



Revisiting HgCl₂: A solution- and solid-state ¹⁹⁹Hg NMR and ZORA–DFT computational study

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ABSTRACT

The ¹⁹⁹Hg chemical-shift tensor of solid HgCl₂ was determined from spectra of polycrystalline materials, using static and magic-angle spinning (MAS) techniques at multiple spinning frequencies and field strengths. The chemical-shift tensor of solid HgCl₂ is axially symmetric ($\eta = 0$) within experimental error. The ¹⁹⁹Hg chemical-shift anisotropy (CSA) of HgCl₂ in a frozen solution in dimethylsulfoxide (DMSO) is significantly smaller than that of the solid, implying that the local electronic structure in the solid is different from that of the material in solution. The experimental chemical-shift results (solution and solid state) are compared with those predicted by density functional theory (DFT) calculations using the zeroth-order regular approximation (ZORA) to account for relativistic effects.

¹⁹⁹Hg spin–lattice relaxation of HgCl₂ dissolved in DMSO is dominated by a CSA mechanism, but a second contribution to relaxation arises from ligand exchange. Relaxation in the solid state is independent of temperature, suggesting relaxation by paramagnetic impurities or defects.

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1. Introduction

Mercury is an element known since ancient times. The first emperor of China, Qin Shi Huang, in an effort to achieve immortality, consumed medicines prepared by Taoist priests with cinnabar (HgS) as an ingredient. When he died, he was buried in a tomb at Xian surrounded by his terra cotta soldiers and “rivers of mercury” [1]. Mercury was also used extensively in the process of hat-making. The inhalation of mercury vapor among workers led, over time, to neurological damage and manifestations such as slurred speech and distorted vision. This apparent mental confusion among members of that profession gave rise to the somewhat clichéd statement, “mad as a hatter” [1].

The interesting and useful features of mercury, frequently given in introductory chemistry texts [2], include the following. As the only metallic element that exists as a liquid at room temperature, it is found in thermometers, sphygmomanometers, electrical switches, and diffusion vacuum pumps. It is used in high-pressure lamps and fluorescent lights as a source of visible and ultraviolet radiation. Its triple point (−38.8344 °C) is a fixed point on the International Temperature Scale 1990. It forms a range of inorganic and organometallic compounds, with many showing biological activity. Although mercury is still commercially useful, toxicity and environmental concerns have restricted the widespread use of mercury and mercury compounds.

The ¹⁹⁹Hg isotope is amenable to observation by nuclear magnetic resonance (NMR) spectroscopy. The spin-½ isotope has a natural abundance of 16.8%, and its receptivity relative to ¹³C at natural abundance is 5.89. The first observation of ¹⁹⁹Hg NMR, the resonance of Hg₂(NO₃)₂ in aqueous solution, was reported in 1951 [3]. Since that report, the NMR properties of a variety of solutions containing mercury compounds have been investigated. A compilation by Wrackmeyer and Contreras [4] contains a substantial tabulation of solution-state ¹⁹⁹Hg chemical shifts.

The ¹⁹⁹Hg relaxation properties of neat mercury-containing liquids and mercury compounds dissolved in solvents ranging from alcohols and water to organic liquids have also been examined [5–9]. For smaller molecules such as dimethylmercury, Hg(CH₃)₂, and for the Hg²⁺ ion in aqueous solution investigated at the low resonance frequencies encountered when using electromagnets with fields of 2.35 T or less, spin–lattice relaxation is generally dominated by the spin–rotation interaction [4,5]. However, many reports indicate that the chemical-shift anisotropy (CSA) mechanism dominates the ¹⁹⁹Hg spin–lattice relaxation in mercury compounds in solution at field strengths greater than 4.7 T [4,6]. Recently, Malariik and Persson [7] have noted that “despite the number of ¹⁹⁹Hg NMR studies undertaken, information on the relaxation behavior of this nucleus is relatively scarce and is mostly related to linear organometallic HgR₂ complexes”. Maciel and Borzo [8] reported that the relaxation in mercuric chloride (HgCl₂) at 1.4 M in ethanol is exponential, with a ¹⁹⁹Hg T₁ of 1.4 s at ambient temperature. A more thorough study of the magnetic-field dependence of spin–lattice relaxation at ambient temperature by Wasylishen et al. [6] demonstrated that

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the ^{199}Hg spin–lattice relaxation of HgCl_2 in an ethanolic solution is dominated by the CSA relaxation pathway [6]. In principle, measurement of the relaxation time together with an independent measurement or estimate of one parameter should allow specification of the correlation time and the magnitude of the chemical-shift anisotropy. However, they found, over the range of fields and temperatures investigated, that it was not possible to estimate either the correlation time or the chemical-shift anisotropy, as an independent measurement of the other parameter was not available.

Most ^{199}Hg spectra are referenced to the position of the resonance of neat $\text{Hg}(\text{CH}_3)_2$. Due to both the high toxicity and “revolting” odor of dimethylmercury, spectroscopists have sought more convenient, practical secondary standards. A 1.0 M solution of mercuric chloride, HgCl_2 , in dimethylsulfoxide (DMSO) has been proposed [9] as an external reference. The resonance position of mercury in this solution is reported to be -1501.6 ppm. As HgCl_2 is a Lewis acid [10–12], its structure in electron-donating solvents may be expected to be different from that of the nearly linear Cl–Hg–Cl (bond angle of 178.9°) in the solid material [13], which may result in a chemical shift that is strongly dependent on concentration and/or temperature. The use of DMSO as a solvent in the present study, as opposed to alcohols or water, is meant to eliminate or minimize hydrogen bonding to the chlorine [14].

The observation of ^{199}Hg NMR in a solid material, obtained with cross-polarization and magic-angle spinning (CP/MAS) [15–18], was first reported by Harris and Sebald [15] for mercury acetate. Although their initial NMR study of the acetate was interpreted in terms of a crystal structure having two inequivalent mercury sites, later studies failed to reproduce the peak doubling reported in Ref. [15]. Upon re-examination by other groups, the spectral structure observed for mercury acetate in the original study was determined to be an artifact caused by a deviation of the angle of rotation from the magic angle [17,18]. In their note on the material, Harris and Sebald [15] remarked that the large number of spinning sidebands observed in the spectrum made mercury acetate “far from ideal as a standard” for cross-polarization. Later work provided alternatives to mercury acetate for setting up ^1H – ^{199}Hg CP/MAS experiments, including $(\text{NET}_4)\text{Na}[\text{Hg}(\text{CN})_4]$ and $(\text{NBu}_4)_2[\text{Hg}(\text{SCN})_4]$ [19] as well as $[\text{Hg}(\text{DMSO})_6](\text{O}_3\text{SCF}_3)_2$ [20], whose spectra could be obtained by cross-polarization from protons. In particular, the resonance of mercury in $(\text{NET}_4)\text{Na}[\text{Hg}(\text{CN})_4]$ is easily detected with cross-polarization, making it a good candidate for optimizing spectroscopic conditions and for use as a secondary standard, with its chemical shift being -434 ppm [19]. Unfortunately, cross-polarization cannot be used in investigations of a species such as HgCl_2 because of the lack of protons. Direct polarization techniques, with their limitations, must be used to obtain the spectra.

The purpose of this investigation is to measure and compare the chemical-shift anisotropy of HgCl_2 in DMSO solution with that of HgCl_2 in the solid state. Such a comparison elucidates structural changes between the two condensed phases. The experimental chemical-shift results are compared with theoretical predictions, providing insights into structure and into strategies for the calculation of chemical shieldings. In addition, an examination of the magnetic-field and temperature dependences of the ^{199}Hg relaxation of HgCl_2 elucidates the mechanisms of relaxation in DMSO solution and the solid state. Analysis of the relaxation properties of the solution provides the molecular rotational correlation time as a function of temperature.

2. Experimental and theoretical methods

The ^{199}Hg NMR data were acquired at various magnetic-field strengths using Bruker Avance 300, DSX 300, MSL 300, DRX 400,

DRX 500, and AV 600 spectrometers. The solution NMR data were obtained from 0.1, 0.555, and 1.0 M samples of HgCl_2 in d_6 -DMSO. NMR data on static polycrystalline samples were measured with a standard Bruker X-nucleus wideline probe with a 5-mm solenoid coil. The ^{199}Hg $\pi/2$ pulse width was $3.75 \mu\text{s}$. Data for determining the ^{199}Hg spin–lattice relaxation (T_1) in solution were acquired with an inversion–recovery sequence (π – τ – $\pi/2$ –acquire) [21]. The significantly longer spin–relaxation times in the solid state were measured by the saturation–recovery technique [21]. Temperature measurements for solution NMR were calibrated with ethylene glycol [22] while the chemical shift of lead nitrate was used to calibrate the solid-state measurements for static [23] and MAS [24–26] experiments.

Simulation of chemical-shift powder patterns for spectra obtained from static samples and from MAS were performed with the solids simulation package (“solguide”) in the TopSpin (Version 2.1) NMR software program from Bruker BioSpin.

Relativistic spin–orbit calculations using the zeroth-order regular approximation combined with density functional theory (ZORA–DFT) were performed using the Amsterdam density functional (ADF) program package [27] and its associated NMR program module [28–31]. The module DIRAC was applied to generate the core potentials for all atom types. Shielding-tensor calculations employed the all-electron ZORA triple-zeta basis with a double set of polarization functions, TZ2P. The local density approximation (LDA) of Vosko, Wilk and Nusair (VWN) [32] was used, augmented with the Becke88–Perdew86 generalized gradient approximation (GGA) (BP86) [33,34].

Calculations were performed on model anionic fragments representing the local structures. The model structures were generated from crystallographic data taken from the Inorganic Crystal Structure Database (ICSD) [35]. To the extent that long-range interactions do not influence the chemical shielding, calculations on fragments should provide an adequate model of the effects of structure on the chemical shielding.

Clusters representing HgCl_2 in DMSO solution were optimized at the same level of theory (ZORA–DFT with VWN and BP86), using an implicit DMSO solution simulation based on the conductor-like screening model (COSMO) implemented in ADF [36–39].

3. Results and discussion

3.1. Solution chemical-shift measurements

As noted in the introduction, the accepted chemical shift reference for ^{199}Hg solution NMR spectroscopy is neat dimethylmercury, defined as $\delta = 0$ ppm. However, the toxicity and odor of this compound often lead to the use of secondary references. Sens et al. [9] propose a 1.0 M solution of HgCl_2 in DMSO as an external reference, with a chemical shift of -1501.6 ppm at ambient temperature. This solution has been used for establishing the chemical-shift scale in this study.

Sens et al. [9] note several issues related to the use of HgCl_2 and other organomercury compounds as external references. These issues include concentration effects, difficulties arising from the dryness of the solvent, pH of the medium, and potential decoupling difficulties. Maliarik and Persson [7] have noted that “the ^{199}Hg chemical shifts can be misleading and non-reproducible unless the temperature is correctly specified or, preferably, the temperature dependence of the chemical shift of the studied species is determined”. To address a possible temperature dependence of the secondary standard, the variation with temperature of the ^{199}Hg chemical shift of HgCl_2 in d_6 -DMSO was carefully evaluated, as shown in Fig. 1. There is a slight temperature dependence of the chemical shift, with the shift reaching a maximum of approxi-

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