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Preparation and Characterization of Some Stereochemically Rigid Seven Coordinate Monocyclopentadienyl Zirconium(IV) Tris-alkyl Xanthate Complexes

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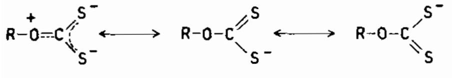
Zirconiun(IV) alkyl xanthates of the type CpZr-(S₂COR)₃ where R = Me, Et have been prepared by the reaction of dicyclopentadienyl zirconium(IV) dichloride with sodium alkyl xanthates in aqueous medium. Molecular weight, conductance and infrared studies point out that these complexes are monomeric non-electrolytes in which all of the xanthate ligands are bidentate. Therefore, a co-ordination number '7' may be assigned to zirconium(IV) ion in these compounds. Proton nmr spectra of these complexes in carbon disulfide or deuterated chloroform indicate that metal centered rearrangement is slow on the nmr time-scale at ambient temperature (30 °C).

Introduction

The xanthate ligands are very similar to the dithiocarbamate ligands which have been known to stabilize the higher coordination states of metals (the authors have already reported the preparation and characterization of some stereochemically rigid seven coordinate complexes of type $CpZr(S_2CNR_2)_3$ where R = Me, Et in another Journal [23]). Both the above ligands are particularly well suited to stabilize the higher coordination states due to their low charge and their relatively small bites (~3 Å).

The xanthate ion can be represented in the following three forms:



1a 1b 1c

Figure 1. Resonating structures for xanthate ion.

Although the literature of metal xanthates is quite extensive, there are very few such complexes and still fewer seven coordinate complexes of the early transition metals. Coutts *et al.* [1] have reported the preparation of xanthates of Ti(III) by reacting stoichiometric quantities of bis(cyclopentadienyl)Ti(III) chloride with sodium salts of alkyl xanthates. In these compounds xanthate groups are supposed to behave as bidentate ligands similar to the corresponding dithiocarbamates [2–4]. Dina Nath *et al.* [5] have reported the preparation of xanthates of Ti(IV) of the type $Cp_2Ti(ROCS_2)_2$ where R = Me, Et, n-Pr, N-Bu or n-Amyl. However, there is no mention in the literature about the stereochemically rigid seven coordinate xanthate complexes. The present communication deals with the preparation and characterization of the seven coordinate cyclopentadienyl zirconium(IV) alkyl xanthate complexes of the type $CpZr(S_2COR)_3$ where R = Me, Et. These complexes are closely related to the seven coordinate dithiocarbamate complexes $Ti(S_2CNR_2)_3Cl$ [3, 6]; $VO[S_2CN(C_2H_5)_2]_3$ [7], $NbO[S_2CN(C_2H_5)_2]_3$ [7], $Mo(NO)[S_2CN(n\text{-}C_4H_9)_2]_3$ [8] and $CpZr(S_2CNR_2)_3$ (R = Me, Et [14, 23]. The reported seven coordinate compounds of zirconium(IV) include $M(acac)_3Cl$ (M = Zr or Hf; acac = $CH_3COCH_2COCH_3$) [9] and $(\pi\text{-}C_5H_5)Zr(CF_3COCH_2COCF_3)_3$ [10]. All the above seven coordinate compounds have been shown to possess pentagonal bipyramidal structures in which the monodentate ligand occupies an axial position. A similar structure for $(\pi\text{-}C_5H_5)Zr(S_2COR)_3$ (R = Me, Et) is suggested by the proton nmr spectrum which exhibits when R = Me two methyl resonances of relative intensity 2:1 and when R = Et two types of signals for CH_2 and CH_3 protons of relative intensity 2:1 at ambient probe temperature (30 °C).

Experimental

Reagents and General Techniques

Potassium alkyl xanthates were prepared by the literature method [11].

Dicyclopentadienyl zirconium(IV) dichloride was prepared by reaction of zirconium tetrachloride with the sodium salt of cyclopentadiene in tetrahydrofuran [12].

Nitrobenzene was purified for conductance measurements by the method described by Fay *et al.* [13].

TABLE I. Proton Chemical Shift (in Hz) and Coupling Constant Data (in Hz) at 30 °C.

Compound	Deuterochloroform Solution			
	π-C_5H_5	$-CH_2-$	$-CH_3$	J
$CpZr(S_2COMe)_3^e$	−374.9	–	−249.2, −245.6[a]	–
$CpZr(S_2COEt)_3^e$	−372.2	−276.2, −271.3, −268.7, −264.2[b]	−92.5, −86.0, −82.5, −76.7[c]	7.0[d]

[a] Two peaks observed (in the intensity ratio 2.05:1.0) are due to two types of methyl groups present in the compound and not to the coupling of protons on adjacent atoms. [b] Position of four most intense peaks (total number of observed peaks = 8). [c] Position of four most intense peaks (total number of observed peaks = 6). [d] Average value. [e] Me = CH_3; Et = CH_3CH_2.

TABLE IIa. Physical Characteristics (Λ in $ohm^{-1}\ cm^2\ mol^{-1}$).

Compound	Mol. Wt		Conductance		M.P. (°C)
	Found	Calcd	Molarity × 10^3		
$(C_5H_5)Zr(S_2COMe)_3$	428	477.2	0.5	0.15	116–121(d)
$(C_5H_5)Zr(S_2COEt)_3$	490	519.2	0.5	0.23	115–120(d)

TABLE IIb. Yields and Analysis.

Compound	Method of Preparation	Yield (%)	Found %			Calculated %		
			C	H	Zr	C	H	Zr
$(C_5H_5)Zr(S_2COMe)_3$	Aqueous	30	27.0	3.2	18.8	27.7	2.9	19.1
$(C_5H_5)Zr(S_2COEt)_3$	Aqueous	25	32.2	3.7	17.0	32.4	3.9	17.6

Preparation of Complexes

The compounds included in this communication have been prepared in aqueous medium:

$$Cp_2ZrCl_2 + 3KS_2COR \longrightarrow CpZr(S_2COR)_3 + 2KCl + KCp$$

The dicyclopentadienyl zirconium(IV) dichloride was dissolved in boiling water, filtered and cooled to room temperature. The potassium alkyl xanthate was dissolved in water and filtered. The filtrate so obtained was added dropwise to the former solution and the precipitated compound was repeatedly extracted by shaking with dichloromethane. The above process was continued until the aqueous layer did not give any more precipitate upon addition of potassium alkyl xanthate solution. The dichloromethane containing the dissolved reaction product was dried over calcium chloride. Colourless crystals of the compounds were obtained by adding petroleum ether (60–80 °C) to the above and allowing the mixture to stand overnight.

Molecular Weight and Conductance Measurements

Molecular weight was determined ebullioscopically in benzene using a Gallen Kamp (U.K.) ebulliometer.

Conductance measurements were made in nitrobenzene at 30.00 ± 0.05 °C with a Beckmann Conductivity Bridge Model No. RC-18A.

Infra-red Spectra

Infra-red spectra were recorded in solid state (KBr pellets) in the region 4000–250 cm^{-1} with a Perkin Elmer 621 grating spectrophotometer.

Nuclear Magnetic Resonance Spectra

The proton nmr spectra were recorded at ambient temperature (30 °C) at sweep width of 100–500 Hz with a Varian A-60 spectrometer. Spectra were recorded in triplicate, and the values reported in Table I are average values; chemical shifts are expressed relative to an internal reference of tetramethylsilane (1% by volume).

Results and Discussion

Table IIa and IIb summarize the important physical characteristics of the complexes. The methods used for preparation and isolation of these compounds (see Experimental) give materials of good

TABLE III. Characteristic Infra-red Bands of $CpZr(S_2COR)_3$ (R = Me, Et) Complexes.

S. No.	Peak Position (in cm^{-1})		Assignment
	Due to $CpZr(S_2COMe)_3$	Due to $CpZr(S_2COEt)_3$	
1	350 m, b	350 m, b	ν(Zr–S)
2	1050 s, b	1045 s, b	ν(C–S)
3	1165 s, b	1150 s, b	ν(C–O)
4[a] (i)	3110 m	3112 m	ν(C–H)
(ii)	1442 vs	1440 s	ν(C–C) (asymmetric ring breathing)
(iii)	1010 sh	1005 sh	ν(C–H) (in plane bending)
(iv)	818 s	808 s	ν(C–H) bending (out of plane deformation)
5 (i)	1228 s, b	1225 s, b	
(ii)	452 s	440 s	ν(C–O–C)
6	2990 w	2995 m	ν(C–H) aliphatic

[a] Infrared bands characterising π-C_5H_5 ring.

purity as judged by satisfactory elemental analysis and by proton nmr spectra of deuterated chloroform solutions (Table I). Both the compounds are new.

The two compounds are colourless and moderately soluble in carbon disulfide, dichloromethane and chloroform. Dichloromethane was used to crystallize them. The two compounds are thermally stable but decompose near their melting points. On keeping in air, they decompose slowly but their solutions are hydrolysed relatively rapidly.

Conductance measurements (Table IIa) show that both the complexes are essentially non-electrolytes in nitrobenzene.

The subject of chief interest in the preparation of these compounds is the stereochemistry. A coordination number of '7' may be assigned if all the three xanthate ligands are bidentate and the cyclopentadienyl group occupies one coordination site. Fay *et al.* [14] have described the X-ray diffraction of $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ in which, because of the relatively small size of the cyclopentadienyl group, it is considered to occupy a single axial coordination site in a pentagonal bipyramidal structure. Therefore the cyclopentadienyl group in the compounds included in this communication is assumed to occupy one coordination site. Xanthate can behave as monodentate and bidentate ligands. But as in dithiocarbamates [15–21] complexes having both monodentate and bidentate xanthate ligands are expected to exhibit additional infra-red bands not found for complexes having only bidentate ligands [15–21].

Characteristic infra-red frequencies for the $CpZr(S_2COR)_3$ complexes are presented in Table III. Assignment of structure of metal xanthates from infra-red is not always reliable. The $ROCS_2$ group has four characteristic bands near 1250, 1100, 1020 and 550 cm^{-1} which may be called xanthate bands. Each of these is a "mixed" band arising mainly from combinations of the (C=S), (C–O), (C–S) and (R–O) bands.

A normal coordinate analysis of nickel(II) ethyl xanthate by Agarwala *et al.* [22] indicates that 1250 cm^{-1} band has about 90% contribution from C–O–R– stretch and 10% from C=S stretch. The band around 1100 cm^{-1} is mainly a contribution of C–O, R–O and C=S stretching modes. The band around 1020 cm^{-1} has a single major contribution of 60% from C=S stretch. In these circumstances, infrared spectra are of little help in determining whether the xanthato ligands are mono- or bidentate. However, by analogy with the dithiocarbamates described earlier [23] in view of the known tendency of zirconium in many $CpZr^{IV}$ compounds to adopt a coordination number of seven and the C=S and C–O infrared band positions pointing to a major contribution of structure 1a [24] (see Introduction), the bidentate structure for xanthato ligands is proposed. It is expected that the bond order of $C\overset{\cdots}{-}O$ will be less than that of $C\overset{\cdots}{-}N$ in the dithiocarbamates due to the lower electron-releasing character of OR groups.

Interpretation of Nmr Spectra

In analogy with metal dithiocarbamates [3, 25–27] the expected and relative intensities of R group resonances for the $CpZr(S_2COR)_3$ (R = Me, Et) complexes are indicated in Table IV for the following two kinetic possibilities: (A) metal centered rearrangement is slow (S_2C–O bond rotation is slow or fast); (B) metal centered rearrangement is fast (S_2C–O bond rotation is slow or fast). The analysis assumes seven coordinate complexes have pentagonal bipyramidal structure and neglects for the moment the possibility of hindered rotation about O–R bonds.

TABLE IV. Predicted Number (Relative Intensity) of R Group Resonances for Various Rearrangement Possibilities.

Compound	Symmetry	(A)	(b)
$CpZr(S_2COMe)_3$	C_s–m	2(2:1)[a]	1
$CpZr(S_2COEt)_3$	C_s–m	4[b](2:1 & 2:1)[c]	2[d]

[a] Each resonance line will be observed as a singlet due to the absence of protons on adjacent carbon atoms. [b] Two resonance lines due to two different types of $-CH_2-$ protons; each signal will be observed as a quartet due to adjacent $-CH_3$ protons; another two resonance lines due to two different types of $-CH_3$ protons, each signal will be observed as a triplet due to adjacent $-CH_2-$ protons. [c] The overall integrated ratio of resonance signals of $-CH_2-$ protons to resonance lines of $-CH_3$ protons is really 2:3. [d] One resonance line due to $-CH_2-$ protons (split into a quartet) and one resonance line due to $-CH_3$ protons (split into a triplet).

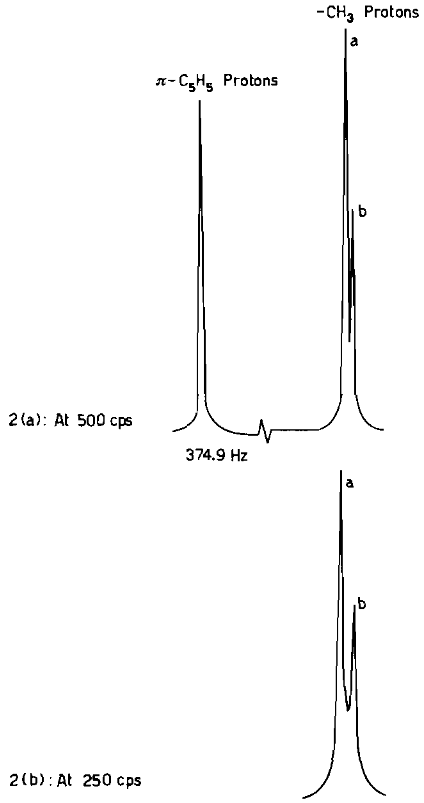


Figure 2. Proton nmr spectrum of $CpZr(S_2COCH_3)_3$. Position of the peaks (in Hz): a, −249.2; b, −245.6.

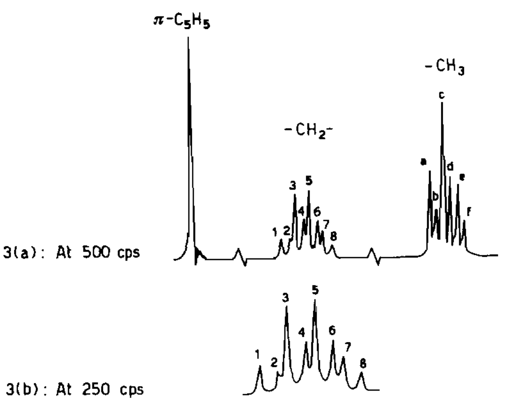


Figure 3. Proton nmr spectrum of $CpZr(S_2COC_2H_5)_3$. Position of the peaks (in Hz):

A, −372.2	1, −282.7	a, −92.5
	2, −278.5	b, −89.3
	3, −276.2	c, −86.0
	4, −271.3	d, −82.5
	5, −268.7	e, −78.7
	6, −264.2	f, −75.4
	7, −261.5	
	8, −257.1	

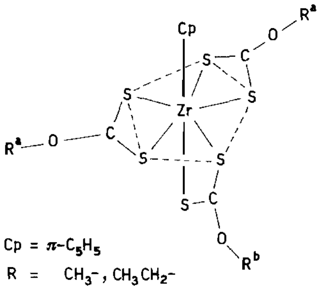


Figure 4. Pentagonal bipyramidal structure of $CpZr(S_2COR)_3$ complex.

The proton nmr spectrum for compounds (π-C_5H_5)$Zr(S_2COR)_3$ (R = Me, Et) is represented in Fig. 2 and Fig. 3 respectively. The resonance lines at −374.9 and −372.2 Hz in the methyl and ethyl compounds respectively are assigned to protons on the cyclopentadienyl ring. The remaining resonance lines in the two figures are due to the methyl and ethyl protons on the xanthate ligands in the methyl and ethyl compounds respectively.

Two distinct methyl resonances are observed (Fig. 2) due to group ^aR and ^bR (Fig. 4) with relative intensities 2:1.

Fig. 3 shows a complex pattern for $-CH_2-$ and $-CH_3$ lines of the ethyl group. In analogy with the above methyl compound the ethyl compound is expected to show two resonance lines (in the ratio as above) for $-CH_2-$ protons (each line split into a quartet due to the adjacent $-CH_3$ protons) and two resonance lines (ratio as above) for $-CH_3$ protons (each line split into triplet due to adjacent $-CH_2-$ protons). The coupling constant (J) for the ethyl compound is the average value (coupling constant differs because of overlapping of peaks). The intensities were determined by planimetric integration of three spectra. The integrated proton ratios correspond to the formula $(C_5H_5)Zr(S_2COR)_3$ (R = Me, Et) for the two complexes.

From the above discussion it must be concluded that observed methyl and $-CH_2-$ proton resonances result from non-equivalent environments for these groups in the $(\pi\text{-}C_5H_5)Zr(S_2COR)_3$ (R = Me, Et) molecule. The existence of a single sharp cyclopentadienyl resonance is attributed to rapid rotation of the ring about the metal ring axis. The resonance lines for the R groups in the two compounds conform to the possibility A in Table IV. Thus the above two seven coordinate compounds have pentagonal bipyramidal structures. The structure is bound to be slightly distorted due to the presence of a cyclopentadienyl group in the molecule.

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