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Preliminary communication

Correlations between nuclear magnetic resonance spectra and crystal structure

II *. The observation of ^{199}Hg–^{13}C scalar coupling in the solid state for some methylmercury derivatives.

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Abstract

Scalar coupling in the solid state between the ^{199}Hg and ^{13}C nuclei is reported for the methylmercury moiety in some MeHgX compounds. Values of $J(^{199}\text{Hg}-^{13}\text{C})$ are 1445, 1807, and 1847 Hz for X = S_2COMe, O_2CMe, and Cl respectively.

As a part of a wider study of crystal structure/solid state NMR correlations, the cross polarized, magic angle spinning (CP MAS) ^{13}C solid state NMR spectra for a series of non-transition metal xanthate (^-S_2COR) complexes have been investigated [1]. During studies on the xanthates of the Zn triad elements, ^{199}Hg–^{13}C scalar coupling was observed for the MeHg group in MeHg(S_2COMe); subsequently a range of MeHgX compounds was examined. Although ^{199}Hg–^{13}C coupling has been reported in the solid state for $Hg(CF_3)_2$ [2] and $Hg(O_2CMe)_2$ [3], to our knowledge no values of $J(^{199}\text{Hg}-^{13}\text{C})$ have been reported for methylmercury derivatives in the solid state.

High resolution ^{13}C NMR spectra of MeHgCl, MeHg(O_2CMe) (Ventron–Alfa Inorganics) and MeHg(S_2COMe) [4] were obtained for the solid state by use of standard cross polarization and high power dipolar decoupling techniques combined with magic angle spinning (2.2–2.4 kHz) to remove ^{199}Hg–^{13}C dipolar coupling [1].

The CH_3Hg region of the three spectra is shown in Fig. 1. MeHgCl, Fig. 1a, exhibits a single resonance (δ 8.31 ppm) with satellites due to ^{199}Hg–^{13}C scalar coupling ($J(^{199}\text{Hg}-^{13}\text{C})$ 1807 Hz). Kendrick et al. [2] have noted that the interpretation of centre band to satellite intensities requires further investigation since the

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* For Part I, see ref. 1.

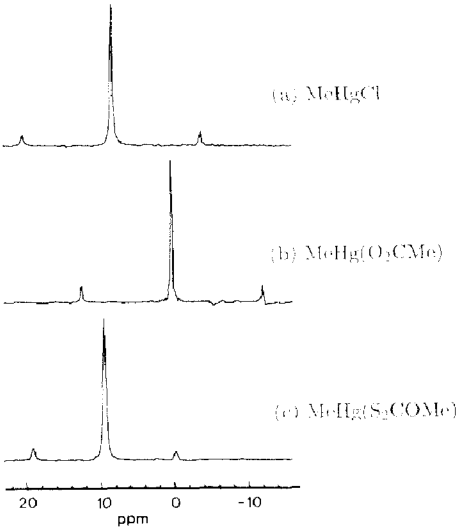

Fig. 1. The CP MAS ^{13}C NMR spectra in the region −16 to 23 ppm for (a) MeHgCl, (b) $MeHg(O_2CMe)$ and (c) $MeHg(S_2COMe)$.

contribution of $J(^{201}Hg-^{13}C)$ (^{201}Hg, spin 3/2, has a natural abundance of 13.24%) is not fully understood. We observed intensities in the approximate ratio 1/8/1, whereas the expected ratio (^{199}Hg, spin 1/2, has a natural abundance 16.1%), assuming no further interactions should be about 1/10/1. The values of δ and $J(^{199}Hg-^{13}C)$ may be compared with the solution state $\delta(CH_3)$ and $J(^{199}Hg-^{13}C)$ values of 8.4; 1674 and 8.6 ppm; 1431 Hz in $(CD_3)_2SO$ and $CDCl_3$ solutions, respectively [5].

For $MeHg(O_2CMe)$ (Fig. 1b) the CH_3Hg resonance occurs at 0.09 ppm and the observed scalar coupling constant $J(^{199}Hg-^{13}C)$ is 1847 Hz. Again these values may be compared with 0.8 ppm and 1695 Hz obtained for $(CD_3)_2SO$ solutions [5]. The ratio of intensities is approximately 1/4/1. The chemical shifts for the O_2CCH_3 and O_2CCH_3 carbons in the acetate group are 25.4 and 177.9 ppm respectively. No evidence was found for scalar coupling between the Hg nucleus and the C atoms of the carboxylate group, whereas the solid state spectrum of $Hg(O_2CMe)_2$ showed both $^2J(^{199}Hg-^{13}C)$ and $^3J(^{199}Hg-^{13}C)$ couplings [3].

Figure 1c shows the CH_3Hg part of the spectrum for a MeHg derivative with a S donor atom, namely $MeHg(S_2COMe)$. A CH_3Hg chemical shift of 9.07 ppm and $J(^{199}Hg-^{13}C)$ 1445 Hz was observed (ratio of intensities approximately 1/10/1). In $CDCl_3$ solution the values are 7.69 ppm and 1324 Hz (ratio of intensities approximately 1/10/1). Chemical shifts observed for the xanthate moiety carbon atoms are 63.5 and 223.9 ppm for S_2COCH_3 and S_2COCH_3, respectively (61.2 and 224.5 ppm in $CDCl_3$ solution).

The solid state NMR spectra for MeHgCl and $MeHg(S_2COMe)$ are consistent with their known crystal structures in which only one formula unit of each compound comprises the asymmetric unit in each structure; only one resonance is observed for each crystallographically distinct site. No crystal structure is yet available for $MeHg(O_2CMe)$, but attempts to grow crystals, suitable for X-ray studies are under way.

The solution state NMR spectra for all three compounds reveal single sites for all chemically distinct carbons. A comparison of chemical shifts and coupling constants for solutions and the solid state leads us to suggest that the basic structures are retained in solution, although some weakening of the Me–Hg bond (evidenced by a general decrease in J in solution) may be caused by solvent effects.

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