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New metallo-organic complex of zirconium (IV) incorporated with internally functionalised oxime: as precursor for nano structured ZrO₂

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Abstract : A new derivative of zirconium (IV), [(acac)₂Zr{ONC(Me)th-2}₂] have been produced by treating bis(acetylacetonato)diisopropoxy zirconium(IV) with internally functionalised oxime HONC(Me)th-2 (where th = thiophene) in 1:2 stoichiometry, while refluxing in anhydrous toluene. After drying and purification, the product appeared as off-white crystalline solid. Physico-chemical analysis of this derivative indicated the monomeric nature of octa-coordinated complex. On subjecting [(acac)₂Zr{ONC(Me)th-2}₂] for sol-gel technology, uniform sized nano particles of zirconia were the ultimate products.

Keywords: Zirconium, Metallo-organic, complex, Zirconia, Nano-particles, Oxime, Acetylacetone.

1. Introduction

Nanostructured zirconia has significant applications in various fields such as oxygen sensors, heat resistant coatings, catalysts, catalyst support, orthopedics, optical coatings etc. Nanostructured zirconia shows improved mechanical, thermal, optical, electrical and chemical properties when compared to micron-sized zirconia¹⁻⁵. Sol-gel is the widely practiced method to synthesize zirconia nano-particles from zirconium alkoxides. Low reaction temperature, simple synthetic route and high homogeneity are the advantages of sol-gel method⁶. The problem involved in the synthesis of nanostructured zirconia from zirconium alkoxides by sol-gel method is formation of precipitate instead of gel due to high rate of hydrolysis and condensation⁷. Modification of these extremely moisture sensitive zirconium alkoxides by replacement of one or more easily hydrolysable alkoxy groups with chelating agents such as β-diketones, β-keto-esters, oximes, Schiff's bases etc. results in zirconium derivatives with enhanced moisture stability⁸⁻¹⁰. Further, sol-gel hydrolysis of these modified zirconium alkoxides results in nano sized zirconia. Therefore, development of zirconium alkoxides with high moisture stability as precursors of nano zirconia is at precedence.

Thus, with an objective of furnishing better precursor for nano zirconia, we are reporting synthesis and characterization of complex [(acac)₂Zr{ONC(Me)th-2}₂]. Further, nano ZrO₂ was prepared by hydrolysis of complex by sol-gel method.

2. Experimental

2.1. General

Synthesis of the Zirconium (IV) derivative was carried out under moisture free environment. Solvents were dried according to the reported methods before use¹¹. Zirconium diisopropoxide bis(acetylacetonate) and oxime were prepared according to the literature^{12,13}. Zirconium was determined gravimetrically as ZrO₂¹⁴ and isopropanol in azeotrope was estimated by oxidimetric method¹⁵. Melting points were recorded on an Elchem digital melting point apparatus. Infrared spectra [4,000-400 cm⁻¹] were collected on SHIMADZU IR affinity 1 spectrometer with anhydrous KBr pellets. ¹H and ¹³C NMR spectra were obtained from Bruker ADVANCE III 400 spectrometer in CDCl₃ using TMS as an internal standard. The elemental analysis of the complex was carried out on Elementar Vario EL III instrument. Powder XRD was recorded on X-ray BRUKER D8 Advance X-ray diffractometer. TEM micrographs were recorded using JEOL JEM 2100 high resolution transmission electron microscope.

2.2. Synthesis of complex [(acac)₂Zr{ONC(Me)th-2}₂]

[Zr(acac)₂(OPrⁱ)₂] (2.50 g, 6.15 mmol) was added to toluene solution of HONC(Me)th-2 (1.73 g, 12.30 mmol). The resulting reaction mixture was refluxed for 4h and the progress of the reaction was checked by determining the liberated isopropanol collected azeotropically with toluene by iodometric titration. After the removal of excess solvent from the reaction mixture under vacuum, an off-white crystalline solid was obtained. Yield, 3.42 g, 98%. mp = 206-208 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ (ppm) 1.90 (s, 6 H, CH₃), 2.01 (s, 6 H, CH₃), 2.27 (s, 6 H, CH₃), 5.42 (s, 2 H, CH), 6.65-6.85 (m, 6 H, CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C): δ (ppm) 10.32, 26.25, 26.79, 103.71, 110.11, 113.24, 142.96, 146.52, 149.37, 186.50, 191.65. FTIR (solid KBr) ν (cm⁻¹) = 2974, 2852, 1613, 1535, 1519, 1368, 613. Anal. Calcd for C₂₂H₂₆N₂O₆S₂Zr: C, 46.4; H, 4.6%. Found: C, 46.3; H, 4.6%.

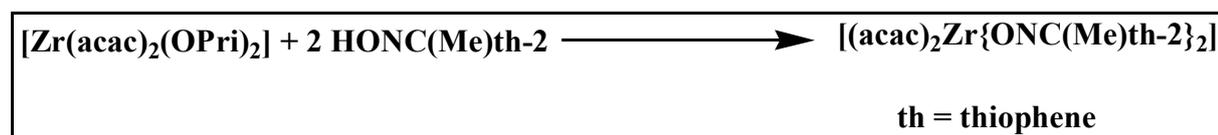
2.3. Synthesis of nano ZrO₂ from [(acac)₂Zr{ONC(Me)th-2}₂] by sol-gel technology

A clear sol was prepared by dissolving 4 g of the complex in dry ethanol (30 ml). Further, to this stirring solution a drop of distilled water-ethanol mixture (1:5) was added to the solution. No immediate gel formation was observed. Excess of water-ethanol mixture was added in small lots intermittently for next 6 h to ensure complete hydrolysis of the complex and the stirring was continued for the next 48 h. The gel obtained was heated in an oven at above 100 °C overnight and the resulting powder was washed thoroughly with distilled water and acetone. The resulting creamy white powder was sintered at 600 °C for 4 h to obtain white colored ZrO₂.

3. Results and discussion

3.1. Synthesis and characterization of complex

Reaction of [Zr(acac)₂(OPrⁱ)₂] with HONC(Me)th-2 in 1:2 ratio in refluxing toluene yielded the monomeric complex [(acac)₂Zr{ONC(Me)th-2}₂] as shown below:



The above reaction was quiet facile and quantitative in yield. Progress of the reaction was monitored by estimating the isopropanol in toluene-isopropanol azeotrope by oxidimetric method. The complex synthesized was off-white crystalline solid with sharp melting point and soluble in common organic solvents like dichloromethane, chloroform, toluene, ethanol, methanol etc. The crude product obtained was washed twice with n-hexane. This newly synthesized complex was characterized by FTIR, ¹H NMR, ¹³C NMR and elemental analysis.

Disappearance of broad peak at 3400 cm⁻¹ due to free OH indicates de-protonation of oxime. Zr-O bond formation was evidenced by bands in the region 615 cm⁻¹. Bidentate quasiaromatic nature of acetyl acetone is confirmed by the presence of strong bands at 1590 cm⁻¹ and 1530 cm⁻¹ corresponding to C=C=O and C=C=C

stretching modes. C–H stretching frequencies of alkyl and alkenyl groups appeared in the region 3050-2860 cm^{-1} .

In the ^1H NMR of the complex, absence of peak corresponding to OH of oxime indicated deprotonation and Zr-O bond formation respectively. Methyl protons of acetyl acetonate moiety appeared as two individual singlets at 1.90 and 2.01 ppm. A sharp singlet at 5.42 ppm could be attributed to methine protons of acetyl acetonate moiety. Singlet at 2.27 ppm is a characteristic peak of methyl protons in oxime. The methine protons of oxime (in thiophene ring) were observed as a multiplet in the region 6.65-6.85 ppm.

3.2. Synthesis and characterization of nano zirconia by sol-gel technique

Synthesis of zirconia nano particles was done by hydrolysis of the $[(\text{acac})_2\text{Zr}\{\text{ONC}(\text{Me})\text{th-2}\}_2]$ by sol-gel technique. Initially, one drop of water-ethanol mixture (1:5) was added and stirred, where no gel formation was observed. Finally, excess of water was added in small lots for 6 h to ensure complete hydrolysis of the complex. The gel obtained after stirring sol for 2 days was heated in an oven at 100 $^\circ\text{C}$ overnight to furnish creamy white solid. Then, the sample was washed several times with distilled water and acetone in order to remove the impurities. The powder obtained was sintered at 600 $^\circ\text{C}$ to get white ZrO_2 which was further characterized by FTIR, powder XRD and TEM analyses.

A strong broad peak at 527 cm^{-1} in the FTIR spectrum of nano ZrO_2 related to Zr-O stretching confirmed zirconia formation. The peak position in the XRD pattern of ZrO_2 was at $2\theta = 30.29^\circ$ (101), 35.38° (110), 50.42° (112), 60.30° (211) and 62.84° (202). Comparison of the obtained powder XRD patterns with standard JCPDS values indicated the tetragonal phase of the synthesized zirconia nano-particles. From the TEM image the particles appear to be spherical and agglomerate. Size of the particles is in the range of 9-22 nm and the average particle size is calculated as 15 nm.

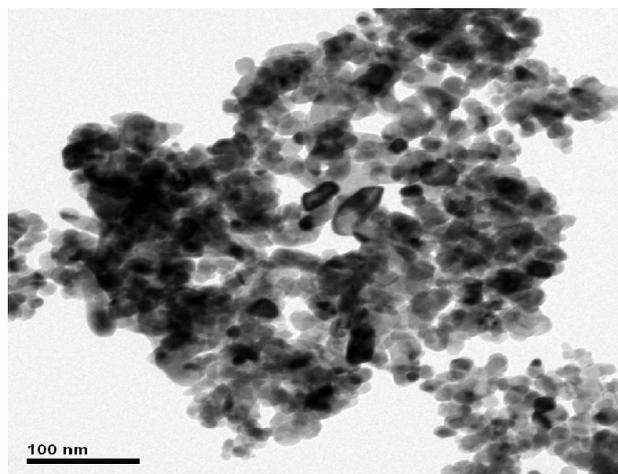


Figure 1: TEM micrograph of ZrO_2 nano-particles

4. Conclusions

Synthesis and characterization of new metallo-organic complex of zirconium (IV) by alcohol elimination reaction of $[\text{Zr}(\text{acac})_2(\text{OPr}^i)_2]$ with $\text{HONC}(\text{Me})\text{th-2}$ in appropriate stoichiometry have been reported in the present manuscript. Further, the complex was subjected to sol-gel hydrolysis to yield tetragonal zirconia nano-particles.

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