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Xanthate Anions in Salts of Biscyclopentadienylzirconium(IV) Chelates

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A series of $[Cp_2ZrL]^+[ROCS_2]^-$ complexes where L is the conjugate base of acetylacetone, benzoylacetone or 8-hydroxyquinoline and $R = Me$, Et or $i\text{-}Pr$ have been synthesised in aqueous medium by the reaction of $[Cp_2ZrL]^+Cl^-$ with $ROCS_2{}^-K^+$. Various physico-chemical studies carried out for these complexes indicate that all the complexes are 1:1 electrolytes in which the ligand L is bidentate, consequently there is a tetrahedral coordination about the zirconium atom.

(Keywords: Acetylacetone; Benzoylacetone; 8-Hydroxyquinoline; Xanthates)

Xanthat-Anionen in Salzen von Biscyclopentadienylzirkonium(IV)-Chelaten

Es wurde eine Reihe von Komplexen des Typs $[Cp_2ZrL]^+[ROCS_2]^-$ mit L = konjugierte Base von Acetylaceton, Benzoylaceton oder 8-Hydroxychinolin und $R = Me$, Et oder $i\text{-}Pr$ in wäßrigem Medium über die Reaktion von $[Cp_2ZrL]^+Cl^-$ mit $ROCS_2{}^-K^+$ dargestellt. Mittels physikalisch-chemischer Untersuchungen wurde festgestellt, daß diese Komplexe als 1:1-Elektrolyte mit einem zweizähnigen Liganden L vorliegen; demzufolge findet um das Zirkonium-ion eine tetrahedrale Koordination statt.

Introduction

Doyle and *Tobias*[1] pointed out that coordination of four oxygen atoms by strong covalent bonds to a Cp_2M^{2+} (M = Ti or V) moiety leads to weakening of the M-C_5H_5 bond. In an earlier communication[2] we have studied the reaction of Cp_2MCl_2 (M = Ti or Zr) with 8-hydroxyquinoline and observed that coordination of two nitrogen and two oxygen atoms to the Cp_2M^{2+} moiety would lead to similar weakening of metal ring bond. Therefore it is not possible to isolate the bis chelate complexes of the type Cp_2ML_2 where L is the conjugate base of β-diketone or 8-hydroxyquinoline. However the complex

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$[Cp_2ML]^+Cl^-$ in which only one bidentate ligand is chelating is readily obtained in solution by the reaction of Cp_2MCl_2 with HL in water. The complex $[Cp_2ML]^+Cl^-$ was found to react with a large number of halogeno, complex halogeno and dithiocarbamate anions (X^-) to give the ionic chelates of the type $[Cp_2ML]^+X^-$.

In this communication we reports an extension of these studies to the xanthate derivatives of $[Cp_2ZrL]^+Cl^-$ where L is the conjugate base of acetylacetone, benzoylacetone or 8-hydroxyquinoline. With the aim that the behaviour of free xanthate anion would provide additional information on the nature of bonding. We undertook the syntheses of a number of $[Cp_2ZrL]^+[ROCS_2]^-$ ($R = Me$, Et or i-Pr) complexes. These compounds possess a low solvation energy which is evident by the ease of their preparation.

Results and Discussion

The chemical reactions involved in the preparation of $[Cp_2ZrL]^+[ROCS_2]^-$ ($R = Me$, Et or i-Pr) complexes may be represented according to following equations:

$$Cp_2ZrCl_2 + H_2O \rightarrow Cp_2ZrOH^+ + HCl$$

$$Cp_2ZrOH^+ + Cl^- + HL \xrightarrow{\text{Water}} [Cp_2ZrL]^+Cl^- + H_2O$$

$$[Cp_2ZrL]^+Cl^- + ROCS_2^-K^+ \xrightarrow{\text{Water}} [Cp_2ZrL]^+[ROCS_2]^- + KCl$$

(where L is the conjugate base of acetylacetone, benzoylacetone or 8-hydroxyquinoline and $R = Me$, Et or i-Pr).

Table 1 lists the analytical data and physical characteristics of the complexes. The complex are quite stable in solid state and in solution. They are moderately soluble in dichloromethane, chloroform, carbontetrachloride and nitrobenzene. All the complexes are thermally stable but decompose slowly at higher temperature without melting. Conductivity measurements reveal that the chelates are 1:1 electrolytes in nitrobenzene.

The assignments of IR bands have been made on the basis of published work. The infrared spectra of all the compounds show the usual peaks for the C_5H_5 group[3] viz. C—H stretching frequency at $\sim 3100\,cm^{-1}$, the perpendicular hydrogen wagging mode at $\sim 820\,cm^{-1}$, the parallel hydrogen wagging vibration at $\sim 1030\,cm^{-1}$. The band owing to the C—C stretching mode ring breathing mode of π-bond occur at ~ 1430 and $\sim 1170\,cm^{-1}$ respectively. Apart from this, an additional band near $440\,cm^{-1}$ can be assigned to Zr-C_5H_5 vibrations[4].

Table 1. *Analytical data (calculated values in parentheses) and physical characteristics*

Compound	Yield (%)	Colour	Dec. temp. (°C)	Elemental analysis % C	H	Zr	S	N
$[Cp_2\mathrm{Zr}acac]^{+}[Me\mathrm{OCS_2}]^{-}$	72	greenish white	> 250	44.80 (44.84)	4.70 (4.67)	21.28 (21.30)	14.90 (14.95)	
$[Cp_2\mathrm{Zr}acac]^{+}[Et\mathrm{OCS_2}{}^{-}]^{-}$	68	greenish white	> 250	46.20 (46.13)	5.00 (4.97)	20.68 (20.63)	14.42 (14.47)	
$[Cp_2\mathrm{Zr}acac]^{+}[i\text{-}Pr\mathrm{OCS_2}]^{-}$	70	light green	210-214	47.38 (47.35)	5.30 (5.26)	20.04 (19.99)	14.08 (14.03)	
$[Cp_2\mathrm{Zr}bzac]^{+}[Me\mathrm{OCS_2}]^{-}$	58	green	138-140	51.38 (51.41)	4.51 (4.49)	18.68 (18.61)	13.00 (13.06)	
$[Cp_2\mathrm{Zr}bzac]^{+}[Et\mathrm{OCS_2}]^{-}$	54	green	140-142	52.38 (52.36)	4.78 (4.76)	18.00 (18.09)	12.72 (12.69)	
$[Cp_2\mathrm{Zr}bzac]^{+}[i\text{-}Pr\mathrm{OCS_2}]^{-}$	60	green	132-134	53.29 (53.26)	5.00 (5.02)	17.52 (17.60)	12.19 (12.35)	
$[Cp_2\mathrm{Zr}ox]^{+}[Me\mathrm{OCS_2}]^{-}$	78	dark green	> 250	50.90 (50.82)	4.26 (4.24)	19.28 (19.32)	13.39 (13.55)	3.00 (2.96)
$[Cp_2\mathrm{Zr}ox]^{+}[Et\mathrm{OCS_2}]^{-}$	76	green	227-228	51.86 (51.83)	4.70 (4.66)	18.68 (18.76)	13.08 (13.16)	2.91 (2.88)
$[Cp_2\mathrm{Zr}ox]^{+}[i\text{-}Pr\mathrm{OCS_2}]^{-}$	80	green	210	52.80 (52.78)	4.84 (4.80)	18.10 (18.24)	12.84 (12.79)	2.78 (2.80)

The band appearing near 1 560 cm^{-1}, 1 520 cm^{-1} and 470 cm^{-1} in the $[Cp_2Zracac]^+[ROCS_2]^-$ and $[Cp_2Zrbzac]^+[ROCS_2]^-$ complexes may be assigned to ν (C⋯O), ν (C⋯C) and ν(Zr—O) vibrations[5]. The C⋯N bond in the 8-hydroxy-quinolinato group in $[Cp_2Zrox]^+[ROCS_2]^-$ chelates shows an intense absorption around 1 320 cm^{-1}. The free 8-hydroxy-quinoline shows this absorption in the 1 450-1 500 cm^{-1} range. The occurrence of the C⋯N stretching frequency at a lower energy in the 8-hydroxyquinolinato complexes indicate that 8-hydroxyquinoline is chelating[6]. Apart from this the bands occurring around 750, 1 100, 530 and 505 cm^{-1} may be assigned to in-plane ring deformation, C—O stretching ν(Zr—O) and ν(C—O) in-plane bending frequencies[7,8]. Besides these the bands occurring consistantly near 1 240 cm^{-1} and 1 020 cm^{-1} in all the complexes under investigation indicate the presence of a free $ROCS_2^-$ group[9].

The proton NMR spectra of $[Cp_2ZrL]^+[ROCS_2]^-$ chelates is represented in Table 2. The resonance signal due to the cyclopentadienyl groups is observed as a singlet near δ 6.60 ppm. The existence of a single sharp C_5H_5 resonance is attributed to rapid rotation of the ring about the metal ring axis.

The γ-protons (—CH=) resonance of the acetylacetone and benzoylacetonate group in the chelate occur at lower field (6.1-6.0 ppm). This is probably due (at least in part) to the net positive charge on the complex ion $[Cp_2ZrL]^+$. The δ values of the methyl protons (2.5 ppm) in the acetylacetonato and benzoylacetonato group as well as the phenyl ring protons (7.2-8.1 ppm) of the benzoylacetonato moiety in the complexes are also lower than the values reported for other acetylacetonato and benzoylacetonato complexes. It may also be due to the cationic charge on the complex ion[10].

The ^1H NMR spectra of 8-hydroxyquinolinato chelates show that the protons at C_2 absorb at a lower field (9.05, q, $J = 4.0$ Hz, 1,8 Hz) then observed for free 8-hydroxy-quinoline (8.78). This supports the conclusion that the 8-hydroxyquinolinato ligand is chelating.

The resonance signals of the alkyl groups of the alkylxanthate moiety occur at almost the same frequencies as for the free alkylxanthate ligands.

Both the IR and ^1H NMR studies carried out for the present complexes indicate that the ligand L is chelating and the Cp_2Zr^{2+} moiety possess a wadge like sandwich structure with essentially tetrahedral coordination about the metal atom similar to that of dichlorides[11]. Typical vibrational frequencies assigned to the xanthate moiety in all the chelates fully support the view that these anions are free anions.

Table 2. ^{1}H NMR *data (δ scale ppm)*

Compound	C_5H_5–	acac/bzac/ox moiety				Xanthate moiety		
		—CH=	CH_3–	C_6H_5	C_2H oxinate	—CH	—CH_2	CH_3
$[Cp_2\mathrm{Zr}acac]^+[Me\mathrm{OCS}_2]^-$	6.60 s	6.02 s	2.50 s	—	—	—	—	3.00 s
$[Cp_2\mathrm{Zr}acac]^+[Et\mathrm{OCS}_2]^-$	6.62 s	6.04 s	2.48 s	—	—	—	3.18 q $J = 7.0$ Hz	1.00 t $J = 7.0$ Hz
$[Cp_2\mathrm{Zr}acac]^+[i\text{-}Pr\mathrm{OCS}_2]^-$	6.58 s	6.04 s	2.52 s	—	—	3.98 sep $J = 7.0$ Hz	—	1.40 d $J = 7.0$ Hz
$[Cp_2\mathrm{Zr}bzac]^+[Me\mathrm{OCS}_2]^-$	6.60 s	6.06 s	2.50 s	7.20–8.10 m	—	—	—	2.98 s
$[Cp_2\mathrm{Zr}bzac]^+[Et\mathrm{OCS}_2]^-$	6.62 s	6.01 s	2.50 s	7.18–8.08 m	—	—	3.20 q $J = 6.8$ Hz	1.02 t $J = 7.0$ Hz
$[Cp_2\mathrm{Zr}bzac]^+[i\text{-}Pr\mathrm{OCS}_2]^-$	6.56 s	6.08 s	2.48 s	7.20–8.20 m	—	4.02 sep $J = 6.8$ Hz	—	1.42 d $J = 7.0$ Hz
$[Cp\mathrm{Zr}ox]^+[Me\mathrm{OCS}_2]^-$	6.60 s	—	—	—	9.02 q $J = 4.0$ Hz, 1.8 Hz	—	—	2.98 s
$[Cp_2\mathrm{Zr}ox]^+[Et\mathrm{OCS}_2]^-$	6.62 s	—	—	—	9.04 q $J = 4.0$ Hz, 2.0 Hz	—	3.20 q $J = 6.6$ Hz	1.40 d $J = 7.0$ Hz
$[Cp_2\mathrm{Zr}ox]^+[i\text{-}Pr\mathrm{OCS}_2]^-$	6.58 s	—	—	—	9.02 q $J = 4.0$ Hz, 1.8 Hz	4.02 sep $J = 7.0$ Hz	—	1.02 t $J = 6.8$ Hz

s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet.

Experimental

All the chemicals and reagents used were of analytical grade. Biscyclopentadienylzirconium(IV) dichloride was obtained from Alfa Inorganic Ventron U.S.A. and used as such without further purification. Nitrobenzene for conductance measurement was purified by the method as described by *Fay* et al.[12]. Potassium salt of alkylxanthates were prepared by the method as described in thr literature[9].

Microanalyses of carbon and hydrogen contents were carried out in our departmental Microanalytical Laboratory. Zirconium, nitrogen and sulphur was estimated by the standard methods as described by *Vogel*[13].

Conductance measurements were made in nitrobenzene at 28 ± 0.05 °C using a Elico Conductivity Bridge Model CM 82. Solid state infrared spectra were recorded with a Perkin-Elmer 621 grating spectrophotometer in KBr pellets in the range 4 000–200 cm^{-1}. Magnetic measurements were performed by *Gouy*'s method using $Hg[Co(SCN)_4]$ as a calibrant. The electronic spectra of the complexes were taken on a Perkin-Elmer 4 000 Å instrument in the range 400–750 nm. Proton NMR spectra were recorded in $CDCl_3$ on a Perkin-Elmer R-32 spectrophotometer at a sweep width of 900 Hz. The magnetic field was calibrated with a standard sample of $CHCl_3$ and *TMS* (1% by volume).

2,4-Pentadionatobiscyclopentadienylzirconium(IV) O-alkylxanthates

To a concentrated aqueous solution of Cp_2ZrCl_2 (2.5 g in 60 ml water) acetylacetone (1.0 ml) was added and the mixture was stirred for 2 h. Any resulting precipitate was removed by filtration. The filtrate was then added slowly with continous stirring to an equimolar quantity of concentrated hot aqueous solution of the appropriate potassium xanthate. The precipitate obtained was digested over water bath for 2 h at 60–70 °C and then allowed to stand overnight. It was filtered, washed with water and then with diethylether, finally dried under vacuum. In order to remove any acetylacetone impurity the precipitate was dissolved in dichloromethane and reprecipitated by adding petroleumether (60–80 °C).

1-Phenyl-1,3-butadionatobiscyclopentadienylzirconium(IV) O-alkylxanthates

A solution of $[Cp_2Zr(bzac)]^+ Cl^-$ was made by stirring for 3 h a suspension of Cp_2ZrCl_2 (2 g in 60 ml of water) containing an excess of benzoylacetone (2 g) followed by filtration. This solution was then added slowly to a hot aqueous solution of potassium xanthates and the mixture was allowed to react for 1 h with stirring. Addition of KCl aids the precipitation. The resulting precipitate was digested over a water bath for 2 h at 60–70 °C and then allowed to stand overnight. It was filtered and dried.

8-Hydroxyquinolinatobiscyclopentadienylzirconium(IV) O-alkylxanthates

An aqueous solution of $[Cp_2Zrox]^+ Cl^-$ was obtained by stirring a solution containing 2 g of Cp_2ZrCl_2 and 1.02 g of 8-hydroxyquinoline in 60 ml of water for 2 h. It was filtered and the filtrate was then added dropwise to an concentrated solution of potassium xanthate until no more precipitate was formed. The resulting precipitate was collected on a glass frit washed subsequently with water and diethylether and dried under vacuum.

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References

[1] *Doyle G.*, *Tobias R. S.*, Inorg. Chem. **6**, 1111 (1967); **7**, 2084 (1968).
[2] *Sharma A. K.*, *Sodhi G. S.*, *Kaushik N. K.*, Bull. Soc. chim. France, in press.
[3] *Fritz H. P.*, Advances in Organometallic Chemistry **1**, 279. New York: Academic Press. 1964.
[4] *Coutts R. S. P.*, *Wailes P. C.*, J. Organometal. Chem. **84**, 47 (1975).
[5] *Salzmann J. J.*, Helv. Chim. Acta **51**, 601 (1968).
[6] *Sodhi G. S.*, *Kaushik N. K.*, Synth. React. Inorg. Met.-Org. Chem. **11**, 641 (1981).
[7] *Tackett J. E.*, *Sawyer D. T.*, Inorg. Chem. **3**, 692 (1964).
[8] *Magee R. J.*, *Gorgen L.*, Talanta **10**, 851 (1963).
[9] *Ramachandra Rao, S.*, Xanthates and Related Compounds. New York: Marcel Dekker. 1971.
[10] *Fackler J. P., jr.*, Prog. Inorg. Chem. **7**, 361 (1966).
[11] *Alekseev, N. V.*, *Ronova I. A.*, Zh. Strukt. Khim. **7**, 103 (1966).
[12] *Fay R. C.*, *Lowry R. N.*, Inorg. Chem. **6**, 1512 (1967).
[13] *Vogel A. I.*, A Text Book of Quantitative Inorganic Analysis, 3rd ed. London: Longmans. 1964.