2.0 kHz (top) and 3.1 kHz (bottom). Moment analysis[16] gives the chemical shift tensor elements σ_{11}, σ_{22}, and σ_{33} found in Table I, from which the chemical shift anisotropy, $\Delta\sigma$, and the axial asymmetry, η, are calculated. $\Delta\sigma$ is a measure of deviation from spherical symmetry and corresponds roughly to the width of the sideband envelope, while $\eta = 0$ for axially symmetric chemical shift tensors.[17] Linear alkyl Hg(II) complexes with no secondary bonding interactions are known to possess huge shift anisotropies (5000–7000 ppm);[18] accordingly, Harris and Sebald were unable to obtain meaningful solid-state spectra for linear organomercury species.[14] The $\Delta\sigma$ obtained for I, −176 ppm (Table I), indicates a high degree of charge symmetry around Hg(II), reflected further in the nearly axially symmetric value for η. Hg(II) in $Hg(SBu^t)_2$ (II) is surrounded by a very distorted tetrahedron of bridging thiolates in the solid state;[19] consequently, a larger shift anisotropy (−478 ppm) is found. Thus, our data reveal that CPMAS ^{199}Hg NMR is sensitive to changes in geometry *within* a given coordination number. The difference between the isotropic solid-state and solution chemical shifts (≈100 ppm) in both I and II highlights the problems implicit to interpretation of solution NMR in rapidly exchanging Hg–thiolate systems that are prone to ligand dissociation; titration of Hg(II) with 4-chlorothiophenolate shows that the chemical shift is dependent on ligand concentration, approaching the solid-state shift at high RS^-/Hg(II) ratios.[20]

Solid-state spectra for two structurally characterized planar three-coordinate Hg(II) thiolates, $[(n\text{-}C_2H_5)_4N][Hg(SBu^t)_3]$[4,5b] (III) and $[(n\text{-}C_4H_9)_4N][Hg(SPh)_3]$[21] (IV), exhibit substantially higher shift anisotropy (−821 and −978 ppm, respectively) and asymmetry (0.6–0.7) than the tetrahedral thiolates (Table I); from differences in $\Delta\sigma$ and η, three- and four-coordinate complexes are easily distinguished. As seen in the four-coordinate compounds, $\Delta\sigma$ values are also sensitive to geometric variations among planar three-coordinate species. The greater distortion of IV toward a T-shape, relative to the more trigonal complex III, is reflected in a 159 ppm increase in $\Delta\sigma$. The close agreement between solid-state and solution isotropic shifts for both three-coordinate species implies that the predominant species in solution is three-coordinate, corroborating X-ray absorption studies on the $Hg(SBu^n)_3^-$ analogue.[22]

Analysis of the published solid-state spectrum[14] for $Hg(OOCCH_3)_2$ (V) yields a large anisotropy, −1656 ppm, that exceeds the $\Delta\sigma$ for trigonal compounds. Contrary to the four-coordinate label employed by Harris and Sebald, the compound is best described as two-coordinate linear, with three additional secondary bonding interactions [2 + 3] with neighboring acetate oxygen atoms ($Hg–O_1 = 2.06$ Å, $Hg–O_2 = 2.09$ Å, $Hg–O_3 = 2.71$ Å, $Hg–O_4 = 2.76$ Å, $Hg–O_5 = 2.75$ Å; $\angle O_1–Hg–O_2 = 176°$).[9,23] The anisotropy is considerably reduced in comparison to purely linear species, but an order of magnitude greater than that observed for complexes with a primary coordination number of 4. Thus, while the secondary oxygens in $Hg(OOCCH_3)_2$ are well outside the covalent-bonding distance for Hg(II)–O, they influence the observed anisotropy.

The ease with which CPMAS ^{199}Hg NMR can distinguish between three- and four-coordinate Hg(II) thiolates, yield information concerning structural distortion within a given coordination number, and clarify the role of secondary interactions makes it a powerful probe of Hg(II) coordination chemistry.

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Computer Software Reviews

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All in all, this appears to be a useful program for collecting and organizing information obtained from on-line data services. The instruction booklet is clearly written and the program itself is quite easy to learn. However, since the nature of the data provided by the various on-line databases is necessarily restricted, the value of this program to a given user will be a function of how that individual collects, stores, and evaluates information gleaned from the current chemical literature.

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