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STEREOCHEMISTRY AND LABILITY OF DIMERIC METHOXY(β-DIKETONATO)TIN DIHALIDES

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Summary

The static stereochemistry of the title compounds has been investigated by ^{1}H NMR techniques. The NMR analysis indicates that these compounds adopt an octahedral conformation with D_{2h} skeletal symmetry. These dimeric products, which are very stable in the solid state, easily decompose in solution to yield dichlorobis(β-diketonato)tin complexes by disproportionation.

Introduction

In 1965 Kawasaki and Okawara [1] reported that methoxy(acetylacetonato)-tin dihalides can be easily obtained by adding a large excess of methanol to a dichloromethane solution of bis(acetylacetonato)tin dihalides, and on the basis of molecular weight determinations and IR analysis they proposed a dimeric structure for these derivatives. In continuation of our studies of stereochemical aspects of β-diketonate complexes [2,3], we have made an NMR study of such dimeric methoxy(β-diketonato)tin dihalides.

Experimental

Dimeric methoxy(acetylacetonato)tin dichloride (I). Compound I was prepared as described by Kawasaki and Okawara [1]; m.p. 228°C (dec) (lit.: 228—229°C (dec)). The ^{1}H NMR spectrum in CDCl$_3$ showed absorptions at δ (ppm) 2.18 (s, 6H, CH_3), 3.87 ((br) s, 3H, OCH_3) and 5.68 (s, 1H, CH).

Dimeric methoxy(dipivaloylmethanato)tin dichloride (II). Compound II was prepared in 70% yield by refluxing a dichloromethane solution of dichlorobis-(dipivaloylmethanato)tin [3] for 45 min with a large excess of methanol. The white solid obtained had m.p. 238°C, and its ^{1}H NMR spectrum in CDCl$_3$ showed absorptions at δ (ppm) 1.25 (s, 18H, $C(CH_3)_3$), 3.87 (br, s, 3H, OCH_3), 6.02 (s, 1H, CH). Found: C, 35.93; H, 5.31; Cl, 17.69; Sn, 29.65. $C_{12}H_{22}Cl_2O_3Sn$

calcd.: C, 35.68; H, 5.49; Cl, 17.55; Sn, 29.38%.

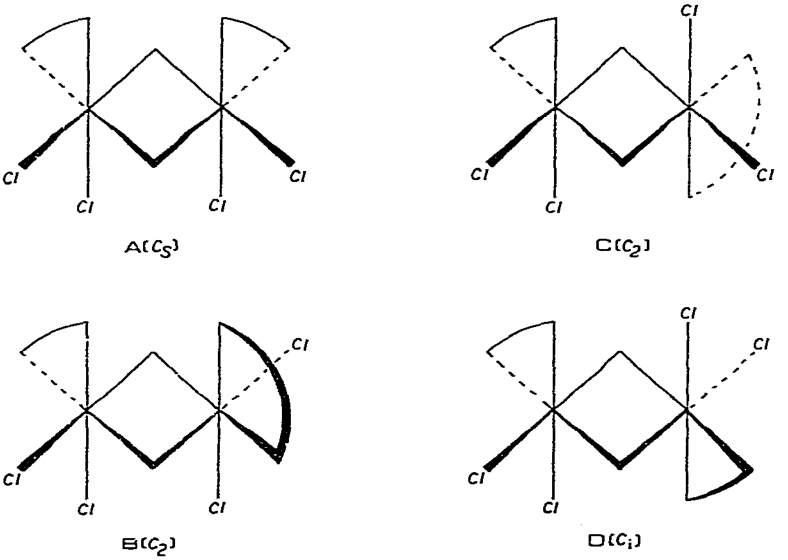
Both derivatives I and II are stable to air, but readily decompose in solution (see below).

Results and discussion

Dimeric methoxy(β-diketonato)tin halides, in which each tin atom is capable of coordinating six ligands, can exist in principle in five stereoisomeric structures, which can be differentiated on symmetry considerations. Four of such diastereomers possess a *cis* arrangement of both chlorine atoms attached to the same tin atom, and they are schematically depicted in Fig. 1. In the symbolism used, the arcs represent any small ring system (the diketonato ring), whereas the four-membered ring is generated by the methoxy oxygen atoms bridging the two tin atoms. The point group symmetry of the molecular skeleton of each diastereomer (assuming a conical symmetry for the methoxy groups) is given in parentheses in Fig. 1. It is evident that two of the structures are chiral (B and C), whereas the other two are achiral (A and D). If, however, both chlorine atoms attached to the same tin atom assume a *trans* configuration, only one skeletal structure (with D_{2h} point group symmetry),is conceivable for such dimeric derivatives (Fig. 2).

The alternative structures, in which the methoxy groups assume a *trans* configuration, would yield a polymeric instead of the dimeric structure, and thus were not considered further.

On the basis of the symmetry considerations above it is evident that the two acetylacetonate methyl groups in I or the dipivaloylmethanato t-butyl groups in II within each β-diketonato ring reside in diastereomeric environments in



A(C_s) C(C_2)

B(C_2) D(C_i)

Fig. 1. Schematic representation of the four diastereomeric forms conceivable for dimeric methoxy-(β-diketonato)tin dichlorides in the *cis* configuration. Skeletal point group symmetry is shown in parentheses.

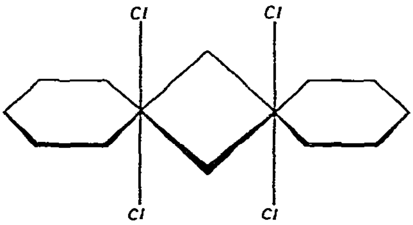


Fig. 2. Schematic representation of dimeric methoxy(β-diketonato)tin dichlorides adopting a *trans* configuration of the chlorine atoms.

each stereoisomer of Fig. 1, and therefore should give rise to separate signals on the ^{1}H NMR spectra. In contrast, the two methoxy methyl groups are homotopic in forms B and D, but diastereotopic in A and C.

On the other hand, if I and II adopt the conformation depicted in Fig. 2, both the methyl (or t-butyl) groups of the diketonate ring and the methoxy methyl groups are homotopic, and therefore only one signal is expected for these derivatives in the methyl and methoxy region, respectively, of their ^{1}H NMR spectra.

The ^{1}H NMR spectra in $CDCl_3$ solution at ambient temperature of derivatives I and II show single signals in the methyl and methine vinyl region, whereas in the methoxy region a broad singlet is observed (Fig. 3a). In addition, this latter signal shows broad satellite bands at ca. 21 Hz upfield and downfield from the main signal due to the ^{117,119}Sn—O—C—H couplings, in agreement

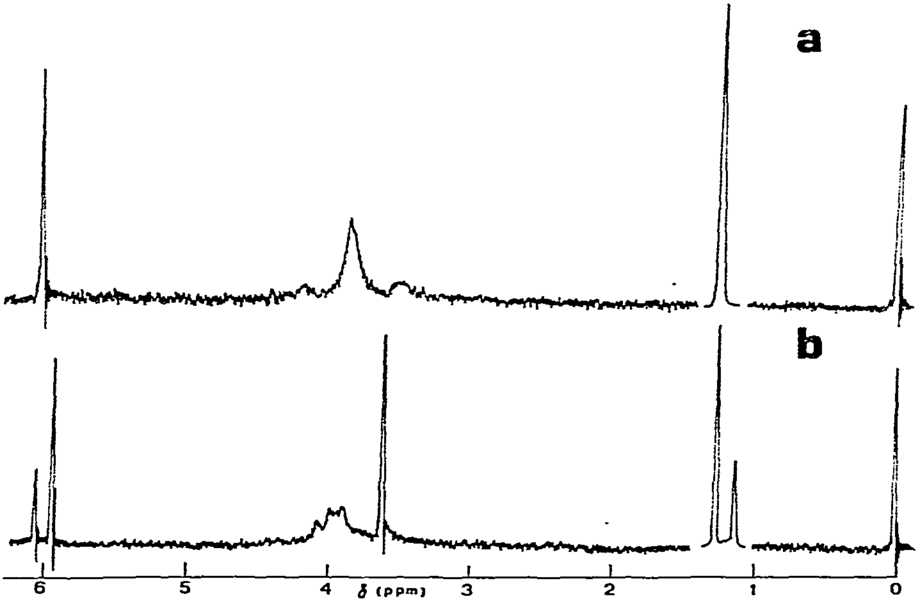


Fig. 3. (a) 60 MHz ^{1}H NMR spectra of a fresh $CDCl_3$ solution of II; (b) aged $CDCl_3$ solution of II. The t-butyl signals were recorded at lower amplitude (ca. 1/10) with respect the other portion of the spectrum.

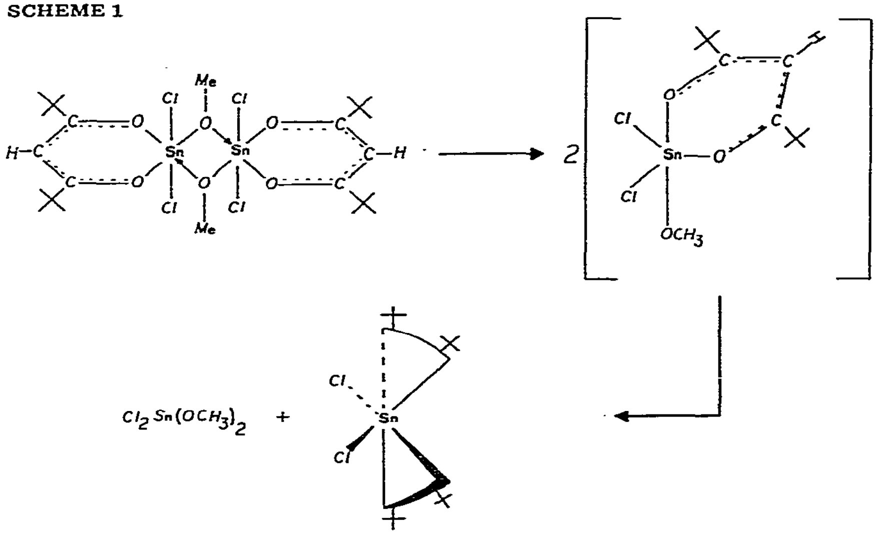
with the fact that the methoxy groups are directly attached to the tin atom [4] and that their exchange between different tin sites is slow on the NMR time scale at this temperature [4,5].

On varying the temperature no drastic changes are observed in the shape and number of signals in the methyl and vinyl methine region, whereas the broad methoxy signal becomes sharper both on lowering or increasing the temperature, although no additional signals arise apart from the low intensity satellite bands mentioned above. Therefore, excluding accidental isochronies, the NMR results above presented strongly favor a structure with D_{2h} skeleton symmetry (Fig. 2) for derivatives I and II.

The most striking feature of these compounds is their ready decomposition in solution to regenerate the bis(β-diketonato) dichloride complexes. In order to investigate this behaviour we made an ^{1}H NMR study of aged solutions in I and II. Because of the greater solubility of II in $CDCl_3$, we confirmed our study to this derivative, although similar behaviour is found for I.

As can be seen from Fig. 3, the aged solution of II shows additional signals in the t-butyl methyl, methoxy and vinyl methine region. The additional signals at δ 1.12, 1.25 and 5.93 ppm (shown in part b of Fig. 3) are superimposable on the signals due to dichlorobis(dipivaloylmethanato)tin (III), formed from II by a disproportionation reaction, according to the proposed scheme 1.

SCHEME 1



When 0.5 g of pure II was refluxed for a few minutes in $CHCl_3$, a white sticky low-melting solid was obtained after evaporation of the solvent. Treatment of this residue with $CHCl_3$ gave two fractions. The soluble one (0.33 g) was shown to contain pure III as shown by a mixed m.p. and by comparing its NMR *, IR and PES [6] spectra with those obtained from authentic III. The portion insoluble in $CHCl_3$ (0.13 g) dissolves in a water/HCl mixture, indicating the formation

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* In addition, coalescence of the two diastereotopic t-butyl groups in the derivative obtained by decomposition of II occurs at the same $\Delta G^{\neq}$ value determined [3] for authentic III.

of some degradation products arising from $Cl_2Sn(OCH_3)_2$, which, readily decomposes in air [7].

The sharp signal in Fig. 3b at δ 3.60 ppm, which increases in intensity with time, must thus arise from $Cl_2Sn(OCH_3)_2$ *, and organotin alkoxides at room temperature are known to show a sharp signal (δ ~3.5—3.6 ppm) in the methoxy region which lacks satellite bands due to the $^{117,119}Sn$ couplings because of fast exchange between different tin sites [4,5].

The stability of II in various solvents was checked, and qualitative investigations indicated that the decomposition rate is enhanced in going from benzene to acetone; in acetone the compound decomposes almost immediately, whereas it can be recrystallized from benzene.

The above analysis explains why the theoretical molecular weight value in I and related species [1,8] is reached asymptotically only in concentrated solutions. Furthermore, the equilibria shown in Scheme 1 cast some light on the disproportionation reactions observed in some simple organotin alkoxides [5] and on the analogous behaviour of alkylmagnesium halides in solution [5b].

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* In contrast to the behaviour of II, the chemical shift of the methoxy groups in $Cl_2Sn(OCH_3)_2$ is strongly affected by the solvent: δ, ppm, (solvent): 3.60 ($CDCl_3$); 3.42 (CD_2Cl_2); 3.32 (acetone); 3.08 (benzene).