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Salicylaldehydo Chelates of Bis(cyclopentadienyl) Zirconium(IV)

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A new series of organometallic ionic chelates of the type $[Cp_2Zr(sal)]^+[ROCS_2/R'R''NCS_2]^-$, where H*sal* = salicylaldehyde; $R = Me, Et, i\text{-}Pr$ or $i\text{-}Bu$ and $R' = R'' = Me, Et, i\text{-}Pr$; $R' = Me$, R'' = benzyl or $R' = Et$, $R'' = m$-tolyl, have been synthesized in aqueous medium by the reaction of $[Cp_2Zr(sal)]^+Cl^-$ and $ROCS_2^-K^+/R'R''NCS_2^-Na^+$. These compounds have been characterized by chemical analyses, electrical conductance, electronic, IR and ^{1}H-NMR spectral studies. These studies indicate that the complexes are 1:1 electrolytes and the salicylaldehyde ligand is chelating in all these complexes. Therefore, a tetrahedral coordination about the zirconium atom is proposed.

[Keywords: Bis(cyclopentadienyl)zirkonium(IV); Conductance measurement; Dithiocarbamate; ^{1}H-*NMR; IR; Salicylaldehydo chelates; UV-VIS; Xanthate]*

Salicylaldehydo-Chelate von Bis(cyclopentadienyl)-zirkonium(IV)

Eine neue Gruppe von organometallischen ionischen Chelaten vom Typ $[Cp_2Zr(sal)]^+[ROCS_2/R'R''NCS_2]^-$ (mit H*sal* = Salicylaldehyd; $R = Me, Et, i\text{-}Pr$ oder $i\text{-}Bu$ und $R' = R'' = Me, Et, i\text{-}Pr$; $R' = Me$, R'' = Benzyl oder $R' = Et$, $R'' = m$-Tolyl) wurde in wäßrigem Medium mittels der Reaktion von $[Cp_2Zr(sal)]^+Cl^-$ mit $ROCS_2^-K^+/R'R''NCS_2^-Na^+$ hergestellt. Die erhaltenen Verbindungen wurden mittels chemischer Analyse, elektrischer Leitfähigkeit und der IR- sowie ^{1}H-NMR-Spektren charakterisiert. Diese Untersuchungen zeigen, daß die Komplexe 1:1-Elektrolyte sind, wobei der Salicylaldehyd-Ligand in allen Fällen an der Chelatbildung beteiligt ist. Es wird daher für das Zirkoniumatom eine tetrahedrale Koordination vorgeschlagen.

Introduction

The organometallic chemistry of titanium has been extensively developed over the past three decades, while that of zirconium is only now beginning to be developed. Although some chelated titanium and zirconium compounds with salicylaldehyde have been reported[1–7] no systematic study on their organometallic derivatives is available. In view of the versatile chelating ability of salicylaldehyde and lack of literature involving organometallic derivatives of zirconium, the reactions of Cp_2ZrCl_2 with salicylaldehyde in aqueous medium have been studied.

Results and Discussion

The reactions involved in the preparation of $[Cp_2Zr(sal)]^+[ROCS_2/R'R''NCS_2]^-$ complexes may be represented according to the following equations:

$$Cp_2ZrCl_2 + H_2O \longrightarrow Cp_2ZrOH^+ + Cl^- + HCl$$

$$Cp_2ZrOH^+ + Cl^- + Hsal \xrightarrow{\text{Water}} [Cp_2Zr(sal)]^+Cl^- + H_2O$$

$$[Cp_2Zr(sal)]^+Cl^- + ROCS_2^-K^+/R'R''NCS_2^-Na^+ \xrightarrow{\text{Water}}$$

$$[Cp_2Zr(sal)]^+[ROCS_2/R'R''NCS_2]^- + KCl/NaCl$$

(where H*sal* = salicylaldehyde, $R = Me$, Et, *i-Pr* or *i-Bu* and $R' = R'' = Me$, Et, *i-Pr*; $R' = Me$, R'' = benzyl or $R' = Et$, R'' = *m*-tolyl).

Even when employing a high concentration of chelating agent, bis-chelate could not be isolated because the free ligand concentration in the solution remained low due to the decomposition of $Cp_2Zr(IV)^{2+}$ moiety with breaking of the Zr—*Cp* bond above *pH* 2.8.

Table 1 lists the analytical and physical data of the complexes. All the complexes were obtained as yellow to yellowish green crystals and are quite stable in solid state and in solution. They are moderately soluble in common organic solvents like dichloromethane, chloroform, methanol, ethanol and *DMSO*. Conductance measurements reveal that the chelates are 1 : 1 electrolytes in *DMSO*.

The electronic spectra of the complexes in ethanol exhibit a single band in the region 404–413 nm. Absence of a d-d transition rules out the presence of any unpaired electron in the zirconium ion confirming the quadrivalent state of zirconium[8, 9].

The assignment of IR bands has been made on the basis of published work. The bands occurring consistently near 1 240 and 1 020 cm^{-1} in the IR spectra of $[Cp_2Zr(sal)]^+[ROCS_2]^-$ complexes may be assigned to $\nu(C \overset{\cdots}{=} O)$ and $\nu(C \overset{\cdots}{=} S)$ vibrations, which are characteristic of free $ROCS_2^-$ group[10]. The IR spectra of $[Cp_2Zr(sal)]^+[R'R''NCS_2]^-$ complexes show a strong thioureide band near 1 475 cm^{-1} supporting

Table 1. *Analytical and physical data*

No.	Compound	Dec. temp. (uncorr.) (°C)	Conductance (ohm^{-1} cm^2 mol^{-1})	% Found (Calc.)		
				N	S	Zr
1	$[Cp_2\mathrm{Zr}(sal)]^+[Me\mathrm{OCS_2}]^-$	132–135	30.2		14.12 (14.25)	20.16 (20.31)
2	$[Cp_2\mathrm{Zr}(sal)]^+[Et\mathrm{OCS_2}]^-$	117–118	29.5		13.70 (13.82)	19.57 (19.69)
3	$[Cp_2\mathrm{Zr}(sal)]^+[i\text{-}Pr\mathrm{OCS_2}]^-$	113–114	32.0		13.33 (13.41)	19.23 (19.11)
4	$[Cp_2\mathrm{Zr}(sal)]^+[i\text{-}Bu\mathrm{OCS_2}]^-$	110–112	28.9		13.13 (13.03)	18.42 (18.57)
5	$[Cp_2\mathrm{Zr}(sal)]^+[Me_2\mathrm{NCS_2}]^-$	127–130	31.4	2.86 (3.03)	13.63 (13.85)	19.60 (19.73)
6	$[Cp_2\mathrm{Zr}(sal)]^+[Et_2\mathrm{NCS_2}]^-$	98–99	32.2	2.73 (2.85)	12.91 (13.05)	18.39 (18.61)
7	$[Cp_2\mathrm{Zr}(sal)]^+[i\text{-}Pr_2\mathrm{NCS_2}]^-$	101–103	28.6	2.53 (2.70)	12.46 (12.35)	17.69 (17.60)
8	$[Cp_2\mathrm{Zr}(sal)]^+[Me, benz\mathrm{NCS_2}]^-$	152–153	31.8	2.49 (2.60)	11.81 (11.89)	16.78 (16.95)
9	$[Cp_2\mathrm{Zr}(sal)]^+[Et, m\text{-}tol\mathrm{NCS_2}]^-$	145–147	28.8	2.44 (2.53)	11.32 (11.59)	16.28 (16.52)

the partial double bond character in the $S_2C\overset{\cdots}{-}NR'R''$ bond, whereas the band near 1 000 cm^{-1} indicates the presence of $C\overset{\cdots}{-}S$ bond[11–13], characteristic of a free dithiocarbamate moiety.

A strong band is observed at ca. 1 668 cm^{-1} in the spectrum of free salicylaldehyde, which is assigned to the carbonyl frequency[14]. Coordination of the oxygen to the metal atom would, however, be expected to reduce the density of the carbonyl linkage and thus lower the carbonyl frequency. In the complexes this band is shifted to the lower wave number (ca. 1 625 cm^{-1}), showing the presence of coordination through carbonyl oxygen. A high intensity band at 1 265 cm^{-1} in the salicylaldehyde may be assigned to the phenolic C—O stretching[15]. In the spectra of the complexes this is shifted to higher wave numbers (ca. 1 310 cm^{-1}) suggesting that the *o*-hydroxy group has entered into bond formation with displacement of hydrogen. This is further supported by the disappearance of the broad ν (O—H) band in the 3 250–3 200 cm^{-1} region, and appearance of a band at ~ 635 cm^{-1} due to ν (Zr—O—C) vibrations in the complexes[16]. Apart from this, an additional band near 440 cm^{-1} can be assigned to Zr—C_5H_5 vibrations[17].

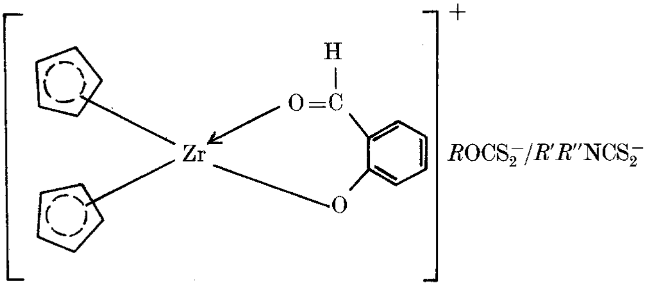
Table 2. ^1H *NMR data* (δ, *ppm*); *for No.'s see Table 1)*

No.	C_5H_5	—CH= (aldehydic)	C_6H_4/C_6H_5	CH—	—CH_2—	CH_3
1	6.32 (s)	9.94 (s)	6.82–7.60 (m)			4.06 (s)
2	6.40 (s)	9.90 (s)	6.80–7.52 (m)		4.12 (q)	1.64 (t)
3	6.42 (s)	9.92 (s)	6.75–7.58 (m)	4.40 (sept)		1.40 (d)
4	6.38 (s)	9.94 (s)	6.80–7.62 (m)	1.95 (m)	4.00 (d)	1.04 (d)
5	6.40 (s)	9.86 (s)	6.72–7.55 (m)			3.35 (s)
6	6.40 (s)	9.90 (s)	6.78–7.54 (m)		3.64 (q)	1.30 (t)
7	6.35 (s)	9.92 (s)	6.76–7.65 (m)	4.42 (sept)		1.46 (d)
8	6.42 (s)	9.88 (s)	6.80–7.60 (m)		3.72 (s)	3.34 (s)
9	6.38 (s)	9.90 (s)	6.84–7.50 (m)		3.70 (q)	1.30 (t) 2.24 (s)

The proton magnetic resonance spectra of the complexes were recorded in $CDCl_3$. Chemical shifts for the protons (δ, ppm) are represented in Table 2. The $[Cp_2Zr(sal)]^+[ROCS_2/R'R''NCS_2]^-$ chelates show four different resonance signals corresponding to (i) the C_5H_5 ring protons, which appear as a sharp singlet at ca. 6.40 ppm (the appearance of a single sharp C_5H_5 resonance is attributed to rapid rotation of the ring about the metal-ring axis), (ii) an aldehydic proton, which appears at 9.92 ppm showing a downfield shift as compared to the free salicylaldehyde (9.76 ppm) indicating coordination of the aldehydic oxygen to the zirconium atom, (iii) aromatic protons which appear as a multiplet in the range of 6.8–7.62 ppm; these also show a considerable downfield shift compared to the corresponding signals of salicylaldehyde (observed at ca. 6.54–7.2 ppm; this downfield shift of aromatic protons in the salicylaldehydo complex is attributed to the coordination of aldehydic oxygen to the metal and the net positive charge on the $[Cp_2\mathrm{Zr}(sal)]^+$ ion), and (iv) the resonance signals due to the alkyl group(s) in the xanthate and dithiocarbamate moieties occur at almost the same frequencies as observed for free xanthate and dithiocarbamate ligands.

The phenolic —OH proton which absorbs at 10.95 ppm in the free salicylaldehyde disappears in the complexes indicating its deprotonation and participation in the bond formation to the metal through oxygen.

The studies carried out for the present complexes indicate that the salicylaldehyde ligand is chelating and the $Cp_2\mathrm{Zr(IV)}^{2+}$ moiety possesses a wedge like sandwich structure with essentially tetrahedral coordination about the zirconium atom similar to that of dichlorides[18]. Typical vibrational frequencies assigned to the xanthate and dithiocarbamate moieties in the chelates fully support the view that xanthate and dithiocarbamate anions are free anions. Therefore, the following structure may be assigned to these complexes:



The possibility of the salicylaldehydo ion binding by simple hardsphere *coulombic* interactions to $Cp_2\mathrm{Zr(IV)}^{2+}$ ion is ruled out because in such a case a bis-chelate, in contrast with the present observations, with four oxygen atoms in the *xy*-plane and parallel cyclopentadienyl rings should be isolated. Such a structure would maximise the coordination number of the metal ion and simultaneously maximise the total metal-cyclopentadienyl ring overlap. Further, the ligand repulsion by the cyclopentadienyl electron clouds may lead to unfavourably long metal—oxygen bonds, i.e., the structure is unreasonable on steric grounds.

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Experimental

Materials and Methods

Analytical grade chemicals (E. Merck, Baker and Alfa Inorganic) were used throughout this study. Zirconium was determined as ZrO_2, nitrogen was estimated by *Kjeldahl*'s method and sulphur as barium sulphate[19]. Conductance measurements were made on a Systronic Digital Direct Reading Conductivity Meter Type 304. Electronic spectra of the complexes were run on a Perkin-Elmer 4000 A° instrument. Solid state IR spectra were recorded in KBr pellets in the 4000–200 cm^{-1} region on a Perkin-Elmer 621 grating spectrophotometer. ^1H-NMR spectra were recorded at a sweep width of 900 Hz with a Perkin-Elmer R-32 spectrometer. Chemical shifts are expressed relative to an internal reference of *TMS* (1% by volume).

Preparation of the Complexes

A solution of $[Cp_2Zr(sal)]^+Cl^-$ was obtained by stirring a mixture of Cp_2ZrCl_2 (0.01 mol) and a slight excess (0.012 mol) of salicylaldehyde in distilled water (ca. 50 ml) for 2–3 h. Any resulting precipitate was removed by filtration. The filtrate was warmed slightly and then added dropwise with continuous stirring to an equimolar quantity of hot aqueous solution of appropriate potassium xanthate or sodium dithiocarbamate. The precipitates so obtained were digested on a water bath at 60–70° for 15–20 minutes and then allowed to stand for ~ 2 h. They were filtered, washed with distilled water and dried under vacuum over P_4O_{10}. The precipitates were recrystallized from dichloromethane solution by adding an excess of petroleum ether (60–80 °C).

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