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Solid-State ^{31}P CP-MAS NMR Study of Phosphine Complexes of Mercury(II)

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The solid-state ^{31}P CP-MAS NMR spectra of several phosphine complexes of mercury(II) with known crystal structures have been measured. In addition, some simple valence bond calculations were performed and an attempt was made to relate calculated s characters of bonding orbitals to the measured Hg–P coupling constants. The correlation predicted by an approximation to the Fermi contact term was not found.

Introduction

The ongoing NMR study of phosphine complexes of mercury(II) has resulted in the accumulation of many data, which have been interpreted in terms of several empirical trends. For example, the following trends have been found that for complexes of the type HgX_2P_2 (P = triorganophosphine, X = anionic ligand): (a) for a given coordinated X, ^1J(Hg–P) increases with increasing phosphine basicity[1–7] but if X is noncoordinating, ^1J(Hg–P) decreases;[8,9] (b) for a given phosphine, ^1J(Hg–P) decreases with increasing Lewis basicity of the coordinated anion;[1,3–6,9–11] (c) ^1J(Hg–P) often varies in direct proportion to the coordination chemical shift, Δ ($\Delta = \delta$(complexed phosphine) − δ(free phosphine)).[1,3–6,10]

These empirical trends have been difficult to interpret in terms of current theory except in a qualitative sense. The reasons for the difficulty include the enormity of the task of carrying out MO calculations on large molecules with heavy atoms, the paucity of information from X-ray studies, and the uncertainty in relating the NMR data obtained from solution studies to the solid-state structures of the compounds. In addition, observation c has no firm theoretical basis at this time.

In spite of these problems, Bürgi et al.[12,13] have attempted to rationalize the solution NMR data of some complexes in terms of their structures in the solid state. As part of their study they made use of some extended Hückel MO (EHMO) calculations on the model compound $HgCl_2(PH_3)_2$. These authors concluded that ^1J(Hg–P) could be expressed as a function of the P–Hg–P and X–Hg–X angles and that it is almost exclusively determined by the Fermi contact mechanism. However, as pointed out by the above authors, the possible differences in the molecular conformation in solution and in the solid state, the approximations involved in the EHMO method, and the choice of the model compound (which itself is an approximation of the compounds of interest) mean that the results must still be considered somewhat qualitative.

A way around the solution–solid-state problem can be found in the application of high-resolution magic angle spinning (MAS) ^{31}P NMR to solid-state samples. The MAS technique, usually used with cross-polarization (CP-MAS), has found many applications in ^{13}C NMR in organic systems,[14] but little use of it has been made of it in ^{31}P NMR and it has never been used to study the compounds described herein. We have found that under favorable circumstances, the resolution of the spectra obtained in the solid state approaches the resolution of those obtained in solution (vide infra).

In this paper we present a ^{31}P CP-MAS NMR study of some phosphine complexes of mercury(II) whose crystal structures are known. Some simple valence bond calculations are presented, and an attempt is made to relate the observed Hg–P coupling constants to the Fermi contact term.

Results and Discussion

Bonding in the Complexes. If only s and p valence orbitals are used by the Hg and P atoms for their σ basis sets, a calculation of the s character (S_i) of each of the hybrid atomic orbitals is possible.[15] The orthogonality of the orbitals requires that not all arbitrary sets of interbond angles are possible, and this leads to the calculation of the s characters from the interbond angles. For a given set of angles, the result is unique. Normalization ($\sum_i S_i = 1$) provides a check of the self-consistency of the calculation.

The results of these calculations are presented in Table I. It can be seen that the σ bonding at P can always be described in terms of an s and p orbital basis set. In contrast, this is true for Hg in only some of the complexes. The validity of the σ scheme implies nothing about the possibility of π bonding except that the d orbitals cannot be involved in the σ system and therefore may be available for π bonding.[16]

The complexes fall into two categories: one containing complexes for which $\sum_i S_i$ at Hg is very close to unity and one in which $\sum_i S_i$ deviates significantly from unity. The former group consists of those complexes with soft[18] anionic ligands whereas the latter group contains complexes with hard anions, that is Cl^- and the O donors. The difference arises from the different overlap characteristics of the hard and soft ligands with the soft Hg acceptor. The more diffuse orbitals of the soft donors are capable of overlapping well with the Hg orbitals, and the best overlap is obtained when the orbitals are directed along the internuclear axes. Bending these bonds would require energy, which, it appears, would be large in comparison to the crystal packing forces. The result is that the interorbital angles are described well by the interatomic angles. The hard anions, on the other hand, have much lower valence orbital energies and therefore do not form strong covalent bonds with Hg. The energy gained by maximizing overlap becomes less significant so that the interligand angles need not reflect the hybridization of the Hg atom. It is, however, expected that the s character would be concentrated in the Hg–P bonds

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(1) Alyea, E. C.; Dias S. A.; Goel, R. G.; Ogini, W. O.; Pilon, P.; Meek, D. W. *Inorg. Chem.* **1978**, *17*, 1697.
(2) Keiter, R. L.; Grim, S. O. *Chem. Commun.* **1968**, 512.
(3) Grim, S. O.; Lui, P. J.; Keiter, R. L. *Inorg. Chem.* **1974**, *13*, 342.
(4) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*.
(5) Grim, S. O.; Shah, D. P.; Haas, C. K.; Ressmer, J. M.; Smith, P. M. *Inorg. Chim. Acta* **1979**, *36*, 139.
(6) Alyea, E. C.; Dias, S. A. *Can. J. Chem.* **1979**, *57*, 83.
(7) Allman, T.; Goel, R. G. *Can. J. Chem.* **1984**, *62*, 615.
(8) Allman, T.; Goel, R. G. *Can. J. Chem.* **1984**, *62*, 621.
(9) Colton, P.; Dakternieks, D. *Aust. J. Chem.* **1981**, *34*, 323.
(10) Allman, T.; Goel, R. G.; Pilon, P. *Can. J. Chem.* **1979**, *57*, 91.
(11) Colton, P.; Dakternieks, D. *Aust. J. Chem.* **1980**, *33*, 955.
(12) Bürgi, H. B.; Kunz, R. W.; Pregosin, P. S. *Inorg. Chem.* **1980**, *19*, 3707.
(13) Bürgi, H. B.; Fischer, E.; Kunz, R. W.; Parvez, M.; Pregosin, P. S. *Inorg. Chem.* **1982**, *21*, 1246.
(14) Andrew, E. R. *Philos. Trans. R. Soc. London, A* **1981**, *299*, 505.
(15) Grim, S. O.; Plastas, H. J.; Huheey, C. L.; Huheey, J. E. *Phosphorus Relat. Group V Elem.* **1971**, *1*, 66.
(16) Some ultraviolet photoelectron spectroscopic data indicate that there is little, if any, interaction between the aromatic π orbitals and the P 3d orbitals.[17] It is also very unlikely that there is any π contribution to the Hg–P bonds.[4]
(17) Weiner, M. A.; Lattman, M. *J. Org. Chem.* **1975**, *40*, 1292.
(18) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. For a very comprehensive overview of HSAB see: Pearson, R. G., Ed. *Hard and Soft Acids and Bases*; Dowden, Hutchinson and Ross, Inc.: Stroudsburg. PA, 1973.
(19) Kunz, R. W. *Helv. Chim. Acta.* **1980**, *63*, 2054. See also: Mitchell, T. N.; el-Behairy, M. *Ibid.* **1981**, *64*, 628.

0020-1669/86/1325-3202$01.50/0

Table I. Summary of s Character Calculations[a]

	s characters of Hg orbitals					s characters of P lone pairs					
compd	P_1	P_2	X_1	X_2	$\sum S_i$	P_1	$\sum S_i$	P_2	$\sum S_i$	$10^2 S_{Hg}S_{P_1}$	$10^2 S_{Hg}S_{P_2}$
$HgCl_2(PPh_3)_2$	0.278	0.175	0.100	0.160	0.713	0.314	0.993	0.326	0.996	8.73	5.71
$HgBr_2(PPh_3)_2$	0.387	0.177	0.202	0.229	0.994	0.312	0.994	0.279	0.993	12.1	4.9
$HgI_2(PPh_3)_2$	0.251	0.226	0.213	0.294	0.985	0.370	0.995	0.353	0.983	9.29	7.98
$Hg(SCN)_2(PPh_3)_2$	0.417	0.294	0.177	0.121	0.949	0.323	0.989	0.301	1.003	13.5	8.85
$Hg(CN)_2(PPh_3)_2$	0.375	0.152	0.244	0.228	0.999	0.330	0.995	0.340	0.980	12.4	5.17

[a] Only those complexes with a $\sum_i S_i$ value that is close to unity are reported. The atom labeling is the same as in the original papers. See the references listed in Table III.

Table II. Summary of s Character Calculation Assuming Equivalent Hg–P Bonds (See Text)

compd	P–Hg–P angle, deg	s character of the Hg orbitals
$HgCl_2(PPh_3)_2$	134.1	0.41
$Hg(NO_3)_2(PPh_3)_2$	131.76	0.40
$Hg(OAc)_2(PPh_3)_2$	123.68	0.36
$Hg(OAc)_2(PCy_3)_2$	153.0	0.47
	146.5	0.45
$Hg(ClO_4)_2(PCy_3)_2$	170.7	0.50

Figure 1. ^{31}P CP-MAS NMR spectra of $Hg(CN)_2(PPh_3)_2$ (upper trace) and $Hg(NO_3)_2(PPh_3)_2$. The effects of the lower symmetry of the cyano complex are clearly shown. The very small, outermost peaks in the upper spectrum are spinning side bands.

in these complexes, and this is reflected in their generally larger P–Hg–P angles. If the two Hg–P bonds are equivalent by symmetry then their s character can be calculated from the P–Hg–P angle.[15] We have assumed that the phosphines are equivalent although only in the nitrato complex is this strictly true. Results based upon this assumption are presented in Table II.

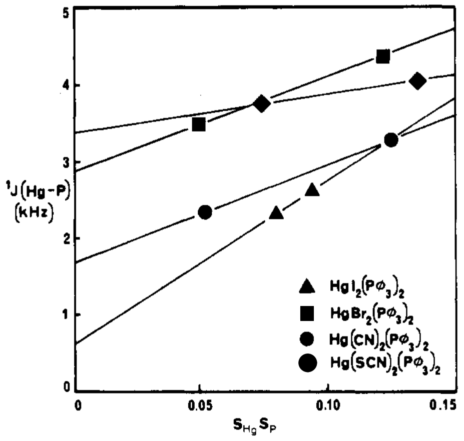

Figure 2. Variation of ^1J(Hg–P) with the product of the s characters in the Hg–P bonding orbitals. The assumption was made that the higher s character is associated with the higher coupling constant although this cannot be independently confirmed. The unit cell constants for the CN and SCN complexes were determined for single crystals taken from the NMR samples in order to confirm that the structures of the samples were identical with the reported structures.

^{31}P CP-MAS NMR Spectra. A summary of the NMR results is given in Table III. Figure 1 shows some typical ^{31}P spectra of powdered samples. The line widths are larger than one would expect to find in the corresponding solution spectra even with careful setting of the instrumental parameters. However, if the chemical shift differences and the coupling constants are large enough, a useful spectrum can be obtained. There was found to be some variation in the line widths in the 50–250 Hz range, and this may reflect varying degrees of restricted motions within the crystal lattices, the narrower lines corresponding to the more rigid lattices.[14]

There is good agreement between the chemical shifts measured in solution and those measured in the solid state. There is much more variation in ^1J(Hg–P), not only between the solution and solid-state values but also between the two values obtained for a given complex with inequivalent phosphines (cf. $Hg(CN)_2(PPh_3)_2$). This inequivalence is due to distortions from the C_{2v} symmetry, which is found in solution. The lower symmetry makes $^2J(P_1–P_2)$ directly observable. Values of this parameter fall within what is generally found to be the normal range.[20] It is expected

Table III. ^{31}P NMR Data

compd	δ(soln)	δ_A(solid)	δ_B(solid)	^2J(A–B), Hz	^1J(Hg–P)(soln), Hz	^1J(Hg–A)(solid), Hz	^1J(Hg–B)(solid), Hz	ref to cryst struct
$HgCl_2(PPh_3)_2$	28.3	30.5	28.7	160	4680	4730	5070	24
$HgBr_2(PPh_3)_2$	22.2	20.8	17.2	160	4230	3480	4380	24
$HgI_2(PPh_3)_2$	7.2	6.1	1.4	150	3070	2340	2620	23
$Hg(CN)_2(PPh_3)_2$	17.9	21.0	16.2	110	2620	2330	3160	13
$Hg(SCN)_2(PPh_3)_2$								
α	31.3	28.7	31.9	160	3730	4050	3770	22
β	31.3	33.9			3730	3700		
γ	31.3	33.5	24.4	180	3730	3700	3590	
$Hg(OAc)_2(PPh_3)_2$	34.4	36.0	32.0	240	5510	4800	5160	26
$Hg(NO_3)_2(PPh_{32}$	40.3	39.3			5930	5560		13
$Hg(OAc)_2(PCy_3)_2$	54.7	64.1			5160	5160		25
$Hg(ClO_4)_2(PCy_3)_2$	78.7	76.1	70.6	180	3800	3390	3350	25

[a] The sold-state ^{31}P resonances are arbitrarily labeled A and B, A being the P atom with the greater chemical shift.

that $^2J(P_1-P_2)$ should show an inverse dependence upon Δ^3E, the triplet excitation energy,[4] and that the largest excitation energies should be associated with the most basic ligands such as Br, I, SCN, and CN. This is borne out by the observation that the hard donor complexes give rise to much higher values of $^2J(P_1-P_2)$ than do the others. The cyano complex has a very small value which is in keeping with its ability to act as a strong donor.

The data obtained to date[4,13] suggest that the Fermi contact term is dominant in determining $^1J(\text{Hg-P})$. Equation 1 gives an expression of this term that utilizes a valence bond description of the bonding, where $|\psi_s(0)|^2$ is the s electron density at the

$$^1J(\text{Hg-P}) \propto |\psi_s(0)_{\text{Hg}}|^2|\psi_s(0)_{\text{P}}|^2 S_{\text{P}}S_{\text{Hg}}(\Delta^3E)^{-1} \qquad (1)$$

nucleus, S is the s character of the hybrid orbital forming the bond and Δ^3E is a mean triplet excitation energy.

Most of these factors are difficult to calculate, but in the context of one molecule with two Hg–P coupling constants several simplifications can be made. The values of $|\psi_s(0)_{\text{Hg}}|^2$ and Δ^3E must be identical for both coupling constants. In addition $|\psi_s(0)_{\text{P}}|^2$ for each phosphine cannot differ significantly.[21] It follows therefore that a plot of $S_{\text{P}}S_{\text{Hg}}$ vs. $^1J(\text{Hg-P})$ for each of the Hg–P bonds in a given molecule should define a line that passes through the origin. The slope of the line would be the product of the other factors. Such a plot is given in Figure 2. The assumption was made that the larger value of $S_{\text{P}}S_{\text{Hg}}$ was associated with the larger coupling constant.

Clearly, the predictions of the above discussion based upon eq 1 are not realized. This could be due to the approximations involved in deriving eq 1 or to contributions from other coupling mechanisms that are larger than expected.

Comments on Some Individual Spectra. $HgBr_2(PPh_3)_2$. The lines were broad (~200 Hz), but the central peaks clearly arose from an AB system and the satellites from an ABX system. However there was some asymmetry to the central peaks, which remained even after recrystallizations from ethanol, acetone, and dichloromethane.

$Hg(SCN)_2(PPh_3)_2$. The published structure of this complex shows that the phosphines are inequivalent, but repeated preparation and recrystallization yielded a complex (labeled β in Table III) whose spectrum indicated the presence of equivalent phosphines. However, one sample, recrystallised from ethanol (purity checked by solution ^{31}P NMR) did show the presence of two species, one with equivalent phosphines (β) and one in which they were inequivalent (γ). Recrystallization of this sample led to the disappearance of the peaks from the lower symmetry species. In an effort to obtain crystals identical with those whose structure was published, many recrystallizations from the solvents CH_3NO_2, $(CH_3)_2CO$, CH_2Cl_2, CH_3OH, and CH_3CH_2OH were performed and the ^{31}P CP-MAS NMR spectra were run. In almost every case the symmetric species was produced. In one case, however, a new unsymmetric species was found. This sample (labelled $\propto$ in Table III) was recrystallized by the slow evaporation of an ethanolic solution that was seeded with the unsymmetric material to give crystals with an identical NMR spectrum. X-ray analysis of these crystals showed them to be identical with those reported previously.

$Hg(OAc)_2(PCy_3)_2$. Although the crystal structure shows the phosphines to be inequivalent, the solid-state ^{31}P NMR spectrum indicates equivalence. No crystallographic work was done by us on this sample.

Experimental Section

Preparation of the Complexes. $HgCl_2$, $HgBr_2$, HgI_2, $Hg(NO_3)_2$, $Hg(OAc)_2$, $Hg(CN)_2$, $Hg(SCN)_2$, and $PCy_3{\cdot}CS_2$ were reagent grade and used as received. PPh_3 was crystallized from hot 95% EtOH and its purity was confirmed by its ^{31}P solution NMR spectrum (singlet at $\delta = -6.3$ in $CDCl_3$).

The PPh_3 complexes were prepared by the direct reaction of stoichiometric quantities of PPh_3 and the appropriate mercuric salt in acetone (NO_3 and OAc complexes) or CH_2Cl_2 (all others). The complexes were recrystallized from acetone (SCN complex) or 95% EtOH (all others). Their purities were confirmed from their solution ^{31}P NMR spectra.

$Hg(OAc)_2(PCy_3)_2$ was prepared as follows. $PCy_3{\cdot}CS_2$ (2 mmol) was refluxed in 95% EtOH (~50 mL) for a few minutes under N_2 until a clear colorless solution of PCy_3 had formed. (The $PCy_3{\cdot}CS_2$ adduct is an air-stable red solid, which dissociates upon heating. The resulting PCy_3 solution must be protected from atmospheric O_2.) Solid $Hg(OAc)_2$ (1 mmol) was added to the solution, which was stirred until the solid dissolved. The complex was isolated by reducing the volume on a rotary evaporator and adding Et_2O. It was recrystallized from hot 95% EtOH.

$Hg(ClO_4)_2(PCy_3)_2$ was prepared by the metathetical reaction of $HgI_2(PCy_3)_2$ (which can be prepared as above) and $AgClO_4$ in EtOH.[8]

X-ray Crystallographic Measurements. Each of the $HgX_2(PPh_3)_2$ (X = Br, I, CN, SCN, OAc) complexes was recrystallized by the slow evaporation of ethanol. Crystals suitable for X-ray analysis were formed by all but the Br and I complexes. The cell constants were determined for X = CN, SCN, and OAc by standard methods in order to show that our samples were identical with those reported in the literature.

(For X = CN: found, orthorhombic, $Pn2_1a$, a = 18.021 (4) Å, b = 18.245 (4) Å, c = 10.035 (2) Å, lit., a = 18.023 (5) Å, b = 18.262 (4) Å, c = 10.032 (3) Å. For X = SCN: found, monoclinic, $P2_1/c$, a = 17.361 (6) Å, b = 10.567 (6) Å, c = 19.262 (5) Å, β = 91.61 (6)°; lit., a = 17.385 (9) Å, b = 10.571 (4) Å, c = 19.304 (5) Å, β = 91.41 (6)°.) The full structure analysis of $Hg(OAc)_2(PPh_3)_2$ was performed and will be reported elsewhere.

^{31}P CP-MAS NMR Measurements. The samples were packed into Delrin spinners along with a small amount of KBr. The ^{79}Br resonance was used to set the spinning angle for each sample. The sample spinning rate was adjusted to 3.5–4.0 kHz.

The spectra were acquired at 81 MHz on a Bruker CXP-200 NMR spectrometer by using the standard CP-MAS probe. The optimum power levels for the transmitter and decoupler power amplifiers were set by observing the ^{31}P resonance of a sample of $[MePPh_3]Br$ and adjusting the transmitter and decoupler output amplifiers to give the maximum signal. The spectra of the complexes were obtained by using the following parameters: spectral width, 20 kHz centered on 0 ppm with respect to 85% H_3PO_4; 90° pulse, 3–5 μs; contact time, 0.5–1.0 ms. The recycle times were set for each sample and usually fell into the range 10–60 s. For samples with sharp resonances often one acquisition was sufficient to obtain useful spectra although typically 16–64 transients were acquired. The spectra were acquired into 2K memory blocks and zero-filled to 4K before Fourier transformation. Line broadenings of 10–50 Hz were found to be useful, depending upon the quality of the individual spectra.

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Registry No. $HgCl_2(PPh_3)_2$, 19543-98-7; $HgBr_2(PPh_3)_2$, 14586-76-6; $HgI_2(PPh_3)_2$, 14494-95-2; $Hg(CN)_2(PPh_3)_2$, 27902-66-5; $Hg(SCN)_2(PPh_3)_2$, 27290-69-3; $Hg(OAc)_2(PPh_3)_2$, 66119-73-1; $Hg(NO_3)_2(PPh_3)_2$, 14057-00-2; $Hg(OAc)_2(PCy_3)_2$, 66161-25-9; $Hg(ClO_4)_2(PCy_3)_2$, 67124-82-7; Hg, 7439-97-6.

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(20) Dakternieks, D. *Inorg. Chim. Acta* **1984**, *89*, 209.

(21) It has been shown[18] that changing the charge on a phosphous atom from 0 to +1 results in a change in $|\psi_s(0)_{\text{P}}|^2$ of only 10.4%. If the electroneutrality principle is followed, much smaller differences in charge and electron density between the two P atoms would be expected and therefore the electron densities must be almost exactly the same. It is also unlikely that there are significant differences among the various complexes.

(22) Makhija, R. C.; Beauchamp, A. L.; Rivest, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2447.

(23) Fälth, L. *Chem. Scr.* 1976, *9*, 71.

(24) Bell, N. A.; Dee, T. D.; Goldstein, M.; McKenna, P. J.; Nowell, I. W. *Inorg. Chim. Acta* **1983**, *71*, 135. Unreported bond angles for $HgBr_2(PPh_3)_2$ were received in private communication from Dr. I. W. Nowell and used in the s character calculations. As noted in this reference, the uncertainties are large due to the poor quality of the available crystals.

(25) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Khan, M. A. *J. Chem. Res., Miniprint* **1979**, 4101.

(26) Allman, T.; Lenkinski, R. E., unpublished results.