A Carbon-13 Nuclear Magnetic Resonance Study of Some Pentanedionato Complexes of Silicon and Germanium

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The ^{13}C NMR spectra of $Si(acac)_2Cl_2$, $Si(acac)_2(acetato)_2$, $Si(acac)_3Cl$, $Ge(acac)_2Cl_2$, $Ge(acac)_2Br_2$ and $Ge(acac)_3I$ are reported. The data is consistent with the disproportionation of $Si(acac)_2Cl_2$ into $Si(acac)_3Cl$ and $SiCl_4$, whereas $Si(acac)_2(acetato)_2$, $Ge(acac)_2Cl_2$ and $Ge(acac)_2Br_2$ each exist in solution as a mixture of cis and trans isomers. The carbon atoms of the cis isomers of these compounds are not exchanging at room temperature.

Introduction

Acetyacetonate (acac) complexes of the type $M(acac)_2Cl_2$ are well known and usually have a *cis* configuration; these have been reported for the dichlorobis(2,4-pentanedionato) complexes of titanium(IV) and tin(IV) [1, 2]. The corresponding germanium(IV) complex, $Ge(acac)_2Cl_2$, has been reported to give a mixture of the *cis* and *trans* isomers in solution [3–5], whereas the silicon analogue, $Si(acac)_2Cl_2$, shows in solution an equilibrium between the *trans* isomer and the tris(pentanedionato)silicon(IV) cation, $Si(acac)_3^+$, [5, 6]. The diacetatobis(pentanedionato)silicon(IV), $Si(acac)_2(acetato)_2$, complex has been reported to give in solution an equilibrium mixture of the *cis* and *trans* isomers in a ratio of the order 1.6 to 1 [7, 8]. The stereochemistry and exchange properties for complexes of this type have been followed by dynamic ^1H NMR with detailed kinetic analysis being carried out for the fluxional *cis*-$Ti(acac)_2X_2$ and *cis*-$Sn(acac)_2X_2$ compounds [1, 2]. Some ^1H NMR data has also been reported for $Ge(acac)_2Cl_2$, $Si(acac)_2Cl_2$ and $Si(acac)_2(acetato)_2$ [3–8].

We have recently reported ^{13}C NMR data as well as IR data on fluxional *cis*-$Ti(acac)_2X_2$ and *cis*-$Sn(acac)_2X_2$ compounds [9, 10]. These results confirm the ^1H NMR studies and point towards a partial bond-rupture as the exchange mechanism. The present paper reports the results of ^{13}C NMR and IR studies on several silicon and germanium compounds to determine their stereochemistry and exchange properties.

Experimental

The compounds $Si(acac)_2Cl_2$ [6], $Si(acac)_2(acetato)_2$ [7], $Si(acac)_3Cl$ [6, 11], $Ge(acac)_2Cl_2$, $Ge(acac)_2Br_2$ [3, 12] and $Ge(acac)_3I$ [3] were prepared as previously reported. The ^{13}C NMR were taken on a JEOL FX60Q NMR spectrometer with TMS used as an internal reference. The IR spectra were taken on a Beckman IR-12 spectrometer.

Results and Discussion

$Si(acac)_2Cl_2$ disproportionates in solution to $Si(acac)_3Cl$ and $SiCl_4$ with $Si(acac)_3Cl$ being the predominant species both at room and low temperatures [6]. The ^{13}C NMR spectra of $Si(acac)_2Cl_2$ taken in chloroform-d gave resonances at 192.9, 191.4, 103.4, 102.6, 26.0 and 25.8 ppm. The spectrum of the cation, $Si(acac)_3^+$, in the same solvent gave resonances at 192.8, 103.8 and 26.0 ppm. These are assigned to the carbonyl, methine and methyl carbons, respectively. Thus the resonances at 191.4, 102.6, and 25.8 ppm are due to the same respective carbon atoms in $Si(acac)_2Cl_2$. None of the resonances assigned to $Si(acac)_2Cl_2$ show any splitting or line broadening down to $-50°$. Previous reported proton data extends to $-60°$ also shows no line broadening [6]. Since the coalescence temperatures for carbon are usually higher than those for proton (for the titanium compounds about $20°$ higher [9]) a *trans* structure in solution for $Si(acac)_2Cl_2$ is now more clearly indicated.

The ^{13}C NMR spectra in deuterochloroform of $Ge(acac)_2X_2$, X is chlorine and bromine, indicates the presence of a mixture of the *cis* and *trans* configurations for each of these compounds with the *cis* configuration being the major isomer. An early ^1H study indicated only the *cis* configuration for the chloro complex [13] while later ^1H and infrared data supported a mixture of the *cis* and *trans* isomers [3, 4]. At $40°$ the ^{13}C NMR spectrum of $Ge(acac)_2Cl_2$ gave resonances at 193.0, 192.8, 190.5 ppm

(carbonyl carbon); 101.1, 100.1 ppm (methine carbon); 26.9, 26.8, 24.7 ppm (methyl carbon). A sample of pure *trans*-Ge(acac)₂Cl₂ was obtained by aging a chloroform solution saturated with the *cis–trans* mixture [3]. *Trans*-Ge(acac)₂Cl₂ gave ¹³C NMR resonances at 190.5, 100.1 and 24.7 ppm. The remaining resonances in the *cis–trans* mixture are due to the two nonequivalent sites of the carbonyl (193.0, 192.8) and methyl carbons (26.9, 26.8) as well as the methine (101.1) carbon of the *cis* isomer.

A sample of *trans*-Ge(acac)₂Cl₂ in CDCl₃ was kept at 50 °C for two weeks and periodically its ¹³C NMR was taken. The spectra showed some decomposition products but no measurable amount of *cis*-Ge(acac)₂-Cl₂ was indicated.

The spectrum of Ge(acac)₂Br₂ at 34 °C also indicates a *cis–trans* mixture (with decomposition products) with the *cis* isomer showing a nonequivalent carbonyl resonance and a broadened methyl carbon resonance. Assignments (ppm) for the *cis* isomer are 192.8, 192.6 (C–O), 100.7, (C–H) and 26.9 (CH₃-line width at half height *ca.* 4.0 Hz) and for the same respective carbon resonances in the *trans* isomer: 190.5, 100.1 and 24.7 ppm. Variable temperature NMR studies were not carried out due to the limited solubility of these germanium compounds, as it was necessary to collect 10,000 or more transients in order to obtain an interpretable spectrum. The corresponding iodo complex, Ge(acac)₂I₂ is not known and Ge(acac)₃I results from the synthetic procedure [3]. The ¹³C NMR spectra of this compound shows resonances at 195.4 (C–O), 103.4 (C–H) and 27.4 ppm (CH₃) from TMS, these are similar to those reported above for Si(acac)₃Cl.

The spectra of diacetatobis(pentadionato)silicon-(IV) are interpretable in terms of a nonexchanging equilibrium mixture of the *cis* and *trans* isomers. Earlier proton work [8] has established a 1.6 to 1 ratio of *cis* to *trans* but no variable temperature work has been reported. The ¹³C data confirms this ratio at room temperature and the spectrum of tetraceto-xysilicon(IV) [167.1 (CO), 22.1 ppm (CH₃)] was used to aid in assignment. The pertinent data with appropriate assignments are displayed in Table I. A total of twelve resonances are recorded for a *cis–trans* mixture of Si(acac)₂(acetato)₂. There are five carbonyl carbon resonances, three from the *cis* isomer (two nonequivalent ligand carbonyl carbons and one from the acetato carbonyl carbon) and two from the *trans* isomer (carbonyl ligand and acetato carbonyl carbons). Two methine carbon resonances (one for each isomer) are observed. Five methyl carbon resonances are expected; three for the *cis* isomer (two ligand methyl and one acetato methyl) and two for the *trans* isomer. These are all observed under high resolution conditions, for a normal spectrum the *trans* ligand methyl carbon

TABLE I. ¹³C NMR Chemical Shift Data for Si(acac)₂(ace-tato)₂.[a]

CD₂Cl₂[b]	CDCl₃[b]	CDCl₃[c]	Assignments
191.9	191.7	191.7	*cis*-ligand CO
191.4	190.8	190.9	*cis*-ligand CO
191.8	191.4	191.4	*trans*-ligand CO
170.3	170.7	170.5	*cis*-acetate-CO
170.1	170.2	170.1	*trans*-acetate-CO
102.5	102.4	102.3	*trans*-CH
102.3	102.2	102.1	*cis*-CH
25.8	25.7	25.6	*cis*-ligand-CH₃
25.6	25.4	25.5	*cis*-ligand-CH₃
25.8	25.6	25.6	*trans*-ligand-CH₃
24.3	24.4	24.3	*cis*-acetate-CH₃
24.1	24.1	24.1	*trans*-acetate-CH₃

[a]In ppm downfield from TMS. [b]Spectra recorded at 30 °C. [c]Spectra recorded at 70 °C.

overlaps with one of the methyl carbons of the *cis* isomer.

Spectra have been obtained from −40° to +70 °C in CDCl₃ and up to 120 °C in C₂D₂Cl₄. No evidence for line broadening is observed over this temperature range. Exchange reactions in acetylacetonate complexes have been suggested to occur by the twist mechanism or by a one-bond-rupture of an acetylacetonate ligand (for example see refs. 1–3, 14–20). We have suggested that the *trans* directing ability of the X group in *cis*-M(acac)₂X₂ is an important factor in determining the rate of reaction for both the titanium and tin systems. The acetato ligand is not normally included in tables of *trans* directors but oxygen based ligands (OH⁻, OR⁻) are generally poor *trans* directors and there is no reason to suspect a different behavior for the acetato ligand.

Complexes of the type Si(acac)₂RCl, where R is phenyl or methyl, adopt a nonrigid *cis* configuration in solution [20]. These complexes decompose with relative ease and variable temperature studies (¹H) have been carried out with activation parameters for the exchange process reported [20]. The major difference between these compounds and the silicon acetate complex seems to reside in the greater *trans* directing ability of the R and chloride ligands *versus* that of the acetato ligand. If these ligands do not make a very great difference in considering a twist mechanism then we suggest that the lack of interconversion of ·the isomers of Si(acac)₂(acetato)₂ may well be the result of the poor *trans* directing ability of acetato ligand leading to no labilization of a silicon acetylacetonate bond and hence no exchange. While there is probably no one mechanism

for the interconversion of complexes of the type $M(acac)_2X_2$ the evidence cited herein could point towards a one bond rupture of the bidentate ligand although a twist mechanism cannot be entirely ruled out nor can any one mechanism be necessarily the sole pathway.

The chemical shift of the methine hydrogen (γ-proton) has been suggested to allow the assignment of *cis* or *trans* configuration in $M(acac)_2X_2$ complexes [11, 21]. This approach has been shown to be questionable in some cases [22] since factors other than electric fields effects arising from a molecular dipole moment may be important. Although there is insufficient ^{13}C NMR data at the present time, a similar conclusion will probably be reached with the methine carbon resonance for the compounds reported herein. For example, in *trans*-$Si(acac)_2$-$(acetato)_2$ the methine carbon resonance is more deshielded than the corresponding *cis* isomer whereas in *trans*-$Ge(acac)_2Cl_2$ and *trans*-$Ge(acac)_2Br_2$ the methine carbon resonance is more shielded than their *cis* counterparts.

Acknowledgements

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