

through boron)]. For a methylcyclopentadienide ion, more isomers may result. Studies have shown that an equilibrium distribution of methylcyclopentadiene contains 95–99% of the 1- and 2-substituted isomers.^{6,7} However, even with boron attachment limited to C-1 or C-2, there are four possible isomers in $\text{Cp}_3\text{B}_3\text{N}_3\text{Me}_3$ resulting from the three different boron atoms in each molecule. For $(\text{MeCp})_3\text{B}_3\text{N}_3\text{Me}_3$, there are 56 such isomeric possibilities. Since it has been shown that a base such as NaC_5H_5 dramatically accelerates rearrangement in substituted cyclopentadienes,⁸ our reaction conditions should have yielded an equilibrium mixture of products. The spectroscopic data obtained tend to confirm this.

Through chemical shift comparisons with the literature,⁹ absorption intensities, and indor data, the nmr spectrum of $\text{Cp}_3\text{B}_3\text{N}_3\text{Me}_3$ has been assigned as follows: the downfield multiplet (3H), vinyl protons; the absorption at *ca.* δ 3.06 (2H), methylene protons; the absorption at δ 2.69 (3H), methyl protons.¹⁰ Broad-band irradiation of the vinyl multiplet led to simplification of the methylene region into two lorentzian singlets at δ 3.11 and 3.07 with relative intensities of *ca.* 58:42, respectively (shapes and area percentages obtained using a Du Pont 310 curve resolver). This result is indicative of two different groups of methylene hydrogens corresponding to 58% borazine substitution at C-2 and 42% substitution at C-1. The peak positions are in agreement with relative positions of the methylene absorptions reported for 1-methyl- and 2-methylcyclopentadiene⁹ and the peak intensities compare well with the equilibrium distribution of cyclopentadiene isomers generally observed.^{6,7} Reverse decoupling led to changes in the vinyl multiplet, but no simple interpretations could be made.

Similarly for $(\text{MeCp})_3\text{B}_3\text{N}_3\text{Me}_3$ the four absorptions are assigned to vinyl protons (δ *ca.* 6.28 (2)), to methylene protons (δ *ca.* 3.06 (2)), and to two groups of methyl protons (δ 2.66 (3) and 2.07 (3)). Indor data and chemical shift comparisons with the $\text{Cp}_3\text{B}_3\text{N}_3\text{Me}_3$ methyl group support assignment of the absorption at δ 2.66 to the methyl protons on the borazine nitrogen. Double-resonance experiments led to spectral changes which did not yield useful information.

Infrared data for both products compared favorably with that reported for cyclopentadiene,¹¹ indicating the presence of methylene and vinyl protons. Both products exhibited their strongest ir absorption at 1399 cm^{-1} indicative of the presence of a borazine ring.

Our nmr data clearly indicate a mixture of 1- and 2-cyclopentadienylborazines, with little if any 5-cyclopentadienyl material. The physical characteristics of the components of such a mixture should be similar

and their separation difficult. Since the usual method for establishing the positions of substituents in cyclopentadienyl compounds consists of preparing Diels-Alder adducts for nmr comparison, we attempted such a preparation using tetracyanoethylene (TCNE) as the dienophile. Reactions involving $\text{Cp}_3\text{B}_3\text{N}_3\text{Me}_3$ and TCNE in chloroform-benzene yielded only dark flocculent suspensions, probably arising from TCNE coordination with the boron atoms in the borazine ring itself.¹² Since our primary interest in these compounds lies with their sodium and potassium salts as reaction intermediates, no further attempts at isomer separation were made.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support in this research.

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Some Anionic Tetrahalo(2,4-pentanedionato)stannate(IV) Complexes

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Received July 23, 1971

Several studies of the interaction of the tin tetrahalides with 2,4-pentanedione have been reported.^{1–10} Thus far, two types of complexes have been isolated: (1) disubstituted six-coordinate oxygen-chelated enolate derivatives, $\text{X}_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$, where X = F, Cl, Br, and I, and (2) a Lewis acid-base adduct $\text{Cl}_4\text{Sn}(\text{C}_5\text{H}_8\text{O}_2)$. This paper reports studies on the interaction of 2,4-pentanedione and SnX_4 (X = Cl, Br, I) in the presence of an amine to form a new series of anionic β -diketonatetin complexes.

Experimental Section

Reagents.—Tin tetrachloride (Fisher Scientific Co.), tin tetrabromide, and tin tetraiodide (Ventron Corp.) were used without further purification. 2,4-Pentanedione (Eastman Organic Chemicals) was distilled prior to use. Pyridine (Fisher Scientific Co.) and triethylamine (J. T. Baker Co.) were distilled from P_2O_5 and stored over Linde Molecular Sieves, Type 4A. All

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TABLE I

Complex	Mp, °C	Color	Ir data, ^a cm ⁻¹		Nmr data ^b -CH ₃ =CH-		Mössbauer data Isomer shift	Line width	Analyses, %						
									Calcd			Found			
									C	H	X	C	H	X	
Pyridinium Salts															
[Cl ₄ Sn(C ₅ H ₇ O ₂)]	248-252	White	3248 1563	1538	-2.06 -5.70	0.47	0.80	27.3	2.98	32.3	27.5	3.03	32.0		
															3130
															3108
															3078
															3075
[Br ₄ Sn(C ₅ H ₇ O ₂)]	242-244	Off-white	3240 1560	1530	-2.04 -5.71	0.70	0.90	19.5	1.95	51.8	19.6	2.00	51.6		
															3180
															3120
															3100
															3075
[I ₄ Sn(C ₅ H ₇ O ₂)]	164-168	Red-orange	3215 1555	1532	-2.01 -5.77	1.10	0.85	14.9	1.49	63.1	14.7	1.58	63.5		
															3155
															3090
															br, sh
															3060
Triethylammonium Salts															
[Cl ₄ Sn(C ₅ H ₇ O ₂)]	122-125	White	3105 1567	1530	-2.06 -5.69	0.45	0.80	28.6	5.02	30.7	28.8	5.15	30.2		
[Br ₄ Sn(C ₅ H ₇ O ₂)]	174-177	Off-white	3100 1563	1530	-2.05 -5.70	0.70	0.90	20.6	3.62	50.0	20.6	3.67	50.3		
[I ₄ Sn(C ₅ H ₇ O ₂)]	131-134	Red-orange	3073 1557	1530	-2.00 -5.74	1.10	0.90	16.0	2.80	61.4	15.9	2.71	60.9		

^a Mull in Nujol. Key: br, broad; sh, shoulder. ^b Solvent is nitromethane. Concentration *ca.* 5×10^{-2} M. Shifts relative to internal TMS.

solvents were purified by distillation under nitrogen or vacuum from suitable dehydrating agents before use. Nitrobenzene was purified in a manner similar to that reported.¹¹

General Preparative Procedure.—The six anionic tin complexes were prepared in a similar manner. All preparations were performed under an atmosphere of dry nitrogen by methods previously described.⁸ For each preparation the tin tetrahalide (*ca.* 2.5×10^{-2} mol) was placed in *ca.* 40 ml of methylene chloride. 2,4-Pentanedione and the amine dissolved in small quantities of methylene chloride were added dropwise at 0°, respectively. The resulting mixtures were stirred for *ca.* 0.5 hr, and the solid products were isolated by filtration. After thorough washing with hexane, the products were dried under vacuum at room temperature. For all preparations the mole ratios of tin tetrahalide to 2,4-pentanedione to amine were 1:1:1. Although the complexes were prepared in a moisture-free atmosphere, later experiments demonstrated that the complexes are not sensitive to moisture. See Table I for data.

Conductance Measurements.—An Industrial Instruments Model RC-18 conductivity bridge operating at 1000 Hz was used for all measurements which were made in nitrobenzene at room temperature using a Freas-type cell (cell constant 0.17 cm⁻¹) with bright platinum electrodes.

Melting Points.—Melting points were measured in sealed capillaries with a Thomas-Hoover apparatus and are uncorrected.

Spectral Data.—Proton nmr spectra were run on a Perkin-Elmer R-20B spectrometer. Infrared spectra were taken with a Perkin-Elmer 457 spectrophotometer. Mössbauer spectra were obtained with a constant-acceleration velocity drive system similar to that developed at the National Bureau of Standards.¹² Velocity calibration of the instrument was accomplished with an iron source of ⁵⁷Co diffused into a chromium matrix and absorbers of iron foil and sodium nitroprusside. A BaSnO₃ ^{119m}Sn source at room temperature with a palladium filter was used to obtain spectra of the samples which were held at the liquid nitrogen temperature. The tin isomer shifts are reported with respect to the centroid of the BaSnO₃ spectrum.

Results and Discussion

Addition of 2,4-pentanedione to SnCl₄ in methylene chloride at room temperature yields the simple diketone adduct of SnCl₄.^{3,4,8} When either pyridine or triethylamine is added to this adduct, a new compound of the type [M][Cl₄Sn(C₅H₇O₂)] is formed where M =

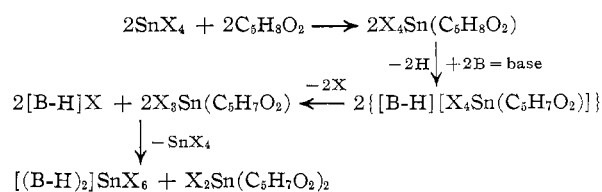
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C₅H₅NH or (C₂H₅)₃NH. With SnBr₄ and SnI₄ analogous complexes are isolated although no evidence for a solid diketone-tin tetrahalide adduct is observed. In the case of pyridine, interaction of 2,4-pentanedione with the tin tetrahalides apparently enhances the acidity of the enolizable proton (*pK_a* ≈ 8.8) to the point where transfer to pyridine (*pK_a* ≈ 5.1), a weaker base than the enolate ion, occurs. For triethylamine (*pK_a* ≈ 10.7), which is a stronger base than the 2,4-pentanedionate ion, complex formation may be interpreted in terms of proton transfer to the amine from an activated diketone or in terms of adduct formation between the enolate anion and the SnX₄ Lewis acid.

The infrared spectra (Table I) in the 3300–3000-cm⁻¹ region (*ν*(N—H)) clearly show the presence of pyridinium and triethylammonium ions. Bands in the 1600–1500-cm⁻¹ (*ν*(C=O) and *ν*(C=C)) region unambiguously indicate the presence of oxygen-chelated 2,4-pentanedionate ligands. Nmr data (Table I) are also consistent with the presence of the enolate ligands. Conductivity measurements presented in Table II are consistent with the complexes being 1:1 electrolytes. All data are consistent with the formulation of the six compounds of empirical formulas [M][X₄Sn(C₅H₇O₂)] as pyridinium or triethylammonium tetrahalo(2,4-pentanedionate)stannate(IV) salts.

Several products which hypothetically could be obtained from the SnX₄–2,4-pentanedione–amine systems are illustrated below



The possibility that the [M][X₄Sn(C₅H₇O₂)] complexes were stoichiometric mixtures of either MCl and X₃Sn(C₅H₇O₂) or [M₂][SnX₆] and the well-known disubsti-

TABLE II
MOLAR CONDUCTANCE VALUES FOR
TETRAHALO(2,4-PENTANEDIONATO)STANNATE(IV)
SALTS IN NITROBENZENE

	$\Lambda_m,^a \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$	
	Pyridinium salts	Trimethylammonium salts
[Cl ₄ Sn(C ₅ H ₇ O ₂)]	17.1 (9.90 × 10 ⁻³)	14.8 (1.40 × 10 ⁻²)
	19.8 (3.95 × 10 ⁻³)	22.5 (2.81 × 10 ⁻³)
	25.4 (1.98 × 10 ⁻³)	25.3 (5.63 × 10 ⁻⁴)
	26.9 (9.88 × 10 ⁻⁴)	24.5 (1.13 × 10 ⁻⁴)
	29.6 (9.88 × 10 ⁻⁶)	26.4 (2.25 × 10 ⁻⁵)
[Br ₄ Sn(C ₅ H ₇ O ₂)]	17.0 (9.23 × 10 ⁻³)	17.8 (9.44 × 10 ⁻³)
	21.5 (1.85 × 10 ⁻³)	23.2 (1.89 × 10 ⁻³)
	23.4 (3.69 × 10 ⁻⁴)	24.4 (3.78 × 10 ⁻⁴)
	26.9 (7.39 × 10 ⁻⁵)	27.5 (7.55 × 10 ⁻⁵)
		28.8 (1.51 × 10 ⁻⁵)
[I ₄ Sn(C ₅ H ₇ O ₂)]	13.3 (5.20 × 10 ⁻³)	17.0 (8.52 × 10 ⁻³)
	14.3 (2.09 × 10 ⁻³)	22.0 (1.71 × 10 ⁻³)
	15.7 (1.05 × 10 ⁻³)	24.9 (3.41 × 10 ⁻⁴)
	16.8 (5.24 × 10 ⁻⁴)	27.4 (6.82 × 10 ⁻⁵)
	20.5 (1.05 × 10 ⁻⁴)	36.6 (1.36 × 10 ⁻⁵)
	29.7 (1.05 × 10 ⁻⁵)	

^a Molar concentrations are in parentheses.

tuted derivatives X₂Sn(C₅H₇O₂)₂ was rejected for several reasons. The possibility of having isolated an X₃Sn(C₅H₇O₂) complex seems remote since no success has been reported in obtaining the monosubstituted derivative by direct reaction of SnCl₄ and 2,4-pentanedione.¹³ Furthermore, all of the pyridinium complexes isolated melt at substantially higher temperatures than expected for the ammonium halide; *i.e.*, C₅H₅NHCl melts at *ca.* 140°. Also, for a mixture of MX and X₃Sn(C₅H₇O₂) the molar conductivity values should be approximately half those expected for 1:1 electrolytes; all values appear to be in the expected range. The possibility that the new compounds are stoichiometric mixtures of [M₂][SnX₆] and X₂Sn(C₅H₇O₂)₂ complexes can be rejected for the following reasons. First, two of the compounds have relatively sharp melting points well above the melting points of the disubstituted product. Second, only a single enolate methyl resonance was observed for each complex in the nmr spectra; all of the disubstituted products have the *cis* configuration and exhibit two enolate methyl resonances.^{6,7} Third, the ¹¹⁹Sn Mössbauer spectra show only a single line of relatively narrow width (see Table I).

Tin-119 Mössbauer spectral data are presented in Table I. Although the complexes do not have cubic symmetry, no quadruple splittings were observed. This fact is consistent with the observations of other workers that octahedrally coordinated nitrogen, oxygen, and halide atoms are not sufficiently different in electrical properties so as to generate significant electrical asymmetry at the tin nucleus.¹⁴ The observed isomer shifts correlate well with the Pauling electronegativity values for the halogens. For the pyridinium series a least-squares analysis generates an equation $IS = -1.26X + 4.46$;¹⁵ for the triethylammonium series the equation is essentially the same.

Attempts were made to extend the reactions of the tin series to germanium and silicon. No analogous anionic complexes were obtained. Reaction of GeCl₄, phenyltrichlorogermane, and phenyltrichlorosilane with

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(15) IS = isomer shift; X = electronegativity value.

2,4-pentanedione and pyridine only led to the isolation of the already characterized disubstituted enolate complexes, *i.e.*, Cl₂Ge(C₅H₇O₂)₂,^{6b,16} Cl(C₆H₅)Ge(C₅H₇O₂)₂,¹⁷ and Cl(C₆H₅)Si(C₅H₇O₂)₂;¹⁸ the reaction of SiCl₄ with 2,4-pentanedione and pyridine yielded the well-known tris(2,4-pentanedionato)silicon(IV) chloride.¹⁸ Thus the formation of the anionic tetrahalo(2,4-pentanedionato) complexes appears to be specific for tin.

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Effects of Nitrogen Donors on the Electronic Structure of Cobalt(II) Bis(dithioacetylacetonate)

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Received July 23, 1971

The X-ray structure² and spectroscopic properties^{3,4} of cobalt(II) bis(dithioacetylacetonate), Co(sacsac)₂, have been extensively studied since its initial synthesis by Martin and Stewart.⁵ The low-spin d⁷ complex was shown by epr studies to have a (d_{zz}, d_{x²-y²}, d_{yz})⁶-(d_{x²})¹(d_{xy})⁰ ground-state electronic configuration (²A_g spectroscopic state).⁶ An interesting feature of the complex is the large in-plane anisotropy (Table I), which results from the combined effects of a small d_{yz}-d_{x²} separation ($\Delta E_{yz-d_x^2} = 1900 \text{ cm}^{-1}$) and a large d_{zz}-d_{x²} separation ($\Delta E_{zz-d_x^2} = 10,000 \text{ cm}^{-1}$). Co(sacsac)₂ has recently been reported to form 1:1 adducts with (C₆H₅)₃M (M = P, As, Sb, Bi).⁷ Martin and Stewart have noted that, in the absence of air, Co(sacsac)₂ gives a green solution in pyridine and correctly suggested that a pyridine complex formed.⁵ In this note we wish to report the results of epr and electronic spectral studies of adducts of Co(sacsac)₂ with the nitrogen donors piperidine and pyridine and to compare them with the parent Co(sacsac)₂ complex. A model for the effects of axial ligation on planar metal chelates originally proposed for Cu(II) chelates⁸ has been extended to these adducts of Co(II) complexes.}

Results and Discussion

The epr spectra and corresponding parameters for Co(sacsac)₂ adducts with piperidine and pyridine are found in Figure 1 and Table I. The splitting of each of the ⁵⁹Co components in the high-field region into three lines results from the coupling with a single ¹⁴N

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