_{net}, 2 θ _{max} = 44.7°; *R* = 0.034, *wR* = 0.030, *S* = 3.00; (Δ/σ)_{max} = 0.004; max. and min. density peaks = 0.790 and −0.480 e Å⁻³. The *NRCVAX* system (Gabe, Lee & Le Page, 1985) was used for all calculations. The structure was solved by the application of direct methods and refined by full-matrix least squares on *F* using weights [*w* = 1/ σ^2 (*F*)] based

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