Metal Complexes with Tetrapyrrole Ligands, LXIX[1]

Facile Synthesis and ^{13}C-NMR Spectrum of Dichloro(octaethylporphyrinato)zirconium(IV)

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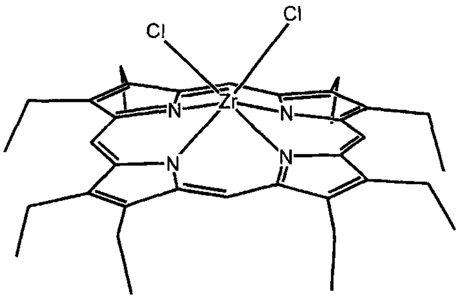
The synthesis of dichloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV), Zr(oep)Cl$_2$, from zirconium tetrachloride and octaethylporphyrin, H$_2$(oep), is described. The reported synthesis is a new and simple route to this precursor of organometallic compounds. Zr(oep)Cl$_2$ was characterized by elemental analyses, ^{1}H- and ^{13}C-NMR, UV/Vis, and mass spectra. Hydrolysis yielded a mixture of mono- and binuclear hydroxy zirconium(IV) porphyrins.

In the last few years there has been a growing interest in the synthesis of group 3 to 6 metalloporphyrin complexes M^n(p)X$_{n-2}$[2,3]. Due to the large ionic radii, the central ion in early transition metal porphyrin complexes is located above the porphyrin mean plane, resulting in a *cis* coordination of further anionic ligands[4]. Besides the long- and well-known porphyrin derivatives with chelating oxygen-donor ligands M(oep)L$_2$[5] (L = acac$^-$, OAc$^-$), the coordinatively unsaturated difluoro complexes of zirconium and hafnium, M(oep)F$_2$, were prepared[6]. Especially, the synthesis of dichloro porphyrinatozirconium(IV) complexes, Zr(p)Cl$_2$, allows the preparation of a variety of new organometallic compounds[7].

Typically, dichloro zirconium(IV) and hafnium(IV) metalloporphyrins were synthesized by metathesis of lithium porphyrins, Li$_2$(p)(Solv)$_n$ (Solv = THF, THT, DME), with cyclic ether or thioether adducts of the respective metal tetrachloride[8]. Solid zirconium tetrachloride with its polymeric structure is not suitable for complexation as it is only sparingly soluble. However, destruction of the ZrCl$_6$ octahedra – and therefore better solubility – could be achieved as well by coordination to solvents like quinoline, polychlorobenzenes, or benzonitrile. The latter was chosen for the preparation of dichloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV), Zr(oep)Cl$_2$ (Figure 1), due to weakly coordinating and basic properties ("benzonitrile method"[4]).

Figure 1. Structural formula of Zr(oep)Cl$_2$; coordinates taken from ref.[7]



A rather high reaction rate for the incorporation of zirconium in porphyrins (eq. 1) was realized with benzonitrile as solvent due to is high boiling point (190 °C) and good dissolving power towards the porphyrin and zirconium tetrachloride.

$$\mathrm{ZrCl_4 + H_2(oep)} \xrightarrow[\text{PhCN, reflux}]{\text{Ar}} \mathrm{Zr(oep)Cl_2 + 2\,HCl} \uparrow \qquad (1)$$

The reaction was carried out to completion by passing a stream of dry argon through the reaction mixture within 7 h. Extraction of the raw material with anhydrous toluene and subsequent crystallization gave dichloro(octaethylporphyrinato)zirconium(IV) Zr(oep)Cl$_2\cdot$0.5 C$_7$H$_8$ as purple-red air-stable needles. This procedure saves the preparation of the dilithium porphyrin and the ether adduct of zirconium tetrachloride.

An elemental analysis showed that per mol of Zr(oep)Cl$_2$ half a mol of toluene is present in the crystals. This was verified by ^{1}H- and ^{13}C-NMR spectra in which signals originating from toluene are clearly seen. Slow vaporization of the sample in a mass spectrometer allowed the spectra of toluene and Zr(oep)Cl$_2$ to be observed successively. Obviously, the same crystalline phase was obtained that Arnold et al.[7] had identified by X-ray structural analysis and a ^{13}C-NMR spectrum the signals of which had not been assigned.

A ^{13}C-NMR spectrum (Figure 2a) with ^{1}H decoupling exhibits five signals stemming from the metal porphyrin moiety. (For δ values see Experimental; the toluene signals are also listed). The (oep)$^{2-}$ signals were assigned on the basis of a ^{13}C-^{1}H coupled spectrum (Figure 2c). The low-field signals at δ = 147.6 and 143.6 are not split into further signals and are therefore assigned to the pyrrole carbon atoms not bearing protons. Differentiation between α- and β-pyrrole carbon atoms was made as described in ref.[9]. The signal at δ = 103.1 in the ^{13}C{^{1}H}-NMR spectrum appears as a doublet in the coupled spectrum with a coupling constant ^1J(C,H) of 157 Hz, characteristic of the sp^2 methyne carbon atoms of (oep)$^{2-}$.

Interestingly, the chemical shift difference of the *meso*-carbon atoms in Zr(oep)Cl$_2$ related to H$_2$(oep) is with its downfield shift

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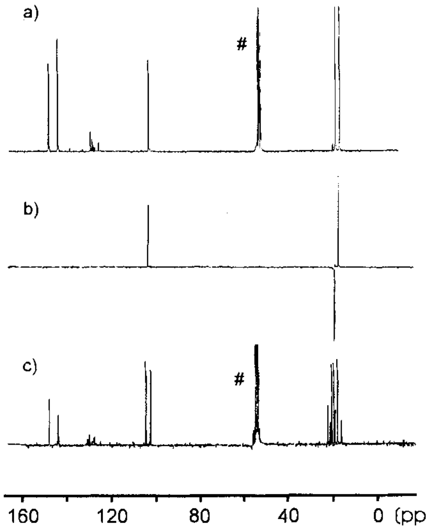
Figure 2. ^{13}C-NMR spectra of $Zr(oep)Cl_2$ in CD_2Cl_2; ^1H-decoupled (a), DEPT (b), ^1H-coupled (c) (#: CD_2Cl_2)



of δ = 7.1 rather high. In the coupled spectrum high-field signals at δ = 20.4 and 18.4 are split into a triplet and a quartet, respectively. Their coupling constant $^1J(C,H)$ of 127 Hz is in good agreement with that of sp^3 carbon atoms. The multiplet at δ = 20.4 was assigned to the methylene carbon atoms of the ethyl groups. Coupling between ^{91}Zr and ^{13}C is not observed.

A DEPT experiment assisted the assignment (Figure 2b): Signals of quaternary carbon atoms are not observed as expected, the methyne C atoms give rise to a signal at δ = 103.1. The ethyl groups give rise to a signal at δ = 18.4 originating from the methyl carbon atoms and a signal with a negative phase at δ = 20.4 assigned to the methylene carbon atoms.

Attempted purification of the raw material via column chromatography, as claimed by Berezin[10] to be performed for $Zr(tpp)Cl_2$, on alumina, silica gel, or polyvinylpyrrolidone gave no pure fraction of the $Zr(oep)Cl_2$ complex. Instead, the chromatographed material shows a remarkable feature in the UV/Vis spectrum: a concentration-dependent hypsochromic shift is observed for the B band and a less intense shift for the Q bands. Guilard[11] as well as Hammerschmitt[12] ascribed this phenomenon to a concentration-dependent equilibrium between monohydroxy porphyrins and hydroxo-bridged binuclear porphyrins. A mass spectrum identified the solid isolated from the solution to be a dihydroxo-bridged binuclear zirconium complex $[Zr(oep)(\mu\text{-}OH)]_2$. The mass spectral observation of this binuclear complex, however, does not prove the existence of this compound after chromatography. It is possible that condensation of hydroxymonoporphyrins occurred during work-up or vaporization in the ion source[13]. Therefore, it seems premature to identify the chromatographed substance as a hydroxo-bridged binuclear complex.

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Experimental

MS: Finnigan MAT 311 A with data system SS 100 MS (direct insertion, ion source at 150 °C, EI, 70 eV). – UV/Vis: Spectrophotometer Bruins Instruments Omega 10, λ = 300–700 nm. – NMR: Bruker WM 300 (300 MHz), 293 K. Chemical shifts (δ) for the ^1H-NMR spectrum are reported relative to residual protons in deuterated dichloromethane, for the ^{13}C-NMR spectra relative to the carbon atom in $[D_2]$dichloromethane. – Elemental analyses: Microanalytical Laboratory, Institut für Organische Chemie der Technischen Hochschule Darmstadt, and Analytische Laboratorien Malissa und Reuter, D-51647 Gummersbach. – Materials: The following chemicals were purchased from the companies indicated in parentheses: zirconium tetrachloride (Fluka), benzonitrile (Fluka, distilled under argon and stored over molecular sieves 4 Å), $[D_2]$dichloromethane [Merck, dried over molecular sieves 4 Å and vacuum transferred]. $H_2(oep)$ was prepared by a variant of a literature method[14]. Standard Schlenk techniques were employed throughout to prevent hydrolysis by moist air.

Dichloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV) $[Zr(oep)Cl_2]$: To a solution of 400 mg (0.75 mmol) of $H_2(oep)$ in 200 ml of benzonitrile was added 490 mg (2.1 mmol) of zirconium tetrachloride. A stream of dry argon was passed through the reaction mixture while heating at reflux until no more hydrogen chloride was detected in the exhaust gas (7 h). UV/Vis spectra showed quantitative transformation of the starting compound when bands originating from the metal-free $H_2(oep)$ were no longer observed. Evaporation of the solvent in vacuo yielded the dark red crude product. This was transferred into a soxhlet thimble and extracted with 50 ml of toluene for 40 h. Concentration of the filtrate to 10 ml and crystallization at −27 °C afforded 347 mg (62%) of $Zr(oep)Cl_2 \cdot 0.5$ toluene as deep purple red needles. – MS; *m/z* (%): 692 (61) $[M^+(^{90}Zr)]$, 657 (100) $[M^+ - {}^{35}Cl]$, 346 (4) $[M^{2+}]$. – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 330 nm (3.98), 400 (5.32), 527 (4.00), 567 (4.40). – ^1H NMR (CD_2Cl_2) δ = 1.93 (t, J = 8 Hz, 24 H, CH_2CH_3), 2.34 (s, 1.7 H, toluene-CH_3), 4.25 (m, 16 H, CH_2CH_3), 7.19 (m, 2 H, aromatic H), 10.66 (s, 4 H, oep-C*H*). – ^{13}C NMR (CD_2Cl_2) δ = 18.4 (q, $^1J(C,H)$ = 127 Hz, CH_2CH_3), 20.4 (t, J = 127 Hz, CH_2CH_3), 21.5 (toluene CH_3), 103.1 (d, J = 157 Hz, oep CH), 125.6–129.3 (toluene aromatic C), 138 (CCH_3), 143.6 (s, C_β), 147.6 (s, C_α). – $C_{36}H_{44}Cl_2N_4Zr \cdot 0.5$ toluene (741.0): calcd. C 64.03, H 6.53, N 7.56, Cl 9.57; found C 64.65, H 6.51, N 7.60, Cl 9.36.

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[2] Abbreviations: $(p)^{2-}$, $(oep)^{2-}$ are the dianions of a general porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin; M^{n+} = early transition metal ion of charge $n+$; X^- = univalent anion; L^- = bidentate anionic chelating ligand.

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