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Conformational analysis and vibrational circular dichroism study of a chiral metallocene catalyst

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ABSTRACT

Metallocene complexes are an important type of catalysts for several applications. In the present work, the Ziegler–Natta-catalyst dichloro[(*S*,*S*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)] zirconium(IV) is investigated using vibrational circular dichroism (VCD) spectroscopy and density functional theory (DFT) calculations. Furthermore the influence of a different central ion as well as different counterions is examined theoretically. From the comparison of the experimental and calculated VCD spectra, it is concluded that the metal ion acts as a placeholder whose function is just to keep the conformation of the ligand in a chiral shape.

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1. Introduction

In the last few years, vibrational circular dichroism (VCD) spectroscopy has become a powerful tool to investigate chiral compounds. Especially the application of a combined experimental and theoretical approach, i.e. VCD spectroscopy and density functional theory (DFT) calculations, yields detailed information about absolute configurations and preferred conformations [1,2]. Previous VCD studies of chiral transition metal complexes were focused up to now on structures consisting of σ-donor ligands that bind the metal ion bidentately via lone electron pairs [3–5], e.g. tris(ethylenediaminato) cobalt(III), short form $[Co(en)_3]^{3+}$. To our knowledge, there is only one investigation concerning complexes with π-donor ligands [6].

A remarkable group of π-complexes are transition metal complexes of group IV metals which are considered a new generation of catalysts for the polymerization of α-olefines. For this application, the catalytic system is formed by a complex L_2MX_2 (L = ligand; M = Ti, Zr, Hf; X = halogen or alkyl) and a co-catalyst with Lewis acid properties like methylaluminoxane (MAO). The complex has a metallocenic type of structure and the ligand L is a π-ligand. When the π-ligand is flexible in its orientation to the central atom, e.g. like cyclopentadienyl, mostly atactic polymers are obtained [7,8]. Catalysts with ethylene-bridged ligands, e.g. ethylenebis(4,5,6,7-tetrahydro-1-indenyl) or ethylenebis(indenyl) are also available (see Fig. 1). These ligands facilitate the synthesis of stereoregulary polymers with high isotactic composition and thus, the precise control of the polymer microstructure. Additionally, these catalysts show a very high catalytic activity [9].

Interestingly, the isotactic content of the obtained polymers is higher when the complex is used in an enantiomeric pure form. The chirality of these complexes originates from the rigid conformation of the bridged ligands since the bridge prevents the rotation of the indenyl groups. Therefore, two chiral forms in which the indenyl groups are pointing to opposite directions and an achiral meso-form with both groups pointing to the same direction can be obtained.

In the present work, the VCD spectrum of dichloro[(*S*,*S*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)] zirconium(IV), short form $en(thind)_2ZrCl_2$ (Fig. 1) is investigated by experiment and density functional theory calculations. Furthermore, the effect of another central metal ion as well as different counterions are evaluated theoretically. It should be examined on the one hand, whether the VCD spectra of π-donor complexes are sufficiently described by the DFT calculations and on the other hand, whether the exchange of the central ion affects the VCD significantly and whether the chirality of the ligand is transferred to an achiral organic ligand. The results are expected to be valuable for further investigations of chiral metallocene and metallocene-like complexes for a better understanding of their structure in solution and catalytic applicability.

2. Materials and methods

2.1. Chemicals

Deuterated chloroform was purchased from Deutero GmbH, Germany, and dichloro[(*S*,*S*)-ethylenebis(4,5,6,7-tetrahydro-1-

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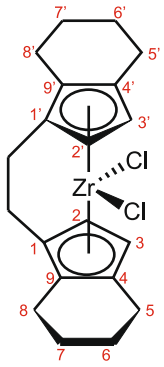

Fig. 1. Structure of dichloro[(*S*,*S*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)] zirconium(IV) (en(thind)$_2$ZrCl$_2$) including the numbering of relevant atoms.

indenyl)] zirconium(IV) was purchased from Sigma Aldrich, Germany. All chemicals were used without further purification.

2.2. VCD measurements

The VCD measurements were carried out using a Bruker Tensor 27 equipped with a PMA 50 module. The resolution was 4 cm^{-1} and the acquisition time was 60 min (coadding approx. 2100 scans). For the measurement, a mountable cell with KBr windows and 50 μm teflon spacer was used. The concentration of en(thind)$_2$ZrCl$_2$ was 0.33 M in chloroform-d_1. Baseline correction was carried out by subtracting the VCD spectrum of the pure solvent.

2.3. Simulational details

The DFT calculations, i.e. the geometry optimization of the conformers and the calculation of the corresponding vibrational absorption (VA) and VCD spectra, were performed using Gaussian 03 [10] and applying the B3PW91 functional and the LanL2DZ basis set. This basis set includes Dunning/Huzinaga full double-zeta for the first row elements and the Los Alamos effective core potential plus double-zeta for the elements Na–La and Hf–Bi [11,12]. Therefore, it is the preferred choice for DFT calculations involving transition metals and it has also been proven to give good results for VCD calculations [3,5,13]. For the VA and VCD spectra, a Lorenzian band shape with half width of 4 cm^{-1} was assigned to each fundamental vibration.

3. Results and discussion

3.1. Conformational analysis of en(thind)$_2$ZrCl$_2$

Without the bridging ethylene fragment the indenyl ligands could rotate nearly independent of each other, but here the bridge inhibits this rotation. The Zr(IV) ion keeps the organic ligand in a chiral conformation. Therefore, the conformations of en(thind)$_2$ZrCl$_2$ that have to be considered for the analysis of the VCD spectrum are reduced to the conformations of the two six-membered rings of the indenyl-ligands. For these rings, there are only two possible conformations each ring can adopt: one for which carbon atom 6 is pointing towards the center of the complex and another for which carbon atom 7 is pointing towards the zirconium (for atom numbering see Fig. 1). Due to symmetry reasons these four theoretically possible conformers are reduced to three. These three were also found to be energetically stable according to geometry optimizations via DFT calculations. The structures of these conformers are shown in Fig. 2.

In Table 1, the relative energies, the relative Gibbs free energies and the corresponding populations of the three stable conformers according to the Boltzmann distribution are given. Regarding the zero-point energies, conformer 1 for which carbon 6 and 6′ are pointing away from the center of the complex is the most favoured structure. This is consistent with conformer 1 being identical to the crystal structure found by Wild et al. [14]. In Table 2 the structural data obtained by XRD are compared with those bond lengths and bond angles that were obtained from DFT calculations. It can be seen that the calculated values are in good agreement with the experimentally obtained structural data.

The other conformers are higher in energy which leads to a lower weighting. This situation changes when the Gibbs free energies are taken into account which needs to be done for free molecules in solution and hence, for the calculation of the VA and VCD spectra in this case. The population of conformer 2 increases while conformer 1 becomes less important and thus, they change their order.

3.2. VCD spectra of en(thind)$_2$ZrCl$_2$

The vibrational absorption (VA) and vibrational circular dichroism spectra of the three conformers of the chiral metallocene complex discussed above were calculated and the results are shown in Fig. 3. Additionally, the ΔE weighted as well as the ΔG weighted VA and VCD spectra are given. In the lower panel, it can be seen that the VA spectra of all conformers are almost identical. The upper panel contains the calculated VCD spectra. Conformers 1 and 2 pos-

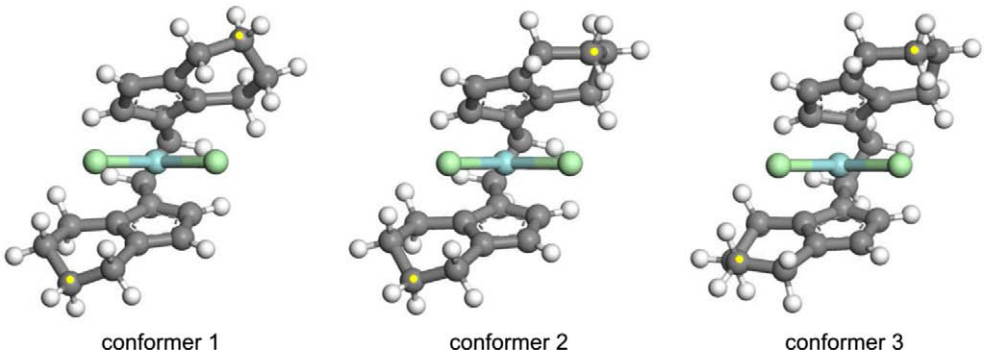

Fig. 2. Atomistic model structures of the three energetically favoured conformers of en(thind)$_2$ZrCl$_2$ as obtained by DFT calculations. Yellow dots mark the C6 and C6′ atom in both six-membered rings to clarify the different conformations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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