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^{199}Hg Chemical Shielding Tensor of the Mercurous Ion in Mercurous Nitrate Dihydrate

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Abstract: Using single-crystal NMR, we have measured the full chemical shielding tensor of the Hg_2^{2+} ion in mercurous nitrate dihydrate, the first tensor determination of a metallic species involved in a metal–metal bond. The tensor is almost axially symmetric; its unique element is directed approximately along the long axis of the diaquomercurous ion, but it lies closer to the ligand metal axis than the metal–metal bond. The shielding anisotropy of mercury is, as would be expected for a linear mercury compound, quite large (3203 ppm).

Introduction

Hg differs from Zn and Cd, the other d^{10} metals, in its ability to accommodate an oxidation number of +1. Compounds of mercury(I) consistently form dimeric mercurous ions (Hg_2^{2+}), notable examples of metal–metal bonding. These ions generally are dicoordinate in solution and the solid state,[1] forming linear species of the general formula $(R–Hg–Hg–R)^{2+}$. Differences in Hg–Hg bond order and length in comparable linear systems suggest significant dependence on the electronic properties of the ligands. Although Hg^{2+} forms more stable compounds, the equilibrium constant for the disproportionation of the aqueous solvated metal ion ($Hg_2^{2+} \leftrightarrow Hg + Hg^{2+}$) indicates that the Hg(I) species is the more energetically favored of the two ions in aqueous solution; however, if the ligands are strong Lewis bases such as amines, disproportionation tends to occur. The driving source for this disproportionation has been suggested to be population of antibonding orbitals by ligand-donated electrons.

Angular-dependent mercury solid-state NMR is therefore an excellent choice for examining these properties, since the orientation and magnitude of the Hg chemical shielding tensor is dependent on the electronic distribution about the nucleus. The metal–metal bond in Hg_2^{2+} has almost pure σ character: it is formed predominantly by overlap of the mercury 6s orbitals. Such σ bonds contribute only to the diamagnetic shielding. On the other hand, ligands coordinating the ion form dative bonds to it predominately between p orbitals, providing π and π^* orbitals which will contribute to paramagnetic shielding. Linear mercury complexes are excellent models for the study of the paramagnetic and diamagnetic contributions to the chemical shift, and may also shed light on the stability of the complexes.

Fourier-transform ^{199}Hg NMR has long been a useful spectroscopic tool in the solution state[2] and recently there has been a growing interest in mercury solid-state NMR. The vast chemical shift anisotropies of mercury[3–5] lead to broadening of the liquid state spectra for many relatively low molecular weight species. Interest in the possibility (yet unrealized) of determining the coordination environment of mercury in the bacterial mercury resistance proteins by NMR,[5,6] paralleling the success of ^{113}Cd NMR studies,[7] has motivated high-resolution CP-MAS studies, which, if properly conducted, can yield the principal values of the chemical shielding tensor.[5,8,9] A complete tensor determination, however, usually requires a single crystal study. Such studies have been carried out on only a limited number of mercuric salts.[10]

Even solution studies of mercurous salts have been limited in extent: in the solution state, mercurous salts are broadened by an as yet undefined mechanism, probably either chemical exchange or chemical shielding anisotropy.[11] While mercury–mercury *J* couplings are not observable in the mercurous ion itself, because of chemical equivalence, a solution NMR study[12] of the next highest linear ions in the series (Hg_3^{2+} and Hg_4^{2+}) revealed the largest *J* couplings yet observed, up to 189 kHz. In contrast with liquids, in the solid state, the two mercury atoms in Hg_2^{2+} may be magnetically inequivalent, potentially allowing *J* couplings to be observed even in the mercurous ion.

The present work describes the NMR studies on a single crystal of $Hg_2(NO_3)_2{\cdot}2H_2O$, a compound whose crystal structure has been extensively studied[13,14] and whose proton solid-state NMR has also been examined.[15] To the best of our knowledge this is the first NMR single-crystal experiment performed on a metal–metal bonded species.

Experimental Section

Large single crystals of $Hg_2(NO_3)_2{\cdot}2H_2O$ were grown from a slightly supersaturated solution of commercial mercurous nitrate (Baker Scientific) in approximately 1 M HNO_3, at room temperature. Seed crystals were obtained by slow cooling of a more concentrated solution from 50 °C to room temperature. The crystals then grew quickly and were stable indefinitely when stored dry in a closed container over a beaker of the mother liquor. In the laboratory atmosphere, however, they rapidly acquired a powdery coating and decomposed within 2–3 days. For this reason, prior to the experiment, they were coated with a thin layer of clear varnish (Hard as Nails, Revlon, New York) which effectively prevented decomposition.

NMR measurements were carried out on a well-formed crystal weighing approximately 500 mg. The bounding faces were determined by optical goniometry. The crystal was then mounted on a cell holder located in

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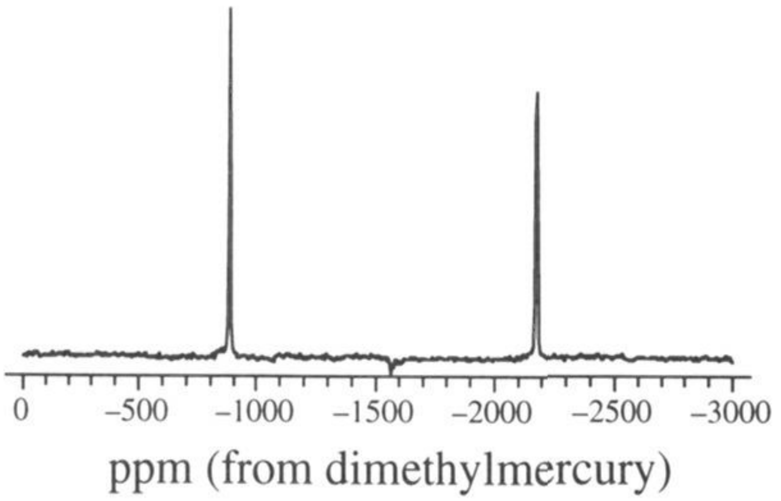

Figure 1. Typical ^{199}Hg NMR spectrum of a single crystal of mercurous nitrate dihydrate, obtained as described in the text. The spectrum corresponds to rotation plot c, angle 345°.

the goniometer head of a doubly tuned probe,[16] and spectra were obtained for a full 2π turn at 7.2° intervals, using a home-built NMR spectrometer operating at a 301.44-MHz ^1H frequency (53.9-MHz ^{199}Hg frequency). The full 2π rotation allows us to compensate for small errors in the orthogonality of the rotation axis with respect to the magnetic field. The same procedure was followed for two other mutually orthogonal orientations. Attempts to cross-polarize the sample were unsuccessful; therefore a simple $\pi/2$ pulse (pulse length 3.0 μs) was applied, and the spectrum was acquired with proton decoupling. Typically 4 or 8 transients were signal averaged with a recycle delay of 20 s and a spectral width of ±125 kHz. To detect possible satellites, several overnight acquisitions were also conducted with a bandwidth of ±250 kHz. All chemical shifts are referenced to dimethylmercury, positive shifts being to higher frequency.

Results

Figure 1 illustrates a typical ^{199}Hg NMR spectrum of a mercurous nitrate dihydrate single crystal taken at 53.9 MHz. Noticeable are the two distinct resonances arising from the two magnetically inequivalent, but chemically identical, mercury nuclei in the unit cell. These molecular sites are generated via the 2_1 symmetry operator. The two mercury atoms within the mercurous ion itself are related by an inversion center. The ^{199}Hg chemical shielding tensor was obtained from three mutually orthogonal plots using standard methods;[17] the structure was refined by using a simultaneous least-squares fit to the full data set. The rotation plots for the ^{199}Hg resonances are shown in Figure 2. Through knowledge of the crystal orientation, established in this case by optical goniometry, the tensor in the goniometer frame was transformed into the more chemically interesting crystal frame of reference. This was chosen with the z axis along the mercury–mercury bond and the x axis perpendicular to the O–Hg–Hg plane. At this point, there was an ambiguity in the assignment of the two magnetically inequivalent molecules to the two 2_1 related molecules in the unit cell; there being no other useful information (such as dipolar splittings), the molecule whose tensor bore the closest relationship to the local molecular symmetry was assigned to that frame.

Figure 3 illustrates the direction of the principal values of the ^{199}Hg shielding tensor. The tensor of the second mercury atom is identical since the mercury atoms are related by inversion symmetry. The ^{199}Hg principal values and direction cosines are listed in Tables 1 and 2. They will serve as the basis for our discussion in the following section. We estimate the uncertainties to be ±20 ppm in the principal values and ±3° in the directions.

Discussion

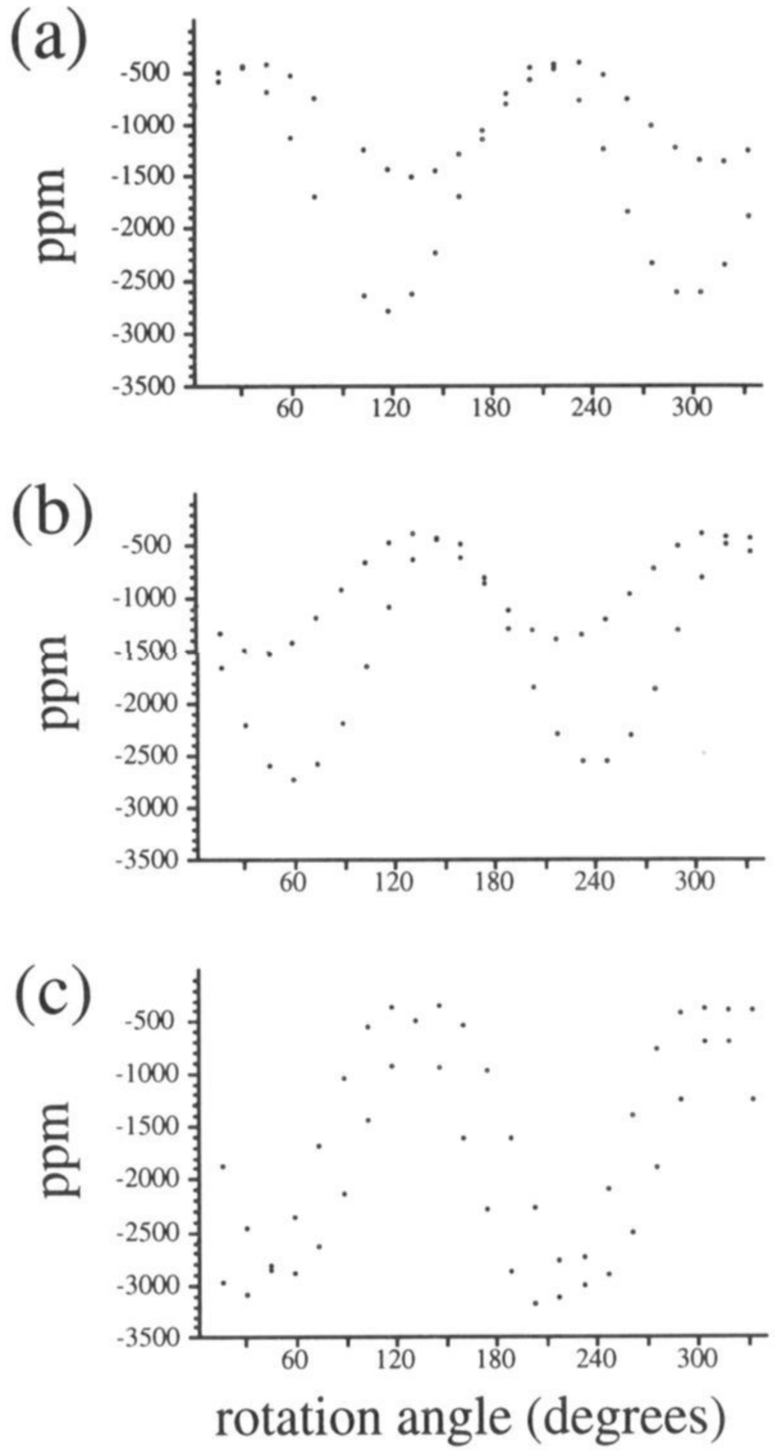

Figure 2. Chemical shifts of the two magnetically inequivalent resonance lines of mercurous nitrate dihydrate, plotted against rotation angle θ, in the three mutually orthogonal rotation plots obtained for this crystal.

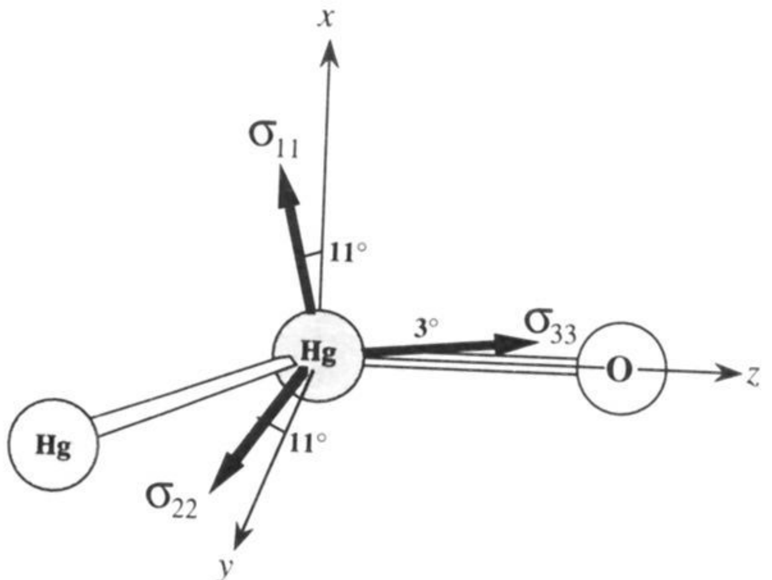

Figure 3. Orientation of the ^{199}Hg chemical shielding tensor in a molecular frame defined as follows: z axis along the Hg–O bond; x axis perpendicular to the O–Hg–Hg plane; y orthogonal to x and z, to form a right-handed basis.

The mercurous nitrate structure is composed of the complex aquo cation [H_2O–Hg–Hg–OH_2] and nitrate anions.[13,14] The hydrogen bonding of the aquo species to the oxygens of the nitrate ion presumably disrupts the linearity of the [H_2O–Hg–Hg–OH_2] dimer, giving rise to an Hg–Hg–O bond angle of 167.5°. As befits a nearly linear cation, the chemical shielding tensor is almost axially symmetric ($\eta = 0.03$), with the σ_{33} element approximately along the long axis of the molecule. However, closer examination

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Table 1. Principal Values and Shielding Parameters of the ^{199}Hg Chemical Shift Tensor of $Hg_2(NO_3)_2{\cdot}2H_2O$, Expressed in Parts per Million with Respect to Dimethylmercury (Estimated Errors Are ±20 ppm)

σ_{11}	−435.2	σ_{iso}	−1533.7
σ_{22}	−496.7	$\Delta\sigma$	−3203
σ_{33}	−3669.3	η	0.03

Table 2. Direction Cosines of the ^{199}Hg Chemical Shift Tensor of $Hg_2(NO_3)_2{\cdot}2H_2O$ and of the Local Molecular Axis System, Given in an Orthogonalized Crystallographic Frame of Reference

	tensor direction cosines				reference frame direction cosines		
	a^*	b	c		a^*	b	c
σ_{11}	−0.2563	0.9035	0.3436	x	−0.0686	0.9472	0.3133
σ_{22}	−0.8714	−0.3698	0.3224	y	−0.9213	−0.1806	0.3443
σ_{33}	0.4183	−0.2168	0.8821	z	0.3827	−0.2650	0.8850

reveals a remarkable feature: the direction of the quasiunique element of the shielding tensor, σ_{33} (Figure 3), is more nearly coincident (within 3°) with the Hg–OH_2 bond vector than with the more plausible Hg–Hg bond vector (deviation approximately 10°). We believe this is a consequence of the nature of the Hg–Hg bond in the mercurous ion. Formed as it is by overlap of 6s orbitals, the field at the position of the nucleus is zero and angular momentum is quenched. The diamagnetic contribution will therefore be small, allowing the paramagnetic contribution (from the p and d orbitals) to be the determining factor to the orientation and magnitude of the shielding tensor. The tensor elements of transition-metal nuclei reflect the environment that is orthogonal to them.[18] Our conjecture here is that the σ character of the metal–metal bond means that it contributes less to the paramagnetic shift than the highly directional π and π^* orbitals involved in ligand binding, and so the unique axis is skewed toward the frame of reference of the ligand–metal rather than the metal–metal bond. The other two tensor elements are almost identical and are directed as predicted by molecular symmetry.

The isotropic shift in the solid state is consistent with that observed for the mercurous ion at infinite dilution in aqueous solution, which has been estimated at −1500 ppm;[12] it is about 200 ppm upfield of mercurous nitrate at high dilution in nitric acid.[11] The magnitude of the chemical shielding anisotropy (3203 ppm) is large but not abnormally so for linear mercury systems; linear Hg(II) thiolates have anisotropies of the order of 4300 ppm,[5] and that of dimethylmercury is even larger.[4] It is doubtful that this shielding anisotropy alone could account for the line width observed for mercurous ions in solution; the observed line width of 700 Hz at the 13.6-MHz Zeeman frequency for an approximately 1 M solution of mercurous nitrate in 1 M nitric acid would require a rotational correlation time of 70 ns, which seems rather slow for an ion of molecular weight only 400. However, if the size of the ion were augmented by bulky ligands, the shielding anisotropy might well be the major contribution to the solution NMR line width.

Despite repeated attempts, we were unable to cross-polarize this compound, either as a single crystal or using magic-angle spinning. This is somewhat curious, because the nearest neighbor protons, while they are distant from the mercury, are less so than is the case in mercuric acetate or the mercury thiolates, which cross-polarize quite efficiently if a long mixing time (5 ms) is used. The feasibility of continuous-wave proton single crystal studies[15] suggest a short proton T_1; possibly the water molecules are hopping in a regime which makes the rotating frame T_1 too short to effect cross-polarization. However, single crystal studies show that the protons exist as nearly isolated spin pairs, with discrete dipolar splittings. Under these circumstances, cross-polarization to the mercury may be expected to show oscillatory behavior, rather than the usual monotonic growth,[19] and it is possible, albeit unlikely, that the maxima of polarization transfer were missed. This remains somewhat of a mystery, albeit an inconsequential one. The short mercury T_1, which was of the order of 5 s, is quite unusual for a rare spin; while some dipolar relaxation of the mercury by the water protons may contribute to it, it is not unlikely also that librational motion and consequent modulation of the large chemical shielding interaction may also contribute.

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