

# Bis(*O*-Alkyl Dithiocarbonate)-Bis(Dicarbonyl- $\eta^5$ -cyclopentadienyliron)Tin(IV) Complexes

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Seven new complexes,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Sn}(\text{S}_2\text{COR})_2$  ( $\text{R} = \text{alkyl}$ ), have been synthesized and characterized by elemental analysis, IR and  $^1\text{H}$  NMR spectra. It has been proved that these *O*-alkyl dithiocarbonates are monobasic bidentate ligands to the tin ion. The coordination number of the central tin ion is six and we suggest an octahedral structure for these complexes.

Although there are some reports concerning the replacement of the chloride ion in dichloro-bis(dicarbonyl- $\eta^5$ -cyclopentadienyliron)tin(IV) by other ligands which are inorganic anions or some simple organic anions [1–4], the central tin atom remained four-coordinate. It is reported that some complexes with Schiff bases are five-coordinate to central tin atom [5, 6]. In this paper, we report that some organic ligands,  $\text{ROCS}_2\text{K}$  (potassium *O*-alkyl dithiocarbonates), react with dichloro-bis(dicarbonyl- $\eta^5$ -cyclopentadienyliron)tin(IV) to produce seven new complexes,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Sn}(\text{S}_2\text{COR})_2$  [ $\text{R} = \text{CH}_3$  (*I*),  $\text{C}_2\text{H}_5$  (*II*),  $\text{C}_3\text{H}_7$  (*III*), *i*- $\text{C}_4\text{H}_9$  (*IV*),  $\text{C}_6\text{H}_{13}$  (*V*),  $\text{C}_{10}\text{H}_{21}$  (*VI*), and  $\text{C}_6\text{H}_5\text{CH}_2$  (*VII*)], in which the central tin atom is six-coordinated.

## EXPERIMENTAL

All solvents were purified by the methods reported [7]. Potassium *O*-alkyl dithiocarbonates were prepared according to the literature [8, 9], recrystallized from diethyl ether, washed with petroleum ether, and checked by melting point, elemental analysis, and  $^1\text{H}$  NMR measurements. Dichloro-bis(dicarbonyl- $\eta^5$ -cyclopentadienyliron)tin(IV) was synthesized by the method of *Bonati* and *Wilkinson* [10], and its purity was determined by elemental analysis.

Microanalyses were carried out in the Microanalytical Laboratory of Lanzhou University by an elemental analyzer, model Elemental Vario El (Germany). IR spectra were recorded in the region of 200–4000  $\text{cm}^{-1}$  with a Nicolet-179SX spectrophotometer using KBr discs.  $^1\text{H}$  NMR spectra were obtained on a DMX-60 or FT-80A spectrometer using  $\text{CDCl}_3$  as solvent and TMS as the internal standard. Melting points were determined using an RY-1 type apparatus, but the temperature was not calibrated.

## Synthesis of the Complexes *I*–*VII*

All reactions were performed under argon atmosphere. The solution of the ligand (2.1 mmol) in anhydrous tetrahydrofuran (20  $\text{cm}^3$ ) was added dropwise with stirring to  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$  (0.54 g, 1 mmol) in anhydrous benzene (20  $\text{cm}^3$ ). KCl precipitated immediately and the colour of the solution turned into reddish orange. The reaction mixture was stirred at room temperature for 3 to 24 h and filtered. The filtrate was concentrated to 10  $\text{cm}^3$ , and then 10  $\text{cm}^3$  light petroleum ether was added. The crystalline product was collected on a Büchner funnel and recrystallized from anhydrous benzene. Yield, elemental analyses, and physical properties of these complexes are listed in Table 1.

## RESULTS AND DISCUSSION

The data in Table 1 indicate that the ligands coordinate to the central tin ion only in the stoichiometry  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SnCl}_2 + 2\text{ROCS}_2\text{K}$ , giving only one product,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Sn}(\text{S}_2\text{COR})_2$ . All complexes are excellent crystals stable to atmosphere, but photosensitive to light. They are soluble in common organic solvents such as benzene, dichloromethane, chloroform, acetone, and tetrahydrofuran, but insoluble in hexane and petroleum ether.

The  $^1\text{H}$  NMR spectral data of these complexes are shown in Table 2. It can be seen that the chemical shifts of the cyclopentadienyl protons of these complexes are observed at about  $\delta = 4.9$  as a singlet (10H). The signals for the aromatic protons appeared at about  $\delta = 7.3$  (singlet) and those of the benzyl protons at about  $\delta = 5.5$  (singlet). Chemical shifts of the alkoxy protons are observed at about  $\delta = 4.0$ – $4.5$ . The mole ratio of dithiocarbonate and  $[\eta^5$ -

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**Table 1.** Analytical Data and Some Physical Properties of the Complexes

Compound	Formula	Colour	Yield	M.p.	$w_i(\text{found})/\%$ ( $w_i(\text{calc.})/\%$ )	
			%	°C	C	H
<i>I</i>	C <sub>18</sub> H <sub>16</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Orange	98	106—108	31.45 (31.47)	2.33 (2.35)
<i>II</i>	C <sub>20</sub> H <sub>20</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Orange	95	120	33.53 (33.60)	2.79 (2.82)
<i>III</i>	C <sub>22</sub> H <sub>24</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Red	90	90	35.56 (35.56)	3.21 (3.26)
<i>IV</i>	C <sub>24</sub> H <sub>28</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Red	82	89	37.19 (37.38)	3.57 (3.66)
<i>V</i>	C <sub>28</sub> H <sub>36</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Dark-red	88	58—60	40.75 (40.65)	4.39 (4.39)
<i>VI</i>	C <sub>36</sub> H <sub>52</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Dark-red	83	46—48	45.69 (46.03)	5.55 (5.58)
<i>VII</i>	C <sub>30</sub> H <sub>24</sub> O <sub>6</sub> S <sub>4</sub> Fe <sub>2</sub> Sn	Dark-red	69	93	43.51 (42.94)	2.90 (2.88)

**Table 2.** <sup>1</sup>H NMR Chemical Shifts of Complexes

Compound	Complex	$\delta^a$					
		C <sub>6</sub> H <sub>5</sub>	C <sub>5</sub> H <sub>5</sub>	ArCH <sub>2</sub>	C <sup>1</sup> H <sub>3</sub>	C <sup>2</sup> H <sub>2</sub>	C <sup>3</sup> H <sub>2</sub>
<i>I</i>	(CH <sub>3</sub> OCS <sub>2</sub> ) <sub>2</sub> SnA <sub>2</sub>		4.9 (s, 10H)		4.0 (s, 6H)		
<i>II</i>	(CH <sub>3</sub> CH <sub>2</sub> OCS <sub>2</sub> ) <sub>2</sub> SnA <sub>2</sub>		4.9 (s, 10H)		1.4 (t, 6H)	4.5 (q, 4H)	
<i>III</i>	( <i>n</i> -C <sub>3</sub> H <sub>7</sub> OCS <sub>2</sub> ) <sub>2</sub> SnA <sub>2</sub>		4.9 (s, 10H)		1.0 (t, 6H)	1.8 (m, 4H)	4.4 (t, 4H)
<i>IV</i>	( <i>i</i> -C <sub>4</sub> H <sub>9</sub> OCS <sub>2</sub> ) <sub>2</sub> SnA <sub>2</sub>		4.9 (s, 10H)		1.0 (d, 12H)	2.1 (m, 2H)	4.3 (d, 4H)
<i>V</i>	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OCS <sub>2</sub> ] <sub>2</sub> SnA <sub>2</sub>		4.9 (s, 10H)		1.0 (t, 6H)	1.0—2.0 (m, 16H)	4.4 (t, 4H)
<i>VI</i>	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> OCS <sub>2</sub> ] <sub>2</sub> SnA <sub>2</sub>		4.9 (s, 10H)		0.9 (t, 6H)	1.0—2.0 (m, 32H)	4.5 (t, 4H)
<i>VII</i>	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCS <sub>2</sub> ) <sub>2</sub> SnA <sub>2</sub>	7.3 (s, 10H)	4.9 (s, 10H)	5.5 (s, 4H)			

a) s - singlet, d - doublet, t - triplet, q - quadruplet, m - multiplet, Ar - C<sub>6</sub>H<sub>5</sub>, A -  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>, [C<sup>1</sup>H<sub>3</sub>(C<sup>2</sup>H<sub>2</sub>)<sub>n</sub>C<sup>3</sup>H<sub>2</sub>OCS<sub>2</sub>]<sub>2</sub>SnA<sub>2</sub> (*n* = 0—8).

**Table 3.** Important IR Spectral Data<sup>a</sup> of Complexes,  $\tilde{\nu}/\text{cm}^{-1}$ 

Complex	$\nu(\text{cp})$	$\nu(\text{CO})$	$\nu(\text{C}\cdots\text{S})$	$\nu(\text{C}-\text{S})$	$\nu(\text{C}=\text{S})$	$\nu(\text{Sn}-\text{S})$
<i>I</i>	3096 m, 1435 m 850 s	2009 vs, 1988 vs 1955 vs	1118 s	627 s		330 m
<i>II</i>	3105 m, 1412 m 847 s	2010 s, 1983 vs 1961 vs, 1931 vs	1113 s	628 s	1288 w	328 m
<i>III</i>	3100 m, 1412 m 843 s	2017 vs, 1984 vs 1963 vs, 1939 vs	1114 s	629 s	1259 m	335 m
<i>IV</i>	3090 m, 1425 m 846 s	2014 vs, 1985 vs 1960 s, 1944 vs	1140 s	627 s	1249 w	320 m
<i>V</i>	3100 m, 1459 m 844 s	2017 vs, 1993 vs 1972 vs	1139 s	627 s	1230 m	324 m
<i>VI</i>	3098 m, 1463 m 843 s	2019 vs, 1994 vs 1996 vs, 1949 vs	1132 s	628 s		330 m
<i>VII</i>	3107 m, 1452 m 842 s	2013 vs, 1986 vs 1963 vs	1162 s	626 s	1219 m	336 m

a) vs - very strong; b) s - strong; m - medium; w - weak; cp - C<sub>5</sub>H<sub>5</sub>.

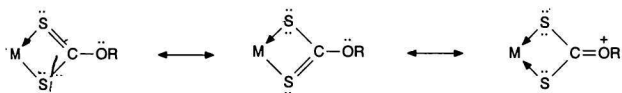
C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sub>2</sub>SnCl<sub>2</sub> is in all cases 2 1.

The important IR frequencies of the complexes are given in Table 3. The characteristic absorption bands of the cyclopentadienyl ring appeared at  $\tilde{\nu}$  = 3110 cm<sup>-1</sup> ( $\nu(\text{C}-\text{H})$  stretching), 1470 cm<sup>-1</sup> ( $\nu(\text{C}-\text{C})$  stretching of  $\pi$ -bond), and 850 cm<sup>-1</sup> ( $\delta(\text{C}-\text{H})$  vibration). The absorption band at 510 cm<sup>-1</sup> is due to the  $\nu(\text{Fe}-\text{C}_5\text{H}_5)$  vibration. Three or four strong bands at about 1930—2010 cm<sup>-1</sup> are attributed to  $\nu(\text{CO})$  vibration [4, 11, 12].

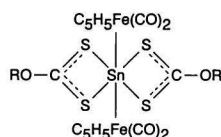
Dithiocarbonates are known to have four characteristic bands in the IR region. The bands oc-

curing at 1260 cm<sup>-1</sup>, 1120 cm<sup>-1</sup>, 1040 cm<sup>-1</sup>, and 630 cm<sup>-1</sup> have been assigned to  $\nu(\text{C}=\text{S})$ ,  $\nu(\text{C}\cdots\text{S})$ ,  $\nu(\text{C}-\text{O})$ , and  $\nu(\text{C}-\text{S})$  vibrations, respectively, which are highly coupled [13]. According to the IR spectral data described in literature [15], EtOCS<sub>2</sub>K (or Na), *n*-BuOCS<sub>2</sub>K, and *i*-C<sub>3</sub>H<sub>7</sub>OCS<sub>2</sub>Na show characteristic absorption bands due to  $\nu(\text{C}=\text{S})$  at about 1260 cm<sup>-1</sup> and  $\nu(\text{C}-\text{S})$  at 650—670 cm<sup>-1</sup>. The band at  $\tilde{\nu}$  = 287 cm, arising from  $\nu(\text{Sn}-\text{Cl})$  [14] in [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sub>2</sub>SnCl<sub>2</sub>, was not present in the spectra of complexes, but there appeared a new band ( $\tilde{\nu}(\nu(\text{Sn}-\text{S})) = 330 \text{ cm}^{-1}$ ). The bands of  $\nu(\text{C}-\text{S})$

are shifted towards lower frequency by about 20–40  $\text{cm}^{-1}$  when compared with standard IR spectra [15]. The band of  $\nu(\text{C}=\text{S})$  became weaker or totally disappeared, and the band of  $\nu(\text{C}\cdots\text{S})$  became stronger. The difference in intensity of  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}-\text{S})$  in the spectra of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Sn}(\text{S}_2\text{COR})_2$  and  $\text{KS}_2\text{COR}$  is due to their joint form. It is shown that  $-\text{C}(\text{C}=\text{S})\text{S}-$  in  $\text{ROCS}_2$  has changed in  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Sn}(\text{S}_2\text{COR})_2$  to conjugate bond of the allylic  $\text{S}\cdots\text{C}\cdots\text{S}$  type rather than to apparent  $\text{C}=\text{S}$  double bond and  $\text{C}-\text{S}$  single bond. The X-ray analysis data of similar coordination complexes had also shown that both  $\text{C}\cdots\text{S}$  bond length equal to 1.675–1.689 Å [16] rather than to 1.56 Å of  $\text{C}=\text{S}(\text{sp}-\text{S})$  and 1.75 Å of  $\text{C}-\text{S}(\text{sp}^2-\text{S})$  [17]. Cotton and McCleverty [18] had synthesized 11 complexes the spectra of which revealed the absorption bands of  $\nu(\text{C}=\text{S})$  at about 1200–1280  $\text{cm}^{-1}$ . The intensities of  $\nu(\text{C}=\text{S})$  are in all cases strong. In fact, two sulfur atoms in ligand are jointed to the central tin atom, therefore the above-mentioned vibrations were little distinct. The ligand is bidentate [16, 17]. X-Ray crystallographic studies are in good agreement with our opinion [17]. The *O*-alkyl dithiocarbonate existed in the following resonance structure



On the basis of the obtained results we suggest the following structure for the studied complexes



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