

Note

# Degradation of a methacrylate-substituted oxozirconium cluster by acetylacetonate

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Dedicated to Professor Nefedov on the occasion of his 70th birthday

## Abstract

Reaction of  $Zr_4O_2(OMc)_{12}$  ( $OMc$  = methacrylate) with acetylacetonate leads to the degradation of the cluster and formation of monomeric  $Zr(acac)_2(OMc)_2$  ( $acac$  = acetylacetonate). The zirconium atom in  $Zr(acac)_2(OMc)_2$  is dodecahedrally coordinated by the eight oxygen atoms of the chelating  $OMc$  and  $acac$  ligands. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Transition metal oxide clusters capped by reactive organic groups are interesting building blocks for the synthesis of inorganic–organic hybrid materials due to their defined shape, and their size in the lower nanometer range [1]. These clusters can be prepared by two strategies. The organic groups can either be grafted to a pre-formed cluster ('surface modification' method) or introduced during the cluster synthesis ('in-situ' method). The latter method has been successfully used for the preparation of carboxylate- or  $\beta$ -diketonate-substituted metal oxide clusters by reaction of metal alkoxides with carboxylic acids or  $\beta$ -diketones [1,2]. One problem associated with the 'surface modification' method is that substitution of reactive groups bonded to the surface metal atoms requires the simultaneous balancing of charges and co-ordination numbers. Sub-

stitution of mono-anionic, monodentate groups ( $OR$ ,  $OH$ ,  $Cl$ , etc.) by mono-anionic, bidentate ligands (carboxylates,  $\beta$ -diketonates, etc.) therefore requires either rearrangement of the cluster and/or changing the co-ordination mode of bridging groups (e.g. bridging  $OR$  or  $OH$  to terminal, or  $\mu_3$  oxygens to  $\mu_2$  oxygens) to make additional co-ordination sites available. A recent example which illustrates this point is the formation of  $Ti_6O_4(OEt)_{14}(OOCPh)_2$  [ $= Ti_6(\mu_4-O)_2(\mu_2-O)_2(\mu_2-OEt)_6(\mu_2-benzoate)_2(\mu_1-OEt)_8$ ] upon reaction of  $Ti_7O_4(OEt)_{20}$  [ $= Ti_7(\mu_4-O)_2(\mu_3-O)_2(\mu_2-OEt)_8(\mu_1-OEt)_{12}$ ] with benzoic acid [3].

In a recent publication [4], the reaction of  $Ti_{16}O_{16}(OEt)_{32}$  with acetylacetonate was spectroscopically investigated, but no products were isolated. When up to four molar equivalents of acetylacetonate per cluster were added, the oxo core remained stable. With a higher proportion of acetylacetonate, the NMR data indicated the formation of larger species, and a small resonance of  $Ti(acac)_2(OEt)_2$  was observed. In the present paper we report an example in which a oxozirconium cluster is completely degraded to monomeric units upon reaction with acetylacetonate.

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## 2. Experimental

### 2.1. Synthesis of $Zr(acac)_2(OMc)_2$ (**2**)

The reaction was carried out in a Schlenk tube under Argon. 0.5 g (0.35 mmol) of  $Zr_4O_2(OMc)_{12}$  was dissolved in chloroform, and 0.28 g (2.82 mmol) of acetylacetonone were added. The solution was stirred at room temperature for 10 min. After 24 h at 4°C, 0.74 g of **2** had precipitated as colorless crystals (yield 75%). Anal. Calc. (Found) for  $C_{18}H_{24}O_8Zr$ : C, 44.8 (44.7); H, 4.9 (5.8)%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  = 1.85 (s, 6 H,  $CH_2C(CH_3)COO$ ), 1.97 (s, 12 H,  $CH_3(acac)$ ), 5.43 (s, 2 H,  $CH(acac)$ ), 5.53 (s, 2 H, *cis*- $CH_2C(CH_3)COO$ ), 6.17 (s, 2 H, *trans*- $CH_2C(CH_3)COO$ ) ppm.  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  = 17.6 ( $CH_2C(CH_3)COO$ ), 26.6 ( $CH_3(acac)$ ), 104.5 ( $CH(acac)$ ), 127.1 ( $CH_2C(CH_3)COO$ ), 136.4 ( $CH_2C(CH_3)COO$ ), 171.4 ( $COO$ ) 190.5 ( $CO(acac)$ ) ppm.

### 2.2. X-ray crystallography

Selected crystals of **2** were mounted on a Siemens SMART diffractometer with a CCD area detector. Crystal data and details of data collection are provided in Table 1. The crystal-to-detector distance was 4.40 cm. A hemisphere of data was collected by a combination of three sets of exposures at 213 K. Each set had a different  $\phi$  angle for the crystal, and each exposure took 20 s and covered 0.3° in  $\omega$ . The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections.

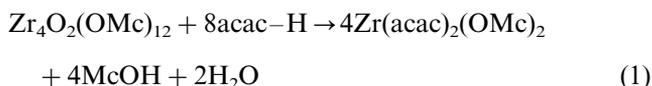
Table 1  
Crystal data and structure refinement for  $Zr(acac)_2(OMc)_2 \cdot 2CHCl_3$

Empirical formula	$C_{20}H_{25}Cl_6O_8Zr$
Formula weight	697.32
Temperature (K)	213(2)
Wavelength (pm)	71.073
Crystal system, space group, Z	Monoclinic, $P2_1/n$ , 4
Unit cell dimensions	
<i>a</i> (pm)	1106.7(2)
<i>b</i> (pm)	1198.6(1)
<i>c</i> (pm)	2305.7(2)
$\beta$ (°)	95.23(1)
<i>V</i> (pm <sup>3</sup> )	3045.6(6)·10 <sup>6</sup>
$D_{calc}$ (g cm <sup>-3</sup> )	1.521
Absorption coefficient (mm <sup>-1</sup> )	0.925
$\theta$ Range for data collection (°)	1.77–26.39
Reflections collected/unique	17862/6229
Goodness-of-fit on $F^2$	1.030
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0291$ , $wR_2 = 0.0740$
<i>R</i> indices (all data)	$R_1 = 0.0342$ , $wR_2 = 0.0769$
Largest difference peak and hole (e Å <sup>-3</sup> )	0.551 and -0.476

The structure was solved by direct methods (SHELXS-86). Refinement was carried out with the full-matrix least-squares method based on  $F^2$  (SHELXL-93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. The asymmetric unit of **2** contains two  $CHCl_3$  molecules.

## 3. Results and discussion

The cluster  $Zr_4O_2(OMc)_{12}$  ( $OMc$  = methacrylate) (**1**) exists in two crystalline modifications which slightly differ by the mutual orientation of the coordination zirconium polyhedra [5]. In both modifications, two of the methacrylate ligands are chelating and the other ten are bridging. In an attempt to substitute the chelating methacrylate ligands by (chelating) acetylacetonate ligands, we reacted a  $CHCl_3$  or toluene solution of **1** with increasing proportions of acetylacetonone. The reaction was monitored by NMR spectroscopy. When eight molar equivalents of acetylacetonone were added, the opaque solution became clear, and the NMR signals of the starting cluster **1** had completely disappeared. Monomeric  $Zr(acac)_2(OMc)_2$  ( $acac$  = acetylacetonate) (**2**) was quantitatively formed, along with methacrylic acid and water, which were spectroscopically detected (Eq. (1)). With smaller proportions of acetylacetonone, the same products were observed, together with the unreacted starting compound **1**. A mixed methacrylate/acetylacetonate cluster was not observed at any stage of the reaction.



There is a marked solvent influence on the degradation reaction. In  $CHCl_3$ , the reaction is complete within 2 min at room temperature, while 3 h at 50°C are needed in toluene. In benzene, no reaction was surprisingly observed within several hours at 50°C.

Crystals of **2** were obtained by recrystallization from  $CHCl_3$ . The X-ray structure analysis (Fig. 1) showed that all ligands are chelating. The eight oxygen atoms are arranged around the Zr atom in a dodecahedral geometry. The Zr–O(methacrylate) distances (average 225.3 pm) are distinctly longer than the Zr–O(acetylacetonate) distances (average 213.8 pm), as expected. While the zirconium atom is more or within the COO plane of the two methacrylate ligands ( $\pm 0.14$  and 0.05 pm), the two acac ligands are tilted (i.e. Zr  $\pm 0.63$  and 0.68 pm above/below the OCCCO plane).

The results reported in this paper demonstrate the difficulty of subsequently modifying preformed metal oxide clusters by organic ligands.

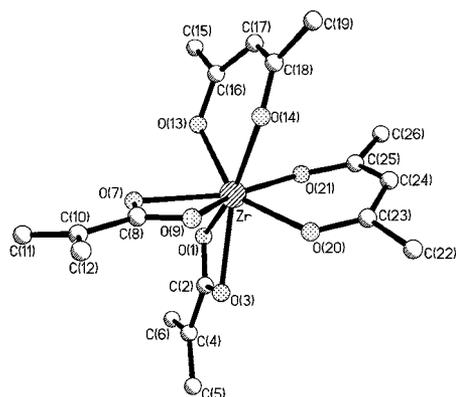


Fig. 1. Molecular structure of  $\text{Zr}(\text{acac})_2(\text{OMc})_2$  (**2**). Selected bond lengths (pm) and angles ( $^\circ$ ):  $\text{Zr}-\text{O}(1)$  224.8(2),  $\text{Zr}-\text{O}(3)$  225.5(2),  $\text{Zr}-\text{O}(7)$  224.4(2),  $\text{Zr}-\text{O}(9)$  226.5(1),  $\text{Zr}-\text{O}(13)$  216.8(1),  $\text{Zr}-\text{O}(14)$  211.4(1),  $\text{Zr}-\text{O}(20)$  215.1(1),  $\text{Zr}-\text{O}(21)$  211.7(1).  $\text{O}(7)-\text{Zr}-\text{O}(20)$  132.46(5),  $\text{O}(7)-\text{Zr}-\text{O}(21)$  149.52(5),  $\text{O}(13)-\text{Zr}-\text{O}(20)$  147.35(5),  $\text{O}(1)-\text{Zr}-\text{O}(14)$  152.24(5),  $\text{O}(3)-\text{Zr}-\text{O}(13)$  132.02(5),  $\text{O}(3)-\text{Zr}-\text{O}(14)$  149.75(5),  $\text{O}(9)-\text{Zr}-\text{O}(21)$  152.36(5).

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157426. Copies of this infor-

mation may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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