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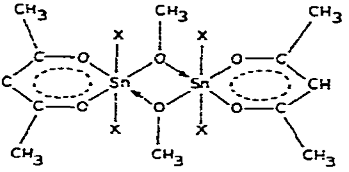
Infrared spectra of alkoxy-bridged tin complexes

Previously we have reported[1] the preparation and properties of methoxy(acetylacetonato)tin dihalides $[(CH_3O)(C_5H_7O_2)SnX_2]_2$ ($X = Cl, Br, I$) and on the basis of their infrared spectra and molecular weight determinations we have suggested a probable configuration (I).



(I)

(X = Cl, Br, I)

In this paper, the infrared spectra in the 1600–400 cm^{-1} region of these complexes and some new alkyl-substituted compounds of (I), $[(CH_3O)(C_5H_7O_2)SnYX]_2$, will be described. These complexes belong to a series of typical compounds having a four-membered ring $\mathrm{Sn}{<}{}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Sn}$. In the chemistry of organotin compounds, this is a structural feature of considerable importance[2]. The infrared spectra of these complexes are rather simple, and these results will be useful in the interpretation of more complicated spectra such as those of the dimeric tetraalkyl-1,3-disubstituted distannoxanes, which are known to have the four-membered ring[3].

The spectra of these complexes are almost identical to those of the corresponding bis(acetylacetonato)tin complexes[4] except for additional strong bands appearing at 1020–970 and 530–480 cm^{-1}. The former band is assigned to a perturbed H_3C–O stretching vibration and the latter to a ring vibration of the Sn–O four-membered ring. The frequencies of these two bands are listed in Table 1. Fig. 1 shows correlations of these bands with the sum of the Hammett's constant[5] σ^* of the substituents X and Y, and it is clear that there are linear relationships between σ^* and the wave numbers of these two bands. It is seen that the weaker the H_3C–O bond, the stronger is the

TABLE 1

RELEVANT INFRARED FREQUENCIES OF METHOXY(ACETYLACETONATO)TIN DIHALIDES AND METHOXY-(ACETYLACETONATO)ALKYLTIN HALIDES IN NUJOL MULLS, AND THE SUM OF THE HAMMETT'S CONSTANT σ^* OF THE SUBSTITUENT X AND Y

Compound $[(CH_3O)(C_5H_7O_2)SnYX]_2$		H_3C–O (cm^{-1})	$Sn{<}^{O}_{O}{>}Sn$ (cm^{-1})	$\Sigma\sigma^*$
Y	X			
Cl	Cl	976	531	2.1
Br	Br	972	523	2.0
I	I	997	506	1.7
CH_3	Cl	1013	490	1.05
CH_3	Br	1013	490	1.0
C_2H_5	Br	1022	484	0.9
n-C_4H_9	Cl	1018	481	0.87

coordination of a methoxy group to tin to form a rigid Sn–O four membered ring. The results indicate that the inductive effect of substituents attached to the tin atom plays a predominant role in the change of infrared frequencies of the bonds described above. The same is true for the shift of frequencies due to the acetylacetonato groups attached to tin[4].

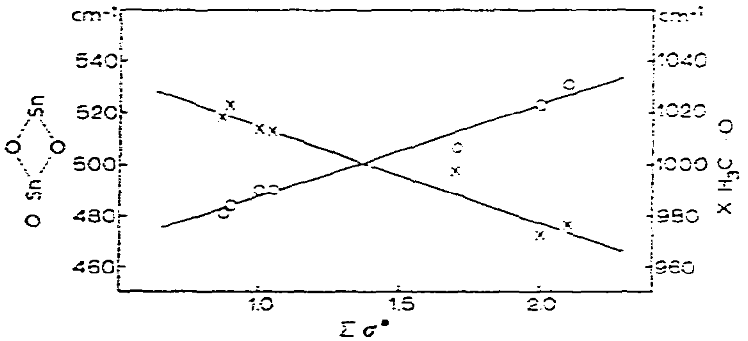


Fig. 1. Relationships between the sum of Hammett's constant σ^* and H_3C–O stretching frequencies (×), and Sn–O ring vibration frequencies (○).

Experimental

Methoxy(acetylacetonato)alkyltin halides. $[(CH_3O)(C_5H_7O_2)SnYX]_2$ ($Y = CH_3$, C_2H_5; $X = Cl$, Br) were prepared by a method similar to that reported for the preparation of methoxy(acetylacetonato)tin dihalides[1] using the following reaction:

$$2\,(C_5H_7O_2)_2SnYX + 2\,CH_3OH \rightarrow [(CH_3O)(C_5H_7O_2)SnYX]_2 + 2\,C_5H_8O_2$$

Methoxy(acetylacetonato)-n-butyltin chloride. To a methanol solution of sodium metal (0.45 g) and acetylacetone (1 g) n-butyltin trichloride (2.8 g) was added and the mixture was heated at reflux for a few minutes. Sodium chloride was filtered immediately from the hot solution. A white crystalline precipitate formed gradually as the filtrate cooled. Analytical data are shown in Table 2.

TABLE 2

METHOXY(ACETYLACETONATO)ALKYLTIN HALIDES: $[(CH_3O)(C_5H_7O_2)SnYX]_2$

Y	*X*	*M.p.* (°C)	% *C*		% *H*		% *X*	
			Found	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*
CH_3	Cl	188 (dec.)	28.17	28.09	4.30	4.38	11.97	11.85
CH_3	Br	187 (dec.)	24.48	24.46	3.81	3.81	23.20	23.25
C_2H_5	Br	175–6 (dec.)	26.99	26.86	4.17	4.23	22.25	22.34
n-C_4H_9	Cl	99–100	35.15	35.18	5.67	5.61	10.51	10.39

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Reaction of *p*-(dimethylamino)bromobenzene with "activated" magnesium

It has been shown by Ehrlich and Sachs[1] that *p*-(dimethylamino)bromobenzene could react with magnesium powder if initially activated by bromoethane (entrainment method). Subsequently, this method for the preparation of *p*-(dimethylamino)phenylmagnesium bromide was employed by several other investigators[2–6]. As a result of the unimpressive yields of this Grignard reagent, however, the lithium reagent is usually preferred. Recently, Owen[7] described the preparation of this Grignard reagent in tetrahydrofuran (THF) after initiation with ethyl iodide or iodine.

In regard to another problem in this laboratory, a procedure has been discovered for the activation of magnesium turnings such that the resultant "activated" magnesium can be caused to react completely with *p*-(dimethylamino)bromobenzene in refluxing tetrahydrofuran *without* the aid of an initiation agent such as iodine or an entrainment reagent such as a haloalkane. The facile activation procedure involves the one day (or longer) room temperature mechanical stirring of magnesium turnings in a nitrogen atmosphere (to prevent oxide formation of the resultant grey-black, finely divided magnesium). Addition of *p*-(dimethylamino)bromobenzene in THF to such magnesium with gentle reflux of the THF results in a black solution with complete or nearly complete reaction of the magnesium.