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SOLID STATE ^{13}C NMR OF MERCURIC(II) ACETATE: SCALAR ^{13}C — ^{199}Hg COUPLING AND CRYSTAL STRUCTURE

PETER F. BARRON

Brisbane NMR Centre, Griffith University, Nathan, Queensland, 4111 (Australia)

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Summary

Solid state ^{13}C CP/MAS spectra of crystalline mercuric(II) acetate have been obtained. Scalar ^{13}C — ^{199}Hg couplings are observed in contrast to solution ^{13}C spectra where rapid acetate group exchange prevents detection of coupling. Two and three bond couplings are compared with typical values found in solution. Two major resonances are observed for both the methyl and carboxyl carbons. This can be rationalized by available crystal structure data which indicates non-equivalence of the two acetate groups attached to mercury.

The recent report of Kendrick et al. [1] of the detection of ^{199}Hg satellites in ^{13}C CP/MAS spectrum of solid $(\text{CF}_3)_2\text{Hg}$ was of interest to us due to our ^{13}C NMR studies of organomercurials and organothalliums [2,3]. ^{13}C NMR has proven to be very useful in these classes of compounds as a probe of electron distribution and bonding characteristics. In particular, the magnitude and variability of ^{199}Hg — ^{13}C and $^{203/205}\text{Tl}$ — ^{13}C scalar couplings has been the subject of considerable study [2–7]. As many organothalliums and organomercurials are only poorly soluble in normally used NMR solvents, and hence ^{13}C spectra are difficult to obtain, the possibility of examination by solid state techniques and the subsequent extraction of chemical shifts and scalar couplings is extremely appealing.

We have begun an examination of soluble organothalliums and organomercurials of the $\text{RM}(\text{OAc})_x$ type in order to compare solution and solid chemical shifts and scalar couplings. Kendrick and coworkers [1], on comparing solid and solution ^{199}Hg — ^{13}C coupling in $(\text{CF}_3)_2\text{Hg}$, comment on the need for more work on this subject. As many of the organometallics we intended to examine were synthesized using mercury(II) and thallium(III) acetates we initially obtained ^{13}C CP/MAS spectra of these. In this paper we wish to report two interesting features of the ^{13}C CP/MAS spectrum of mercuric(II) acetate $(\text{CH}_3\text{CO}_2)_2\text{Hg}$ which demonstrate the value of solid state ^{13}C examination of organometallics.

In the organomercurials and organothalliums we have previously examined in solutions [2,3] we have never observed scalar ^{13}C -M couplings to the acetate methyl and carboxyl carbons and have presumed this to be due to either rapid acetate group exchange or the ionic nature of M-OAc bonding. The former is the more likely explanation with the lack of observed coupling being due to scalar relaxation of the first kind. For no coupling to be observed, the rate of exchange must be significantly larger than $2\pi J(^{13}\text{C}-\text{M})$.

The solution state spectrum of mercuric(II) acetate obtained in D_2O is shown in Fig. 1a and exhibits two resonances at δ 178.9 and 20.8 ppm which can be assigned to the carboxyl and methyl carbons respectively. No scalar

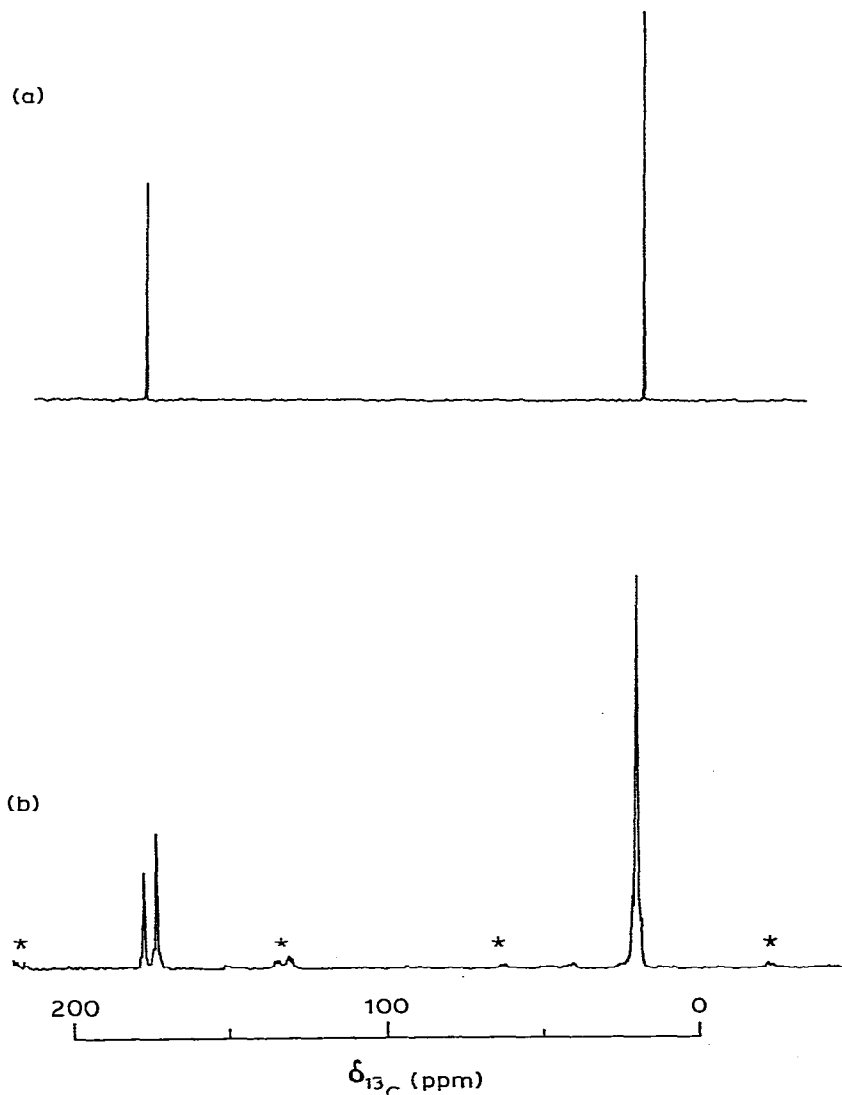


Fig. 1. 75.46 MHz ^{13}C spectra of $(\text{CH}_3\text{CO}_2)_2\text{Hg}$: (a) in D_2O , sweep width 18.5 kHz; (b) solid state by CP/MAS, sweep width 20 kHz, residual spinning sidebands are indicated (*). Block multiplication of spectra at different spinning speeds was used to reduce carboxyl spinning sidebands.

^{199}Hg — ^{13}C satellites are evident presumably implying that, in D_2O , the rate of acetate group exchange is greater than $2\pi J(^{13}\text{C}$ — $^{199}\text{Hg})$. The other possibility, that no coupling occurs as $(\text{CH}_3\text{CO}_2)_2\text{Hg}$ is dissociated in solution, can be dismissed as it is well known that it exists largely in a covalent state. In order to detect the certainly present couplings in solution, spectra would need to be obtained at low temperatures where the exchange rate would be sufficiently slow. As mercuric(II) acetate is only soluble in water and alcohol, obtaining spectra at sufficiently low temperature would be difficult if not impossible.

However the solid state ^{13}C CP/MAS spectrum (Fig. 1b) exhibits a number of resonances. Two major peaks occur in each of the methyl region (δ 24.7 and 24.3 ppm) and carboxyl region (δ 180.9 and 176.8 ppm) which can be assigned tentatively to either two types of acetate groups in the crystal structure or two crystallographic forms of mercuric(II) acetate. Expansion of each region (Fig. 2) reveals additional pairs of small peaks symmetrical about each major peaks which are most certainly ^{13}C — ^{199}Hg scalar coupling satellites. As pointed out by Kendrick [1], it is difficult to predict satellite intensities due to the uncertain

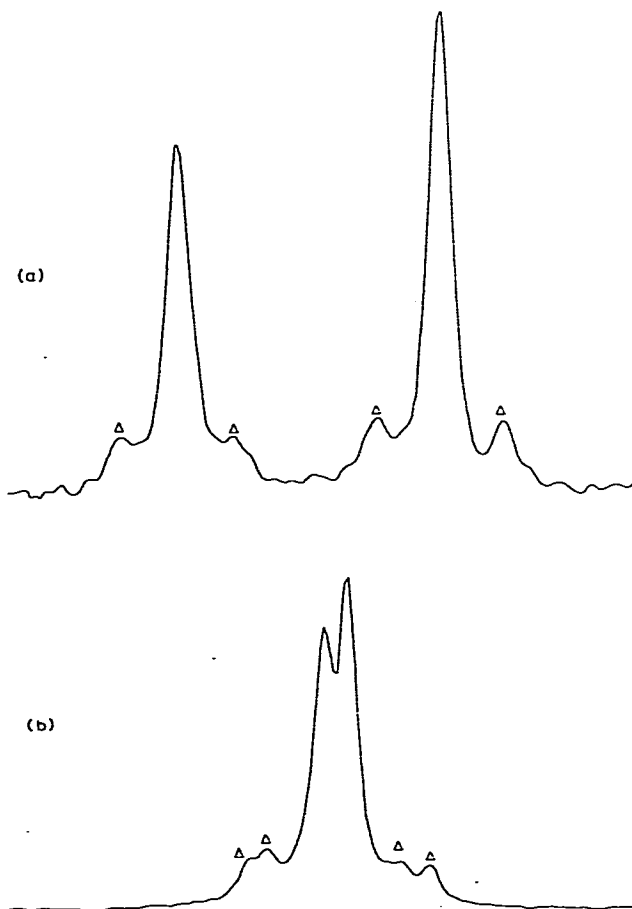


Fig. 2. Expanded sections of Fig. 1b: (a) carboxyl region, plot width 750 Hz; (b) methyl region, plot width 750 Hz. ^{13}C — ^{199}Hg satellites are indicated (Δ).

contribution of carbons bonded to spin $3/2$ ^{201}Hg . However, the ratios of satellite to centreband are ~ 0.12 and within reasonably expected limits.

The two bond couplings, $^2J(^{13}\text{C}-^{199}\text{Hg})$ are 118 and 156 Hz for the low and high field carboxyl resonances respectively whilst the three bond couplings, $^3J(^{13}\text{C}-^{199}\text{Hg})$, are 176 and 195 Hz for the low and high field methyl carbons respectively. Discussion of these solid state scalar couplings can only be on a very qualitative basis at present given the absence of any previous detailed work on the subject. Two bond couplings in solution are generally of order of 50–70 Hz [2–4]. An oxygen substituent (OCH_3 , OAc) on the carbon β to mercury has been found to generally increase the coupling to ~ 100 – 150 Hz [2,4]. Under certain circumstances, however, this coupling can be less than 50 Hz [2,4]. Hence, the situation for two-bond $^{13}\text{C}-^{199}\text{Hg}$ coupling in solution where the carbon has one or more oxygen substituents is somewhat unclear. In mercuric(II) acetate the two bond coupling is via oxygen and to a carboxyl and no analogous couplings in solution are available for comparison as a result of rapid acetate group exchange. The observed values of 118 and 156 Hz are within the range of two bond couplings found in solution but are more consistent with those values found for mono-oxygenation of this β -carbon to mercury.

In solution, three bond couplings to mercury have been shown to exhibit a Karplus type dependence [2,3] on dihedral angle with values as large as ~ 280 Hz being found. Oxygenation of the intervening β -carbon has also been found to greatly reduce the coupling from expected values. The couplings of 176 and 195 Hz are significantly larger than the two bond couplings and hence suggest that $^3J(^{13}\text{C}-^{199}\text{Hg})$ may exhibit a Karplus type dependence in the solid state. If carboxyl and methyl signals are paired according to intensity, the less intense acetate group exhibits smaller coupling to both carbons.

The existence of two centre-band methyl and carboxyl signals can be clarified by the crystal structure determination performed by Allman [8]. Resolution of different crystal environments in solid state ^{13}C spectra has been observed previously [9,10]. The space group of mercuric(II) acetate was determined to be $P2_1/a$ and found to exist as chains in which each mercury is bonded to two oxygens with a bond length of 2.07 \AA . Furthermore each mercury has two additional oxygen linkages at a distance of 2.73 \AA to adjacent molecules in the same chain. Hence within each chain both acetate groups are identical within experimental error. However, it is the location of chains within the crystal which renders the acetate groups non-equivalent. One acetate group approaches the Hg atoms of two neighbouring chains. This interaction presumably results in a significant deshielding of one carboxyl carbon and a smaller deshielding of the methyl of this acetate group. Furthermore, this extra interaction would appear to reduce the $^{199}\text{Hg}-^{13}\text{C}$ scalar couplings, even though no change in bonding lengths or angles is evident.

In conclusion, the detection of scalar couplings in solids when not detectable in solution due to exchange should be of value in many other organometallic compounds. For example, we have examined the analogous thallium(III) acetate, $(\text{CH}_3\text{CO}_2)_3\text{Tl}$, and similar effects appear evident. However, to date we have not been able to analyse this spectrum completely due to the complexity of both the carboxyl and methyl regions. This complexity probably results from different crystal environments, large scalar $^{13}\text{C}-^{203/205}\text{Tl}$ couplings and possibly

broader lines due to the incomplete removal of ^{13}C — $^{203/205}\text{Tl}$ dipolar couplings at the spinning speeds used. However, before scalar couplings in solids can be interpreted with confidence, systematic studies of coupling in solids need to be undertaken. The clear resolution of the nonequivalence of the acetate groups in mercuric(II) acetate indicates that solid state ^{13}C NMR examination of organo-metallics may prove useful as a simple means of detecting crystal structure variations.

Experimental

^{13}C spectra were obtained on a Bruker CXP-300 spectrometer operating at 75.46 MHz. Chemical shifts are quoted relative to external TMS with dioxane used as internal reference for solution and external adamantane for solid. Solid state ^{13}C CP/MAS spectra were obtained using a Bruker Z32 DR/MAS probe with ^{13}C and ^1H fields of 48 and 12G respectively, single 1 ms contacts repeated at 20 s intervals and spin-temperature alternation. Samples were packed in Andrews type rotors free from background signals and spun at speeds of 3–4 kHz [11]. The magic angle was accurately set by observing the ^{79}Br resonance of a small amount added KBr. Linewidths of less than 50 Hz for ^{199}Hg satellites in the CP/MAS spectra indicate that the ^{13}C — ^{199}Hg dipolar coupling is effectively removed at these spinning speeds, as expected [1].

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- 11 Spinning speeds used, 3–4 kHz, whilst sufficient to remove large carboxyl chemical shift anisotropy, are not fast enough to completely remove the spinning side bands.