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^{19}F and ^{199}Hg NMR of trimeric perfluoro-*ortho*-phenylenemercury

R.E. Taylor [a,*], François P. Gabbaï [b,*]

[a] Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095-1569, USA
[b] Department of Chemistry, Texas A&M University College Station, TX 77843-3255, USA

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Abstract

^{19}F and ^{199}Hg high-resolution solution NMR spectra were acquired for cyclic trimeric perfluoro-*ortho*-phenylenemercury. Even with the high superconducting magnetic fields currently available, the ^{19}F spectrum was not interpretable with a simple first-order analysis. Spectroscopic parameters for chemical shift and scalar coupling interactions in the NMR spectra were extracted from four- and five-spin simulations. Differential line widths in the ^{19}F spectrum result from scalar coupling to the ^{199}Hg.

Keywords: NMR; ^{19}F NMR; ^{199}Hg NMR; Lewis acid; Mercury; Trimeric perfluoro-*ortho*-phenylenemercury; Strong scalar coupling

1. Introduction

Cyclic trimeric perfluoro-*ortho*-phenylene mercury (the “trimer”) is a tridentate Lewis acid which complexes a number of neutral and anionic electron rich substrates and its chemistry has been recently reviewed [1,2]. The structure is shown in Fig. 1. In the case of halides, complexation leads to the formation of adducts in which the halide anion forms secondary coordination bonds with the three mercury centers. A similar tridentate complexation is observed with the electron rich center of various donor substrates including organic carbonyls, nitriles, sulfoxides and dialkylsulfides. Formation of these complexes substantiates the unusual Lewis acidic properties of the trimer. These properties result from the electron-withdrawing nature of the fluorinated backbone, the accessibility of the mercury centers as well as from cooperative effects arising from the proximity of the mercury(II) centers. Structural investigations also point to the propensity of this trinuclear derivative to engage in non-covalent interactions including mercuriophilic interactions and dispersion interactions [3]. For example, free trimer forms compact cofacial dimers whose structure has been determined by single crystal X-ray diffraction. As shown by recent developments, the trimer is also a remarkable supramolecular building block which readily forms binary stacks with various arenes including benzene and naphthalene [3,4]. The formation of these stacks, which results from secondary π interactions occurring between the mercury centers and the π-system of the arene, is likely assisted by attractive electrostatic and dispersion forces between the individual components.

For nuclear magnetic resonance (NMR) spectroscopy, all nuclei present in this derivative are NMR-active and variation of their chemical shift upon addition of a substrate can sometime reflect adduct formation. This principle is nicely exemplified by the work of Shur and coworkers [5] who witness the complexation of electron rich substrates by ^{199}Hg NMR. For example, coordination of dimethylformamide to the trimer leads to a 12.3 ppm down field shift of the mercury resonance [6]. The fluorine nucleus constitutes another obvious NMR handle. As shown by Fackler and Burrini, the trimer forms binary stacks with trinuclear cyclic basic Au^{I} compounds such as $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ (bzim = 1-benzylimidazolate). Remarkably, a ^{19}F, ^{1}H-HOESY NMR measurement carried out on these adducts in THF-d_8 shows intermolecular

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[*] Corresponding authors. Tel.: +1 310 206 2074 (R.E. Taylor).
E-mail addresses: taylor@chem.ucla.edu (R.E. Taylor), gabbai@mail.chem.tamu.edu (F.P. Gabbaï).

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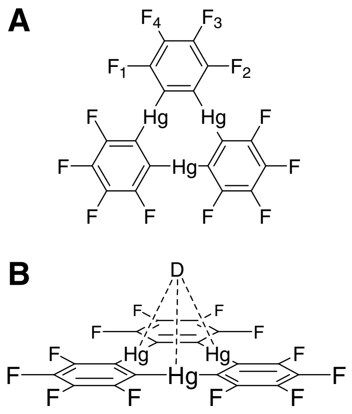

Fig. 1. The structure of cyclic trimeric perfluoro-*ortho*-phenylenemercury is shown in (A). For spectral assignments, the individual ^{19}F atoms in the above structure are subscripted one through four. The chemical shifts and coupling constants are given in Table 1. The general structures of the donor adducts of the trimer (D = donor) are shown in (B).

cross-peaks of the adduct indicating that adducts between the trimer and [Au(μ-C^2,N^3-bzim)]$_3$ subsist in solution [7,8]. These two examples indicate that the NMR properties of the trimer are useful for monitoring and therefore understanding the chemistry of this tridentate Lewis acid. For these reasons, a detailed analysis of the NMR spectroscopic features of the trimer appears highly desirable.

2. Experimental

The ^{19}F NMR spectrum was acquired with a Bruker ARX-400 spectrometer at ambient temperature. One milligram of sample was dissolved in 0.5 ml of CD$_2$Cl$_2$ to minimize interaction between solute and solvent. The ^{19}F spectrum is referenced to an external sample of CFCl$_3$. The data were acquired with 512 scans using a 30 degree pulse every 5 s. A total of 128k time domain data points were acquired with a spectral width of 21739.13 Hz, yielding a total acquisition time of 3.015 s for each scan. The size of the Fourier transform was 256k data points, yielding a digital resolution of 0.083 Hz/pt. The high sensitivity allowed resolution enhancement to be applied for the spectral analysis. One common method of resolution enhancement is the Lorentz-Gauss transformation [9]. This technique uses a negative line-broadening in Hertz to enhance the latter part of the free induction decay (FID) while using a second function to shift the point during acquisition when the FID reaches its maximum but forces the tail of the FID to zero. While this technique is implemented in many commercial software packages, it does suffer a drawback due to a decrease in the apparent signal-to-noise ratio (S/N).

The ^{199}Hg spectrum was acquired with a Bruker AV-600 spectrometer at ambient temperature. Nine milligrams of sample was dissolved in 0.5 ml of CD$_2$Cl$_2$. A total of 240,946 scans were acquired with a 90 degree pulse using a recycle delay of 100 ms. A total of 32k time domain data points were acquired with a spectral width of 53763.44 Hz, yielding a total acquisition time of 0.305 s for each scan. The size of the Fourier transform was 32k data points, yielding a digital resolution of 1.640 Hz/pt. The ^{199}Hg spectrum is referenced to Hg(CH$_3$)$_2$ at zero ppm by using an external sample of 1.0 M HgCl$_2$ in *d*-dimethylsulfoxide assigned to −1501.0 ppm.

Spin–lattice T_1 relaxation times for both ^{19}F and ^{199}Hg were measured with the 180–tau–90 inversion recovery technique.

Attempts to observe the ^{201}Hg spectrum in the sample of 1.0 M HgCl$_2$ in *d*-dimethylsulfoxide and in the trimeric perfluoro-*ortho*-phenylenemercury were unsuccessful.

3. Results and discussion

The ^{19}F NMR spectrum of trimeric perfluoro-*ortho*-phenylenemercury, consisting of the two groups of resonances around −121.6 and −155.7 ppm shown in Fig. 2, has been described [5] as that of an AA′XX′ spectrum, a four-spin problem. However, an analysis extracting the coupling constants was not reported. In those molecules showing coupling to the ^{199}Hg, this turns into a five-spin problem. Expansions of each group of resonances are shown in Figs. 3 and 4. The ^{199}Hg spectrum, shown in Fig. 5, of this compound was analyzed as a "triplet of triplets of triplets" [6] to report both the mercury shift and the Hg–F coupling constants. The full analyses of both the ^{19}F and ^{199}Hg spectra of this compound are presented in the following.

The spin-1/2 isotope ^{19}F is 100% naturally abundant while mercury has two NMR-active isotopes. The spin-1/2 isotope ^{199}Hg has a natural abundance of 16.84% while the spin-3/2 isotope ^{201}Hg has a natural abundance of 13.22%.

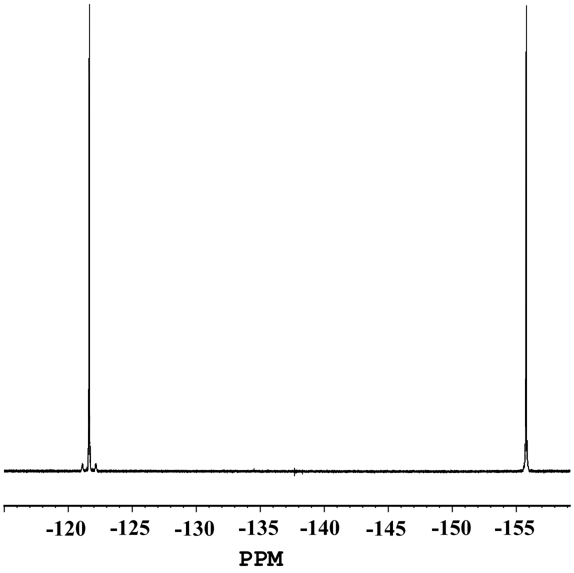

Fig. 2. ^{19}F NMR spectrum of cyclic trimeric perfluoro-*ortho*-phenylenemercury.