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^{199}Hg Nuclear Magnetic Resonance Studies of the Mercury(II) Halides

PAUL PERINGER
Institut für Anorganische und Analytische Chemie der Universität, Innrain 52a, A-6020 Innsbruck, Austria

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The ^{199}Hg chemical shifts of HgX_2 ($X = Cl, Br, I$) in a number of nonaqueous solvents cover a range of 2400 ppm. Solvent and temperature dependence and the difference of $\delta(Hg)$ for HgX_2 can be related to the donor abilities of the solvent. The solvent effects upon $\delta(Hg)$ are smallest for $HgCl_2$ and largest for HgI_2 (over 1800 ppm).

Introduction

Mercury(II) halide solvent adducts [1] in solution have been studied recently by vibrational spectroscopy [2–4], thermochemical [5–7] and solution X-ray methods [8, 9]. The sensitivity of $\delta(^{199}Hg)$ of mercuric cyanide upon solvents was noted very early [10] and ^{199}Hg NMR has been used to investigate interactions between solvents and organomercurials [11–14].

In view of the intensive and successful application of metal NMR to solvation topics [15], ^{199}Hg NMR studies of HgX_2 ($X = Cl, Br, I$) could be expected to allow interesting comparisons and to complement conclusions obtained by other techniques.

Bonds in HgX_2 are of rather covalent character. Mercuric halides preserve molecular structure in the gas phase, in solution, and with the exception of the red modification of HgI_2, in the solid state. As can be seen from numerous crystalline solvates [1], mercury(II) halides are tractable Lewis acids.

After some controversy [16], linear X–Hg–X groups seem to be accepted in noncoordinating solvents (*e.g.* benzene [17]). Solution X-ray [8] and Raman [3, 4] data (appearance of ν_3) indicate bent structures in donor solvents, the deviation of linear geometries being proportional to donor abilities of the solvent. Bent HgX_2 groups of solvates in the solid state are often associated with two ligands forming a distorted tetrahedron [18], but the number of coordinating molecules in solution is not definite. Four DMSO ligands were assumed for example in solution X-ray on HgX_2 [8]. On the other hand only crystalline solvates of stoichiometries HgX_2L_n ($n = 2$) are known, whilst for ionic mercuric compounds, whose octahedral coordination in solution is established, compounds of composition $Hg^{2+}L_6$ can be isolated.

In addition to solvent coordination, association via halogeno bridged species has to be taken into account [19–22].

Experimental

The mercury compounds used in this investigation were of reagent grade and not further purified before use. The solvents were either of spectral grade and not purified further or of reagent grade and distilled and dried prior to use.

^{199}Hg NMR spectra were recorded in the FT mode on a Bruker WP-80-DS multinuclear magnetic resonance spectrometer operating at 1.88 T. The spectrometer was interfaced to a Bruker Aspect 2000 (24 K 24-bit words) computer. Quadrature phased detection was used. The stability of the applied field was ensured by the use of external deuterium (D_2O) field frequency lock. Except where indicated, measurements were carried out on 0.5 *m* solutions at 308 K. Temperatures were adjusted using a Bruker B VT-1000 variable temperature unit with a temperature stability at the sample better than ±0.3 K. Samples were measured in 10 mm OD tubes with coaxial 4 mm tubes containing the reference substance. The spectral resolution was 2.44 Hz per data point or better.

Chemical shifts in this work have been measured using an aqueous mercuric perchlorate solution (2 mmol HgO/ml 60% aqueous $HClO_4$) as a reference.

The 'high frequency-positive sign' convention of chemical shifts according to the IUPAC convention has been employed [23]. Corrections for bulk susceptibilities were not made.

Results and Discussion

Large solvent effects upon $\delta(^{199}Hg)$ have been observed (Table I). In general more polar solvents cause decreased shielding of the ^{199}Hg nucleus. This corresponds with predictions of the paramagnetic

TABLE I. Chemical Shifts of HgX_2 in Different Media.[a]

	$HgCl_2$	$HgBr_2$	HgI_2
Ethylenediamine		1112.0	566.2
Pyridine	1104.8	762.1	29.2
Aniline			−346.8
Hexamethylphosphoramide	951.2		−694.0
Methylsulfoxide	887.5	322.2	−734.7
Methylsulfoxide[d]	885.5	316.9	−746.8
N,N-Dimethylacetamide	888.5	280.3	−873.0
N,N-Dimethylformamide	859.9	265.7	−853.3
1-Methyl-2-pyrrolidinone	876.5	258.6	−905.9
1,1,3,3-Tetramethylurea	877.5	245.2	−930.5
N-Ethylacetamide	873.7	240.0	−976.3[b]
Ethyl alcohol	894.2	229.6	
Methyl alcohol	870.6	222.5	
2-Ethoxyethanol	861.1	208.9	−992.8
Triethyl phosphate	860.7	201.9	−1034.0
Tributyl phosphate	865.7	191.0	−1062.1
Tributyl phosphate[d]	864.9	184.7	−1076.1
Tetrahydrofuran	839.5	171.2	−1062.6
2-Methoxyethylether	808.6	160.1	−1026.9
Acetonitrile	826.9	115.7[b]	
2-Butanone	804.9	84.5	
n-Butyl acetate	812.3	84.0[b]	
Ethyl acetate	804.5	81.5[b]	
p-Dioxane			−1109.2[c]
Tetramethylene sulfone	772.6[b]	64.0	−1205.2[c]
Nitrobenzene			−1298.1[c,e]

[a] 0.5 *m*, 308 K, in ppm to high frequency of aq. $Hg(ClO_4)_2$. [b] Supersaturated (0.5 *m*). [c] Saturated. [d] 1 *m*. [e] 408 K.

shielding term. Equation (1) of Jameson and Gutowsky [24] simplified in neglecting d-orbital terms states:

$$\sigma_p = -(2e^2\hbar^2\mu_0/12\pi\Delta E m^2)\langle r^{-3}\rangle P_u \qquad (1)$$

P_u, representing the p-orbital populations, depends largely on the donor qualities of the ligands: P_u has a maximum of 1 for linearly bonded mercury whilst being 3/2 for 3 or 4 coordinate mercury.

A good correlation can be found between the solvent dependence of $\delta(^{199}Hg)$ and the solvent dependence of vibrations of HgX_2 [2–4]. In analogy to the stretching modes, the solvent shifts can be related to Gutmann's donor numbers [25] of the solvents. Shifts to lower frequencies with increasing solvent polarity have been observed on the other hand for various organomercurials [12–13]. Solvent mercury coordination has been suggested for explanation [14] (solid solvates are known for diorganomercurials R_2Hg with electron withdrawing groups R [26–27]) although the direction of shifts is opposite to that expected from eq. (1). In a recent compilation of data for Me_2Hg and MeHgCl this effect was therefore discussed in terms of interactions of the quadrupolar Me_2Hg with the fields produced by the polar solvents in a solvation shell [28].

The solvent effects for HgX_2 are larger than for organomercurials according to the smaller polarity of the Hg–C bond. Along with the diminishing positive charge of the mercury atom the molecule should be less sensitive to perturbation upon interaction with donor molecules.

The ionic character of the Hg–X bonds, estimated from the classical electronegativity scale of Pauling is: Hg–Cl 26%, Hg–Br 19%, Hg–I 9%. The usual tendency to solvate formation is $HgCl_2 > HgBr_2 > HgI_2$. For example HgI_2 can be recrystallized from DMSO, whilst $HgCl_2$ and $HgBr_2$ form crystalline solvates. Accordingly heats of solvation were determined [5] to increase in the order $HgI_2 < HgBr_2 < HgCl_2$ and the solvent dependence of the HgX_2 stretching modes is largest for $HgCl_2$ and smallest for HgI_2 [2–4]. Rather surprisingly therefore the NMR effects for HgX_2 are largest for HgI_2 and smallest for $HgCl_2$. Similar results have been obtained for mixed cyano–halogeno–mercury compounds XHgCN (X = Cl, Br, I) [29]. The situation may be compared with the effect on $\delta(^{199}Hg)$ going from HgX_2 to RHgX (R = alkyl, aryl, CN). Formation of a C–Hg bond results

TABLE II. Shifts of HgX_2, $Hg(CN)_2$ and XHgCN.[a]

$Hg(CN)_2$	1034[b]
ClHgCN	997[b]
$HgCl_2$	887[c]
BrHgCN	828[b]
IHgCN	520[b]
$HgBr_2$	322[c]
HgI_2	−735[c]

[a] 0.5 *m* in DMSO, 308 K, in ppm to high frequency of aq. $Hg(ClO_4)_2$. [b] Taken from Ref. 29. [c] This work.

in confining the chemical shifts of RHgX to a range of only a few hundred ppm (Table II). The size of this range depends on the nature of R (Me: 305 ppm [30], Ph: 270 [31], CN: 477 [29],) but no theoretical explanation seems to exist for this *trans* influence.

The shift associated with the introduction of the Hg–C bond appears to be largest for $HgI_2 > HgBr_2 > HgCl_2$.

The differences of $\delta(^{199}Hg)$ of HgX_2 (X = Cl, Br, I) in some definite solvent decreases with increasing solvent–HgX_2 interactions (Pyridine: 1076 ppm, Tributyl phosphate: 1925, Tetramethylene sulfone: 1975).

As has been already noted for ionic mercury compounds [33], ^{199}Hg chemical shifts are very sensitive to temperature and concentration. Some examples for the concentration dependence of $\delta(^{199}Hg)$ are given in Table 1. Table III shows the rather complicated temperature dependence of $\delta(^{199}Hg)$. The effects are again largest for HgI_2 and smallest for $HgCl_2$. For $HgBr_2$ and HgI_2 solvents with increasing donor numbers lead to increasing shifts to lower frequencies while the opposite was observed for $HgCl_2$. Several factors are expected to contribute to these effects. Firstly, alteration of the separation of the ground and excited states [34], secondly, alteration of the number of solvating molecules and thirdly a competition of solvation and molecular association.

In solution (as in the gas or the molten state) mixtures of HgX_2 and HgY_2 (X, Y = Cl, Br, I; X ≠ Y) are known to be in equilibrium with the respective mixed species [35], *e.g.*:

$$HgCl_2 + HgI_2 \rightleftharpoons 2HgClI$$

According to preliminary results exchange of these species is rapid on the NMR time scale.

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TABLE III. Temperature Dependence of Chemical Shifts.[a]

		$HgCl_2$	$HgBr_2$	HgI_2
Pyridine	0.5 *m*[b]	68	−92	−283
Methylsulfoxide	0.5 *m*[b]	19	−74	−241
Methylsulfoxide	0.5 *m*[c]	15	−75	−235
Methylsulfoxide	1 *m*[b]	17	−71	−243
Methylsulfoxide	1 *m*[c]	15	−73	−234
Tributyl phosphate	1 *m*[b]	−3	−68	−176

[a] In Hz. [b] ν318 K − ν308 K. [c] ν328 K − ν318 K.

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