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A ^{199}Hg NMR SPECTROSCOPIC STUDY OF TWO AND THREE-COORDINATE METHYLMERCURY(II) COMPLEXES, [MeHgL]NO_3

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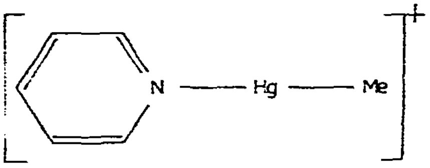
Summary

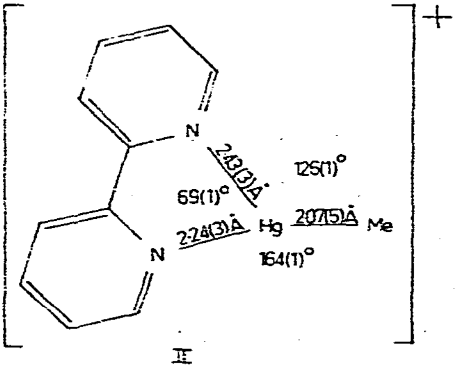
^{199}Hg NMR spectra are reported for the complexes [MeHgL]NO_3 containing either two- (e.g. L = pyridine) or three-coordinate mercury (e.g. L = 2,2'-bipyridyl). For unidentate and bidentate ligands of similar basicity chelation with bidentate ligands to give three-coordinate mercury results in upfield shifts of ^{199}Hg resonances from that of the linear complexes. For complexes of unidentate ligands shifts correlate with changes in base strength of the ligands, and methyl substitution in the 2 position of pyridine appears to result in an upfield shift of ca. 30 ppm. Effects of substitution in the 2 position are very strong in complexes of unidentate 2-benzylpyridine and 3,3'-dimethyl-2,2'-bipyridyl. Comparison of the ^{199}Hg shifts with J(^{1}H-^{199}Hg) shows the coupling constant to be insensitive to substitution in the 2 position in linear complexes and is a function only of the ligand base strength.

Introduction

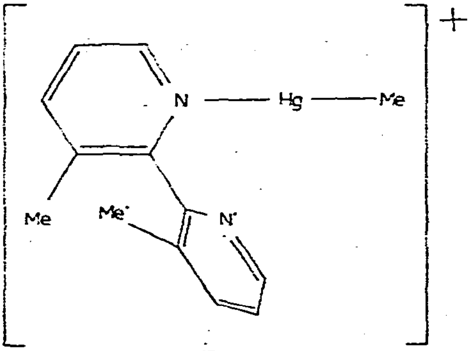
Methylmercury(II) complexes involving linear and three-coordinate mercury have been reported recently [1-3]. Linear complexes [MeHgL]NO_3 were obtained with pyridine and substituted pyridines (I), and an X-ray crystal structure of the 2,2'-bipyridyl complex (II) showed presence of unsymmetrical three-coordinate mercury [3]. Methyl substituted 2,2'-bipyridyls and 1,10-phenanthrolines gave complexes whose ^{1}H NMR spectra indicated structures related to II, except for 3,3'-dimethyl-2,2'-bipyridyl (3,3'-dmbpy) which functions as a unidentate (III) because steric interaction between 3,3'-methyl groups prevents coplanarity of the rings required for chelation [2].



I



II



III

^{199}Hg NMR spectra for these complexes have been measured, as ^{199}Hg shifts are very sensitive to the immediate environment of mercury [4-6], and might be expected to yield empirical information about structures of the complexes.

Results and Discussion

Comparisons of ^{199}Hg NMR shifts, $J(^1H-^{199}Hg)$, and pKa of LH^+ are given in Table 1 and Fig. 1. All of the complexes have δ ^{199}Hg upfield from $MeHgNO_3$, indicating increased shielding on coordination of ligands.

In ^{1}H NMR spectroscopic studies correlations between values of $J(^1H-^{199}Hg)$ for a large range of MeHgX compounds and values of stability constants of MeHgX [9-11], pKa of HX [10-15], or electronegativity of X [15,16] have been explained by assuming that the relative magnitude of the coupling constant is due mainly to the Fermi contact interaction, specified by the s-electron density on the coupled nuclei and carbon [15,16]. An increase in electronegativity of X is expected to increase the s character of the hybrid orbital of mercury involved in bonding to carbon and to increase the effective nuclear charge for the mercury 6s orbital resulting on a contraction of that orbital [8,15,16]. These effects are consistent with the increase in coupling constant observed with increasing electronegativity of X. Thus, for $[MeHgL]NO_3$, $J(^1H-^{199}Hg)$ increases with decreasing pKa of LH^+ with separate relationships for unidentate and bidentate ligands, as a lower basicity of L corresponds to a greater "electronegativity" of the nitrogen donor atom of L [2] [Table 1, Fig. 1(a)].

Application of this approach to the ^{199}Hg NMR results is not straightforward. Thus, plots of δ ^{199}Hg vs pKa of LH^+ (Fig. 1(b)] and $J(^1H-^{199}Hg)$ [Fig. 1(c)] give only approximately linear correlations for the unidentate ligands, with 2-benzylpyridine (2-Bzlpy) and 3,3'-dmbpy well removed from the correlations, and "correlations" for the bidentate ligands are poor.

TABLE 1

NMR PARAMETERS FOR THE METHYLMERCURY GROUP IN COMPLEXES [MeHgL]NO$_3$, TOGETHER WITH pKa of LH$^+$

Complex	$\lvert J(^{1}H-^{199}Hg)\rvert$[a,b]	δ ^{199}Hg[c]	pKa of LH^{+}[a]
MeHgNO$_3$	251.8		
[MeHg(py)]NO$_3$	229.6	-87	4.09
[MeHg(2-mpy)]NO$_3$	227.9	-132	4.71
[MeHg(3-mpy)]NO$_3$	228.2	-91	4.49
[MeHg(4-mpy)]NO$_3$	227.5	-98	4.72
[MeHg(2,4-dmpy)]NO$_3$	225.7	-148	5.44
[MeHg(2,6-dmpy)]NO$_3$	225.2	-171	5.28
[MeHg(2-Bzlpy)]NO$_3$[d]	229.6	-165	3.97
[MeHg(bpy)]NO$_3$	238.8	-236	3.18
[MeHg(6,6'-dmbpy)]NO$_3$.H$_2$O[d]	235.9	-255	3.99
[MeHg(5,5'-dmbpy)]NO$_3$	237.0	-229	3.76
[MeHg(4,4'-dmbpy)]NO$_3$	235.1	-278	3.97
[MeHg(3,3'-dmbpy)]NO$_3$	230.4	-187	3.59
[MeHg(phen)]NO$_3$[e]	239.8	-351	4.03

[a] From ref. 2. [b] 0.1M solutions in CD$_3$OD at 100 MHz. Accuracy to ca. ± 0.5 Hz. The sign of the coupling constant is assumed to be negative [7,8]. [c] ca. 0.1M solutions in CH$_3$OH. Shifts are ppm upfield from MeHgNO$_3$. Accuracy to ± 2 ppm. [d] 2-Bzlpy = 2-benzylpyridine, 6,6'-dmbpy = 6,6'-dimethyl-2,2'-bipyridyl, other ligands similarly abbreviated. [e] Complexes of methyl substituted 1,10-phenanthrolines [1,2] were insufficiently soluble for ^{199}Hg NMR.

In Fig. 1(b) the shifts for linear complexes reflect greater shielding of mercury with the more basic ligands (——), and suggest that methyl substitution in the 2 position may also result in an additional upfield shift of ca. 30 ppm as separate correlations can be drawn for py, 3-mpy, 4-mpy, and 2-mpy, 2,4-dmpy (---). Double substitution, as in 2,6-dmpy, causes a further 30 ppm shift.

Two linear complexes, 2-Bzlpy and 3,3'-dmbpy, correlate neither with the other linear complexes nor with the chelated ligands, and have values of δ ^{199}Hg higher than complexes of unidentate ligands of similar basicity. In addition to a possible effect from substitution in the 2 position, as observed for methylpyridines, the high values may indicate presence of a weak interaction between mercury and the aromatic ring similar to that present in some γ-substituted propyl mercurials, e.g. $ClHgCH_2C(Me)(OMe)CH_2(p\text{-}OMePh)$ which has Hg...Ph 3.05Å [17], and suggested by Sens et al. to account for the ^{199}Hg resonance of Me_2Hg in benzene (50.4 ppm upfield from neat Me_2Hg [6]). Increased shielding of the MeHg(II) proton in these complexes (0.26-0.51 ppm upfield from all other complexes [2]) can then be explained as a result of a diamagnetic ring current effect with the aromatic ring interacting with mercury and thus close to the methyl group.

The correlation between δ ^{199}Hg and J(^{1}H-^{199}Hg) for linear complexes is as expected [Fig. 1(c)]. Complexes with a greater effective nuclear charge on mercury, i.e. ones with lower δ ^{199}Hg and lower pKa of LH^+, have higher values of J(^{1}H-^{199}Hg). The complexes of 2-Bzlpy and 3,3'-dmbpy are again exceptions, but when J(^{1}H-^{199}Hg) is plotted against pKa these complexes conform with the other linear complexes. This suggests that J(^{1}H-^{199}Hg) is insensitive to some of the factors determining the ^{199}Hg chemical shift, in particular, substitution in the 2 position of pyridine.

The bpy, 6,6'-dmbpy, 5,5'-dmbpy, and 4,4'-dmbpy and phen ligands have been shown by ^{1}H NMR spectroscopy to give three-coordinate mercury [2]. For these complexes the shifts correlate less well with pKa, and J(^{1}H-^{199}Hg) is higher than for linear complexes although the mercury atom is more shielded. As for the complexes of 2-Bzlpy and 3,3'-dmbpy J(^{1}H-^{199}Hg) may be insensitive to some of the factors determining the ^{199}Hg chemical shift.

Experimental

The ^{199}Hg spectra were obtained at 16.08 MHz, on a Bruker HX-90 modified for multi-nuclear operation, using the PFT technique. Modifications consisted of addition of a Bruker Multi-nuclear Accessory combined with a Schomandl frequency synthesizer type ND 100M (300 Hz - 100 MHz). An external D_2O lock was used and all spectra were proton noise decoupled. Spectra were recorded using a 90° pulse (ca. 18 μsec), 5000 Hz sweep width, 2.4 or 8K data points giving pulse repeat times of

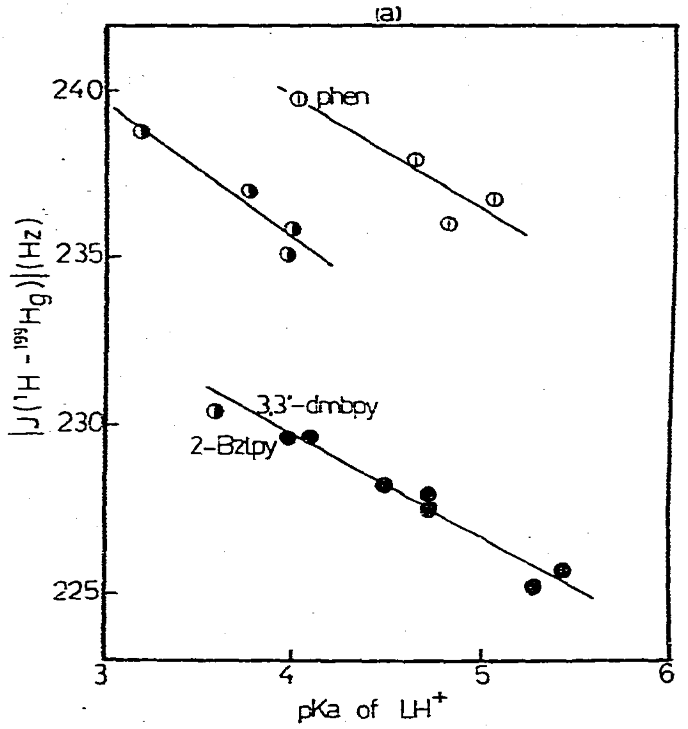
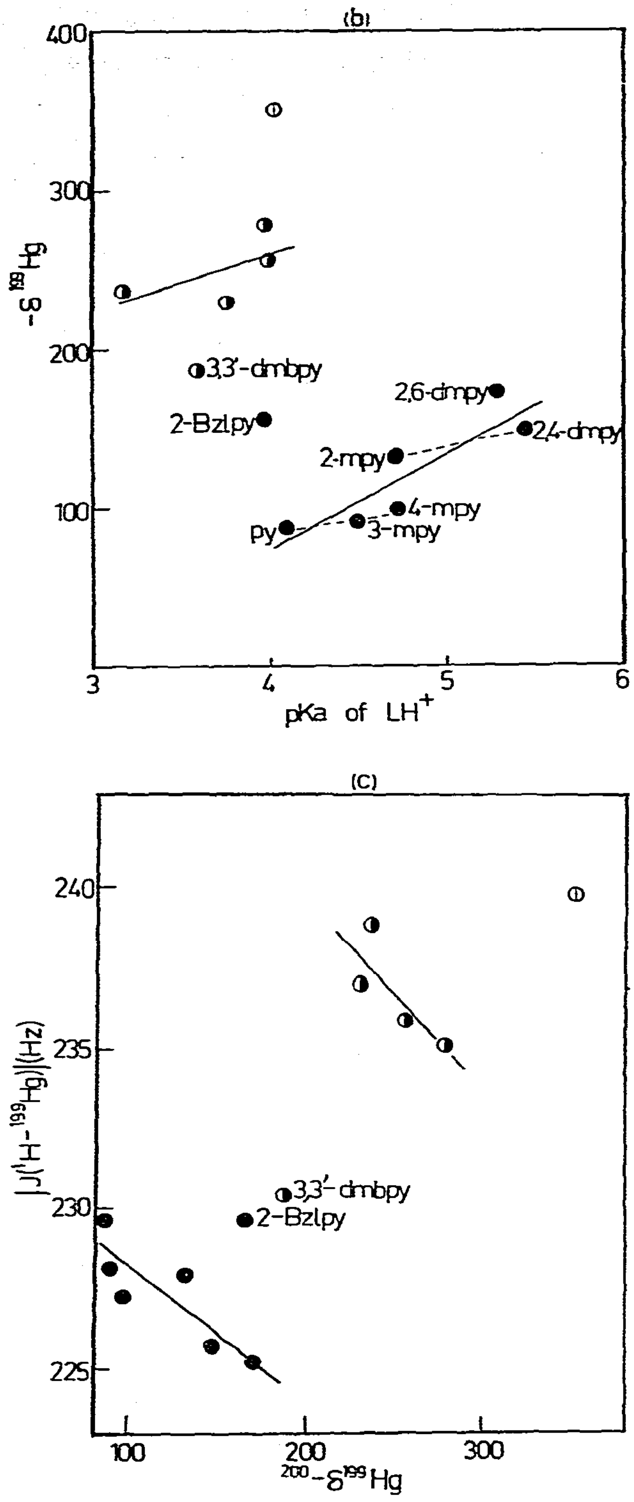


Fig. 1. Relationship between (a) $|J(^1H-^{199}Hg)|$ and pKa of LH^+, (b) δ ^{199}Hg and pKa of LH^+, (c) $|J(^1H-^{199}Hg)|$ and δ ^{199}Hg in the complexes $[MeHgL]NO_3$, where L = pyridines (●), 2,2'-bipyridyls (◑), and 1,10-phenanthrolines (⦶). Least-squares lines are drawn for each group of ligands, with 3,3'-dmbpy excluded in (a), and both 3,3'-dmbpy and 2-Bzlpy excluded in (b) and (c).


(b)
400
300
200
100
$-\delta^{199}Hg$
3,3'-dmbpy
2-Bzlpy
2,6-dmpy
2,4-dmpy
2-mpy
4-mpy
py
3-mpy
3
4
5
6
pKa of LH^+
(c)
240
235
230
225
$|J(^1H-^{199}Hg)|$(Hz)
3,3'-dmbpy
2-Bzlpy
100
200
300
$^{200}-\delta^{199}Hg$

ca. 2, 4 or 8 secs respectively. Chemical shifts are referred, for convenience, to external $MeHgNO_3$ in CH_3OH. Samples were prepared using spectroscopic grade methanol. Concentration effects on shifts, although noticeable, have been ignored as these are not significant compared with the range of shifts between compounds.

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