An Investigation of the Acceptor Properties of Some Organomercurials by Molecular Weight Measurements and X-ray Photoelectron Spectroscopy*

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Stability constants from molecular weight measurements for the complexes \( R_2Hg \text{bpy} \) (bpy = 2,2'-bipyridyl) in carbon tetrachloride and benzene at 25°C decrease in the order \( R = \text{CaF}_5 > \text{p-HC}_6\text{F}_4 = \text{p-MeOC}_6\text{F}_4 > \text{o-HC}_5\text{F}_4 \), and for \( R_2Hg\text{OPPha} \), in the order \( R = \text{o-HC}_5\text{F}_4 > \text{C}_5\text{F}_5 > \text{p-HC}_5\text{F}_4 = \text{p-MeOC}_5\text{F}_4 \) with higher values in the former solvent. The unexpectedly greater stability of \( (\text{o-HC}_5\text{F}_4)_2Hg\text{OPPha} \) than \( (\text{C}_5\text{F}_5)_2Hg\text{OPPha} \) has been related to the structures of the parent mercurials. X-ray photoelectron spectroscopy shows that the acceptor properties of mercury compounds decrease in the order \( \text{HgCl}_2 > (\text{C}_5\text{F}_5)_2\text{Hg} = (\text{p-HC}_5\text{F}_4)_2\text{Hg} = (\text{o-HC}_5\text{F}_4)_2\text{Hg} > (\text{p-MeOC}_5\text{F}_4)_2\text{Hg} > (\text{C}_5\text{Cl}_3)_2\text{Hg} > \text{Ph}_2\text{Hg} > \text{Hg}_2 \). A similar study of \( RHgX \) compounds suggests that there is reasonable additivity of the electrophilic effects of different \( R \) and \( X \) groups on the mercury 4f binding energy.

INTRODUCTION

Molecular weight measurements provide a convenient method for examining complex formation between diorganomercurials and uncharged ligands in organic solvents.1-6 Thus, they have been used to establish orders of acceptor strength for bis(perfluoroalkyl)mercurials in benzene6 and to show that diphenylmercury has negligible acceptor properties in the same solvent.8 Stability constants for formation of \( R_2HgL \) complexes have been calculated from molecular weight data.4,5,7 There is reasonable agreement between the values6 for \( (\text{C}_5\text{F}_5)_2\text{HgL} \) [\( L = \text{2,2’-bipyridyl} \) (bpy) and 1,10-phenanthroline (phen)] and those determined thermochemically7 [but see also ref.8]. However the method is unsuitable for very stable or very unstable complexes since the number of particles formed per molecule of \( R_2HgL \) does not differ significantly from values for no or complete dissociation respectively.

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.
An alternative approach to the acceptor strength of mercurials is to measure binding energies of electrons on mercury. As the electron-withdrawing character of attached organic groups is increased, an increase in binding energy may be expected. X-ray and UV induced ionization of mercury compounds has been studied, but the relationship to acceptor properties has not been explored.

We now report a study of the acceptor properties of bis(polyfluorophenyl)-mercurials by molecular weight measurements and X-ray photoelectron spectroscopy.

RESULTS AND DISCUSSION

Complex Formation with 2,2'-Bipyridyl and Triphenylphosphine Oxide

Stability constants for formation [reaction (1)] of the complexes $R_2HgL$ ($R = C_6F_5$, p-HC$_6$F$_4$, p-MeOC$_6$F$_4$ or o-HC$_6$F$_4$; $L = bpy$ or Ph$_3$PO) in benzene and carbon tetrachloride at 25 °C were calculated from molecular weight data for either preformed complexes or ligand/mercurial mixtures (mole ratio 1:1). The results are given in Table I.

$$R_2HgL + L \rightleftharpoons R_2HgL$$ (1)

The assumption of 1:1 stoichiometry in the calculations is supported by isolation of $(C_6F_5)_2Hgbpy$, $(C_6F_5)_2HgOPPh_3$, and the new complexes $R_2HgOPPh_3$ ($R = p$-HC$_6$F$_4$ or o-HC$_6$F$_4$), as well as by thermochemical studies of the $(C_6F_5)_2Hg/bpy$ system. For solid $R_2HgOPPh_3$ ($R = p$-HC$_6$F$_4$ or o-HC$_6$F$_4$), the phosphorus-oxygen stretching frequency is at 1160-1150 cm$^{-1}$ and is lower than the free ligand value (1193 cm$^{-1}$) as expected on coordination of the phosphine oxide.

Stabilities of $(C_6F_5)_2HgL$ ($L = bpy$ or Ph$_3$PO) in benzene are in satisfactory agreement with values calculated (this work) from earlier molecular weight data (Table I), whilst the value for $(C_6F_5)_2Hgbpy$ is in reasonable agreement with the stability constant from one thermochemical study. There is more divergence from the value for $(C_6F_5)_2Hgbpy$ obtained in another calorimetric investigation (Table I). However, the difference is partly encompassed by errors in the present determinations where errors of ±2% in molecular weights can give likely an error range of ±8 → 12 for the stability constant of $(C_6F_5)_2Hgbpy$ in benzene and of ±96 → 134 in carbon tetrachloride. In addition, the errors in the reported values, ±5–10% may be conservative studies. Calculations of stability constants in the present work are based on the assumption that any lowering of the observed molecular weight from the value for $R_2HgL$ is solely due to dissociation into $R_2Hg$ and $L$.

The greater stabilities in carbon tetrachloride than benzene are consistent with earlier results for $(C_6F_5)_2HgL$ (L = bpy or py) in these solvents. This has been attributed to differences between the ligand-solvent interactions in the two solvents rather than to acceptor-solvent interaction differences. The stability order for the $R_2Hgbpy$ complexes, $R = C_6F_5 > p$-HC$_6$F$_4 = p$-MeOC$_6$F$_4 > o$-HC$_6$F$_4$ (Ph), shows little sensitivity to change in the polyfluoroaryl group apart from the greater stability of the pentafluorophenyl derivative. Although the last result is consistent with the greater inductive electron with-
drawing capacity of the C₆F₅ group, the lack of differentiation between the other complexes indicates insensitivity to small changes in electronic effects. In particular, in terms of inductive effects, it is surprising that removal of an ortho fluorine has only slightly greater effect than removal of a para fluorine.

Stabilities of \( \text{R}_2\text{HgOPPh}_3 \) complexes are significantly higher than those of the corresponding \( \text{R}_2\text{Hgbpy} \) complexes (Table I). The difference is the more remarkable since there is good evidence that \((\text{C}_6\text{F}_5)_2\text{Hgbpy}\) in solution has chelating 2,2'-bipyridyl ligands and a similar situation is likely for the other \( \text{R}_2\text{Hgbpy} \) complexes. Two possible sources of this difference are (i) a major difference in the solvation energies of the ligands and (ii) hard acid character for bis(polyfluorophenyl)mercurials since Ph₃PO is harder than bpy. There is independent evidence that \((\text{C}_6\text{F}_5)_2\text{Hg}\) is a hard acid,14 by contrast with \( \text{Hg}_2^{2+} \). The stability order for the \( \text{R}_2\text{HgOPPh}_3 \) complexes, \( \text{R} = \text{o-HC}_6\text{F}_4 > \text{C}_6\text{F}_5 > \text{p-HC}_6\text{F}_4 = \text{p-MeOC}_6\text{F}_4 \), reveals an anomalously high stability for the 2,3,4,5-tetrafluorophenyl derivative, which should have the lowest stability on simple electronic grounds. This cannot be attributed to a major difference between the solvation energies of \((\text{o-HC}_6\text{F}_4)_2\text{Hg}\) and those of the other mercurials, since a similar stability order is not observed for \( \text{R}_2\text{Hgbpy} \) complexes and the order is the same in both benzene and carbon tetrachloride. A possible reason for the stability sequence can be found in the structures of the parent mercurials. Bis(2,3,4,5-tetrafluorophenyl)mercury15 has linear \( \text{C}--\text{Hg}--\text{C} \) stereochemistry with coplanar phenyl rings (as in diphenylmercury16) and transoid fluorine atoms. Coordination of the phosphine oxide into a vacant orbital normal to the aromatic plane is readily possible giving either T shape stereochemistry or only slight \( \text{C}--\text{Hg}--\text{C} \) bending so that there is no substantial reorganisation of the mercurial structure. By contrast, whilst bis(pentafluorophenyl)mercury has approximately linear \( \text{C}--\text{Hg}--\text{C} \) stereochemistry, the rings are tilted to give an angle of 59° between them.17 This minimises repulsion between ortho fluorine atoms of the two rings. A similar structure is likely for \((\text{p-XC}_6\text{F}_4)_2\text{Hg} \) (X = H or MeO). Coordination of the phosphine oxide with this configuration of aryl rings would lead to significant oxygen...ortho-fluorine repulsion, whilst twisting the rings towards planarity would lead to substantial re-

**Table I**

<table>
<thead>
<tr>
<th>Complex</th>
<th>( K ) (mol(^{-1}) dm(^3))</th>
<th>Complex</th>
<th>( K ) (mol(^{-1}) dm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_6\text{F}_5)_2\text{Hgbpy})</td>
<td>9.9 113</td>
<td>((\text{C}_6\text{F}_5)_2\text{HgOPPh}_3)</td>
<td>25 320</td>
</tr>
<tr>
<td>((\text{p-HC}_6\text{F}_4)_2\text{Hgbpy})</td>
<td>11° 55.5°</td>
<td>((\text{p-Ph}_3\text{PO})_2\text{HgOPPh}_3)</td>
<td>11 117</td>
</tr>
<tr>
<td>((\text{p-MeOC}_6\text{F}_4)_2\text{Hgbpy})</td>
<td>19.2°</td>
<td>((\text{p-MeOC}_6\text{F}_4)_2\text{HgOPPh}_3)</td>
<td>10 82</td>
</tr>
<tr>
<td>((\text{p-HC}_6\text{F}_4)_2\text{Hgbpy})</td>
<td>5.7 32</td>
<td>((\text{o-HC}_6\text{F}_4)_2\text{HgOPPh}_3)</td>
<td>70 592</td>
</tr>
<tr>
<td>((\text{o-HC}_6\text{F}_4)_2\text{Hgbpy})</td>
<td>6.1 32</td>
<td>((\text{o-HC}_6\text{F}_4)_2\text{HgOPPh}_3)</td>
<td>70 592</td>
</tr>
</tbody>
</table>

* Average of several determinations.  
* Calculated from previously reported molecular weight data at 25°C.  
* From reported calorimetric data at 25°C.  
* Insufficiently soluble.
pulsion between ortho-fluorines, leading to reduced stability with either arrangement. This factor is clearly not relevant to the stabilities of the $R_2Hg$gly complexes (see above). Possibly weaker mercury-ligand bonding in $R_2Hg$gly than $R_2Hg$OPPh$_3$ complexes owing to hard acid character for bis(polyfluoro-phenyl)mercurials makes energy terms associated with donor-ortho fluorine interaction (or inter-ring ortho-fluorine repulsion) much less significant for the bipyridyl complexes. This can be related not only to the lower stability of $R_2Hg$gly complexes than the corresponding Ph$_3P$O complexes (Table I) but also to the rather low enthalpy of formation of (C$_6$F$_5$)$_2Hg$gly$^{7,8}$ [cf. (C$_6$F$_5$)$_2Hg$phen$^7$]. However illumination from crystal structures of $R_2HgL$ (R = C$_6$F$_5$ or o-HC$_6$F$_4$; L = Ph$_3$PO or bpy) is needed. It is of interest that structures of (CF$_3$)$_2Hg$tpy$^{18}$ (tpy = 2,2':6',2''-terpyridyl), (CCl$_3$)$_2Hg$tmp$^{19}$ (tmp = 3,4,7,8-tetramethyl-1,10-phenanthroline) and (PhCC)$_2Hg$phen$^{20}$ show relatively weak Hg—N bonding (2.6—2.7 Å) and substantially linear C—Hg—C angles (160—170°). Phenanthroline complexes with mercurials are more stable than those with bipyridyl$^4$—$^7$ whilst (CF$_3$)$_2Hg$ gives much more stable complexes than (C$_6$F$_5$)$_2Hg$.²

X-ray Photoelectron Measurements

The mercury 4f binding energies of some $R_2Hg$ derivatives recorded using Al K$_x$ X-radiation are presented in Table II. The binding energies are relative to the gold 4f$_{7/2}$ line at 84.0 eV, on which scale the corresponding Hg$^0$ line is at 100.0 eV. For some compounds where irradiation caused some reduction to mercury metal, it was convenient to use the Hg$^0$ line as an internal standard.

The binding energy sequence Hg$^0$ < Ph$_2$Hg < (C$_6$Cl$_5$)$_2$Hg < (C$_6$F$_5$)$_2$Hg < HgCl$_2$ is as expected for increased electron withdrawing character of the attached ligands. (Electronegativities of Ph, C$_6$Cl$_5$, C$_6$F$_5$, and Cl are 2.5,$^{21}$ 2.6,* $^{22}$ 3.0,$^{23}$ and 3.2$^{24}$ respectively.) On the other hand no differentiation within experimental error was observed between mercury 4f binding energies in (C$_6$F$_5$)$_2Hg$, (p-HC$_6$F$_4$)$_2$Hg, and (o-HC$_6$F$_4$)$_2$Hg. The 4f binding energy in (p-MeOC$_6$F$_4$)$_2Hg$ is significantly less than those of the other bis(polyfluoroaryl)-mercurials suggesting that the resonance electron donating effect of the p-MeO substituent may be giving detectably higher electron density at the mercury atom. There is thus some correlation with the relatively low stability constants for complexes of this mercurial with Ph$_3$PO and bpy (Table I).

On the basis of the binding energy shifts (Table II), a 'photoelectron group shift' on the mercury atom can be determined to provide a measure of the electron withdrawing character of the various substituents, viz. Ph, 0.95; C$_6$Cl$_5$, 1.05; p-MeOC$_6$F$_4$, 1.35; o-HC$_6$F$_4$, 1.71; C$_6$F$_5$, 1.75; p-HC$_6$F$_4$, 1.80; Cl, 2.5 eV. In view of the difficulties in measuring the binding energies of insulating materials, the values are considered accurate to ± 0.3 eV.

To establish whether the group shifts are additive, a series of mercury compounds of the type RHgX was investigated (Table III). The chemical binding energy shifts relative to Hg$^0$ are compared with the predicted shifts based on the additivity of the group shifts (above). In all cases, the measured shift is less than the predicted shift, although only for C$_6$F$_5$HgCl is the result

* On a scale with Ph, 2.6 and C$_6$F$_5$, 2.7$^{22}$
TABLE II
Mercury 4f Binding Energies for some R₂Hg Compounds (eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Binding Energy*</th>
<th>Relative 4f7/2 to Hg*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4f7/2</td>
<td>4f5/2</td>
</tr>
<tr>
<td>Hg*</td>
<td>100.0</td>
<td>104.1</td>
</tr>
<tr>
<td>(C₅H₅)₂Hg</td>
<td>101.9</td>
<td>106.0</td>
</tr>
<tr>
<td>(C₅Cl₅)₂Hg</td>
<td>102.1</td>
<td>106.2</td>
</tr>
<tr>
<td>(p-MeOC₅F₄)₂Hg</td>
<td>102.7</td>
<td>106.8</td>
</tr>
<tr>
<td>(o-HC₅F₄)₂Hg</td>
<td>103.4</td>
<td>107.5</td>
</tr>
<tr>
<td>(C₆F₆)₃Hg</td>
<td>103.5</td>
<td>107.6</td>
</tr>
<tr>
<td>(p-HC₅F₄)₃Hg</td>
<td>103.6</td>
<td>107.7</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>105.0</td>
<td>108.9</td>
</tr>
</tbody>
</table>

* Relative to Au 4f7/2 = 84.0 eV

well outside experimental error. In general, there is reasonable additivity of the electron withdrawing effects in mercurials.

CONCLUSIONS

Both molecular weight measurements for R₂HgL complexes and X-ray photoelectron spectra of parent R₂Hg compounds provide information about the acceptor properties of bis(polyfluorophenyl)mercurials but both are generally insensitive to small variations in the substituents. The high stability of (o-HC₅F₄)₂HgOPPh₃ relative to (C₆F₅)₂HgOPPh₃ is unexpected since a simple electronic model predicts C₆F₅ to be more electron withdrawing than o-HC₅F₄, whilst the photoelectron measurements suggest the two groups have similar electrophilic character.

TABLE III
Mercury 4f Binding Energies for some RHgX Compounds (eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Binding Energy*</th>
<th>Group Shift Relative to 4f7/2 Hg*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4f7/2</td>
<td>4f5/2</td>
</tr>
<tr>
<td>Hg*</td>
<td>100.0</td>
<td>104.1</td>
</tr>
<tr>
<td>C₅H₅HgC₅Cl₂</td>
<td>101.9</td>
<td>106.0</td>
</tr>
<tr>
<td>C₅H₅HgCl</td>
<td>103.1</td>
<td>107.1</td>
</tr>
<tr>
<td>C₅Cl₅HgCl</td>
<td>102.8</td>
<td>106.8</td>
</tr>
<tr>
<td>C₆F₆HgCl</td>
<td>102.8</td>
<td>108.9</td>
</tr>
<tr>
<td>Cl—Hg—Hg—Cl</td>
<td>103.1</td>
<td>107.1</td>
</tr>
<tr>
<td>p-HC₅F₄HgCl</td>
<td>104.2</td>
<td>108.3</td>
</tr>
</tbody>
</table>

* Relative to Au 4f7/2 = 84.0 eV. a,b Uncertainty ±0.3 eV. * Uncertainty ±0.6 eV.
**EXPERIMENTAL**

**General**

Microanalyses were by the Australian Microanalytical Service, Melbourne. Infrared spectra (4000-650 cm⁻¹) of compounds as Nujol and hexachlorobutadiene mulls were recorded with Jasco IRA-1 or Perkin-Elmer 621 spectrophotometers. Molecular weights of either preformed R₂HgL complexes or equimolar amounts of ligand and mercurial were determined at 25 °C in benzene or carbon tetrachloride with a Hewlett Packard 302 osmometer, which was calibrated with solutions of benzil. Some molecular weights of R₂HgOPPh₃ (R = C₆F₅ or p-HC₆F₄) were determined at 25 °C in benzene or carbon tetrachloride with a He wlett Packard 302 osmometer, which was calibrated with solutions of benzil. Some molecular weights of R₂HgL complexes were calculated using the expression $K = 2 - i/(i-1)^2$ where $i$ is calculated molecular weight of R₂HgL/observed molecular weight, and $c$ is the initial concentration of the complex. X-ray photoelectron spectra of pelleted samples were recorded using Al Kα radiation with an AEI ES-100 spectrometer modified by addition of an UHV sample preparation chamber and an improved vacuum system. Data were collected with a DS-100 data system and the spectra were calibrated with the gold 4f7/2 line.

**Solvents and Reagents**

'Pronalys' grade benzene and carbon tetrachloride (May and Baker) were used for molecular weight determinations. The latter was passed through an alumina column and was stored over molecular sieves (5A). For determinations under nitrogen, benzene was distilled from calcium hydride under nitrogen. Bis(pentafluorophenyl)mercurials, R₂Hg (R = C₆F₅, p-HC₆F₄, p-MeOC₆F₄ or C₆F₅C₆F₄), were prepared by reported mercuration and symmetrization reactions, and were characterized by melting points and infrared spectra.¹¹-²⁵ Triphenylphosphine oxide (Koch-Light) and 2,2'-bipyridyl (May and Baker) were recrystallized from hexane. Preparations and sources of the mercurials in Table III have been given previously.²²-²⁶

**Complexes**

2,2’-Bipyridylbis(pentafluorophenyl)mercury(II) and bis(pentafluorophenyl)(triphenylphosphine oxide)mercury(II) were prepared by reported methods and had melting points and infrared spectra in agreement with those reported.¹¹-¹

**Bis(2,3,4,5-tetrafluorophenyl) (triphenylphosphine oxide)mercury(II)**

Hot saturated solutions of triphenylphosphine oxide (0.32 mmol) in petroleum spirit (b.p. 100-120 °C) and bis(2,3,4,5-tetrafluorophenyl)mercury (0.32 mmol) in hexane were mixed. On cooling, the title compound was precipitated (yield, 30%), m. p. 120 °C.

Anal. C₃₀H₁₇F₈HgOP (777.02) calc’d: C 46.4; H 2.2; F 19.6%; found: C 46.7; H 2.1; F 19.6%

Infrared absorption: 3035w, 1620w, 1590w, 1510m, 1455s, 1450s, 1308m, 1158m, 1120m, 1080s, 1070m, 995m, 985m, 890m, 810m, 750m, 690m cm⁻¹.

**Bis(2,3,5,6-tetrafluorophenyl) (triphenylphosphine oxide)mercury(II)**

A similar preparation gave initially crystals of triphenylphosphine oxide (infrared identification). Further crystallization from the filtrate gave the title compound (yield, 20%), m. p. 121-122 °C.

Anal. C₃₀H₁₇FsHgOP (777.02) calc’d: C 46.4; H 2.2; F 19.2%; found: C 46.2; H 2.2; F 19.2%

Infrared absorption: 3035w, 1595w, 1495sh, 1485s, 1455s, 1450s, 1420w, 1350m, 1230w(br), 1185w(br), 1185m, 1154m, 1120m, 1090w, 1075w, 1023w, 995w, 905w, 890w, 850m, 745w, 725s, 705sh, 700m, and 695s cm⁻¹.

Similar attempts to isolate (p-MeOC₆F₄)₂HgOPPh₃ were unsuccessful.
Molecular Weight Results

The molecular weight data from which the stability constants were calculated follow. Concentrations are given as \(\%\) w/v, either of the preformed complex or of an equimolar mixture of ligand and mercurial.

\((C_{6}F_{5})_{2}HgOPPh_{3}\)
Calc'd: mol. wt., 813. Found: mol. wt. (in benzene): 503 (1.70%), 513 (1.90%), 509 (1.92%), 493 (1.95%); (in benzene under \(N_{2}\)), 462 (0.642%), 451 (0.670%), 478 (1.01%); (in CCl\(_{4}\)): 595 (0.563%), 590 (0.569%).

\((p-\text{MeOC}_{6}F_{4})_{2}HgOPPh_{3}\)
Calc'd: mol. wt., 837. Found: mol. wt. (in benzene): 462 (1.66%), 459 (1.84%), 448 (1.94%); (in CCl\(_{4}\)): 486 (0.563%), 493 (0.613%), 492 (0.620%).

REFERENCES


SAZETAK

Istraživanje akceptorskih svojstava nekih organomerkurijala mjerenjem molekulske težine i rendgenskom fotoelektronskom spektroskopijom

G. B. Deacon, A. Florenti, M. Hughes i F. P. Larkins

Konstante stabilnosti dobivene mjerenjem molekulske težine kompleksa R₂Hg(bpy) (bpy = 2,2'-bipiridil) u tetraklormetanu i benzenu na 25 °C smanjuju se u nizu R = C₆F₅ > p-HC₆F₄ > p-MeOC₆F₄ ≥ o-HC₆F₄, a za R₂HgOPPh₃, u nizu R = o-HC₆F₄ > ≥ p-HC₆F₄ = p-MeOC₆F₄ s većim vrijednostima u tetraklormetanu. Nenečekivano veća stabilnost (o-HC₆F₄)₂HgOPPh₃ prema onoj (C₅H₅)₂HgOPPh₃ u vezi je sa strukturama tih merkurijala. Rendgenska fotoelektronska spektroskopija pokazuje da se akceptorska svojstva živinih spojeva smanjuju u nizu HgCl₂ > (C₅F₅)₂Hg = = (p-HC₆F₄)₂Hg = (o-HC₆F₄)₂Hg > (p-MeOC₆F₄)₂Hg > (C₅Cl₂)₂Hg ≥ Ph₂Hg ≥ Hg. Slične studije spojeva RHgX pokazuju da ima razloga za pretpostavku o aditivnosti elektrofilnih efekata različitih grupa R i X na 4f-energiju vezanja žive.