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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 weigth measurements for the complexes R_2Hgbpy (bpy = 2,2'-bipyridyl) in carbon tetrachloride and benzene at 25 °C decrease in the order $R = C_6F_5 > p\text{-}HC_6F_4 \simeq p\text{-}MeOC_6F_4 \geq o\text{-}HC_6F_4$, and for $R_2HgOPPh_3$, in the order $R = o\text{-}HC_6F_4 > C_6F_5 > p\text{-}HC_6F_4 \simeq p\text{-}MeOC_6F_4$ with higher values in the former solvent. The unexpectedly greater stability of $(o\text{-}HC_6F_4)_2HgOPPh_3$ than $(C_6F_5)_2HgOPPh_3$ 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 $HgCl_2 > (C_6F_5)_2Hg \simeq (p\text{-}HC_6F_4)_2Hg \simeq (o\text{-}HC_6F_4)_2Hg > (p\text{-}MeOC_6F_4)_2Hg > (C_6Cl_5)_2Hg \geq Ph_2Hg > Hg^0$. 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.[1–5] Thus, they have been used to establish orders of acceptor strength for bis(perfluoroalkyl)mercurials in benzene[2] and to show that diphenylmercury has negligible acceptor properties in the same solvent.[5] Stability constants for formation of R_2HgL complexes have been calculated from molecular weight data.[5,6,7] There is reasonable agreement between the values[6] for $(C_6F_5)_2HgL$ [L = 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen)] and those determined thermochemically[7] [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.

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* 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,[9,10] 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_6F_4, p-$MeOC_6F_4$, or o-HC_6F_4; $L =$ bpy or Ph_3PO) 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.

$$R_2Hg + L \leftrightharpoons R_2HgL \qquad (1)$$

The assumption of 1 : 1 stoichiometry in the calculations is supported by isolation of $(C_6F_5)_2Hg$bpy,[4,11] $(C_6F_5)_2HgOPPh_3$,[4] and the new complexes $R_2HgOPPh_3$ ($R = p$-HC_6F_4 or o-HC_6F_4), as well as by thermochemical studies of the $(C_6F_5)_2Hg$/bpy system.[7,8] For solid $R_2HgOPPh_3$ ($R = p$-HC_6F_4 or o-HC_6F_4), the phosphorus-oxygen stretching frequency is at 1160—1150 cm^{-1} and is lower than the free ligand value (1193 cm^{-1})[12] as expected[13] on coordination of the phosphine oxide.

Stabilities of $(C_6F_5)_2HgL$ ($L =$ bpy or Ph_3PO) in benzene are in satisfactory agreement with values calculated (this work) from earlier molecular weight data[4] (Table I), whilst the value for $(C_6F_5)_2Hg$bpy is in reasonable agreement with the stability constant from one thermochemical study.[7] There is more divergence from the value for $(C_6F_5)_2Hg$bpy obtained in another calorimetric investigation[8] (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 $8 \rightarrow 12$ for the stability constant of $(C_6F_5)_2Hg$bpy in benzene and of $96 \rightarrow 134$ in carbon tetrachloride. In addition, the errors in the reported values,[8] ± 5—10% may be conservative studies.[7,8] 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.[8] This has been attributed to differences between the ligand-solvent interactions in the two solvents rather than to acceptor-solvent interaction differences.[8] The stability order for the R_2Hgbpy complexes, $R = C_6F_5 > p$-$HC_6F_4 \simeq p$-$MeOC_6F_4 \geqslant$ $\geqslant o$-HC_6F_4 ($>$ Ph[5]), 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-

TABLE I

Stability Constants for R_2HgL (L = bpy or Ph_3PO) Complexes in Benzene and Carbon Tetrachloride at 25 °C

Complex	K(mol^{-1} dm^3)[a]		Complex	K(mol^{-1} dm^3)[a]	
	C_6H_6	CCl_4		C_6H_6	CCl_4
$(C_6F_5)_2Hgbpy$	9.9	113	$(C_6F_5)_2HgOPPh_3$	25	320
	11[b]	55.5[c]		15[b]	
	14.0[d]		$(p\text{-}HC_6F_4)_2HgOPPh_3$	11	117
	19.2[c]		$(p\text{-}MeOC_6F_4)_2HgOPPh_3$	10	82
$(p\text{-}HC_6F_4)_2Hgbpy$	5.7	[e]	$(o\text{-}HC_6F_4)_2HgOPPh_3$	70	592
$(p\text{-}MeOC_6F_4)_2Hgbpy$	6.1	32			
$(o\text{-}HC_6F_4)_2Hgbpy$	3.9	33			

[a] Average of several determinations. [b] Calculated from previously reported molecular weight data at 25 °C.[4] [c] From reported calorimetric data at 25 °C.[8] [d] From reported calorimetric data at 30 C.[7] [e] Insufficiently soluble.

drawing capacity of the C_6F_5 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 $R_2HgOPPh_3$ complexes are significantly higher than those of the corresponding R_2Hgbpy complexes (Table I). The difference is the more remarkable since there is good evidence that $(C_6F_5)_2Hgbpy$ in solution has chelating 2,2'-bipyridyl ligands[7,8] and a similar situation is likely for the other R_2Hgbpy 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 Ph_3PO is harder than bpy. There is independent evidence that $(C_6F_5)_2Hg$ is a hard acid,[7] by contrast with Hg^{2+}.[14] The stability order for the $R_2HgOPPh_3$ complexes, $R = o\text{-}HC_6F_4 > C_6F_5 > p\text{-}HC_6F_4 \simeq p\text{-}MeOC_6F_4$, 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 energy of $(o\text{-}HC_6F_4)_2Hg$ and those of the other mercurials, since a similar stability order is not observed for R_2Hgbpy 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)mercury[15] has linear C—Hg—C stereochemistry with coplanar phenyl rings (as in diphenylmercury[16]) 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 C—Hg—C bending so that there is no substantial reorganisation of the mercurial structure. By contrast, whilst bis(pentafluorophenyl)mercury has approximately linear C—Hg—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 $(p\text{-}XC_6F_4)_2Hg$ (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 repulsion between *ortho*-fluorines, leading to reduced stability with either arrangement. This factor is clearly not relevant to the stabilities of the R_2Hgbpy complexes (see above). Possibly weaker mercury-ligand bonding in R_2Hgbpy than $R_2HgOPPh_3$ complexes owing to hard acid character for bis(polyfluorophenyl)mercurials makes energy terms associated with donor atom-*ortho* fluorine interaction (or inter-ring *ortho*-fluorine repulsion) much less significant for the bipyridiyl complexes. This can be related not only to the lower stability of R_2Hgbpy complexes than the corresponding Ph_3PO complexes (Table I) but also to the rather low enthalpy of formation of $(C_6F_5)_2Hgbpy$[7,8] [cf. $(C_6F_5)_2Hgphen$[7]]. However illumination from crystal structures of R_2HgL ($R = C_6F_5$ or o-HC_6F_4; $L = Ph_3PO$ or bpy) is needed. It is of interest that structures of $(CF_3)_2Hgtpy$[18] (tpy = 2,2′ : 6′,2″-terpyridyl), $(CCl_3)_2Hgtmp$[19] (tmp = = 3,4,7,8-tetramethyl-1,10-phenanthroline) and $(PhCC)_2Hgphen$[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 $(C_6F_5)_2Hg$.[2]

X-ray Photoelectron Measurements

The mercury 4f binding energies of some R_2Hg derivatives recorded using Al K_α 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 $Hg^0 < Ph_2Hg \leqslant (C_6Cl_5)_2Hg < (C_6F_5)_2Hg < < HgCl_2$ is as expected for increased electron withdrawing character of the attached ligands. (Electronegativities of Ph, C_6Cl_5, C_6F_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 $(C_6F_5)_2Hg$, $(p$-$HC_6F_4)_2Hg$, and $(o$-$HC_6F_4)_2Hg$. The 4f binding energy in $(p$-$MeOC_6F_4)_2Hg$ 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_3PO 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_6Cl_5, 1.05; p-$MeOC_6F_4$, 1.35; o-HC_6F_4, 1.71; C_6F_5, 1.75; p-HC_6F_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_6F_5HgCl is the result

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* On a scale with Ph, 2.6 and C_6F_5, 2.7.[22]

TABLE II

Mercury 4f Binding Energies for some R_2Hg Compounds (eV)

Compound	Binding Energy[a]		Relative $4f^7/_2$ to Hg^0
	$4f^7/_2$	$4f^5/_2$	
Hg^0	100.0	104.1	0.0
$(C_6H_5)_2Hg$	101.9	106.0	1.9
$(C_6Cl_5)_2Hg$	102.1	106.2	2.1
$(p\text{-}MeOC_6F_4)_2Hg$	102.7	106.8	2.7
$(o\text{-}HC_6F_4)_2Hg$	103.4	107.5	3.4
$(C_6F_5)_2Hg$	103.5	107.6	3.5
$(p\text{-}HC_6F_4)_2Hg$	103.6	107.7	3.6
$HgCl_2$	105.0	108.9	5.0

[a] Relative to Au $4f^7/_2 = 84.0$ eV

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

CONCLUSIONS

Both molecular weight measurements for R_2HgL complexes and X-ray photoelectron spectra of parent R_2Hg 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 $(o\text{-}HC_6F_4)_2HgOPPh_3$ relative to $(C_6F_5)_2HgOPPh_3$ is unexpected since a simple electronic model predicts C_6F_5 to be more electron withdrawing than $o\text{-}HC_6F_4$, whilst the photoelectron measurements suggest the two groups have similar electrophilic character.

TABLE III

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

Compound	Binding Energy[a,b]		Group Shift Relative to $4f^7/_2$ Hg^0[b]	Shift Based upon Additivity of Group Shifts[c]
	$4f^7/_2$	$4f^5/_2$		
Hg^0	100.0	104.1	0.0	
$C_6H_5HgC_6Cl_5$	101.9	106.0	1.9	2.0
C_6H_5HgCl	103.1	107.1	3.1	3.45
C_6Cl_5HgCl	102.8	106.8	2.8	3.55
C_6F_5HgCl	102.8	106.9	2.8	4.25
Cl—Hg—Hg—Cl	103.1	107.1	3.1	
$p\text{-}HC_6F_4HgCl$	104.2	108.3	4.2	4.3

[a] Relative to Au $4f^7/_2 = 84.0$ eV. [b] Uncertainty ±0.3 eV. [c] 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 521 spectrophotometers. Molecular weights of either preformed R_2HgL 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 $R_2HgOPPh_3$ ($R = C_6F_5$ or o-HC_6F_4) in benzene and the corresponding calibrations were measured under solvent-saturated nitrogen, which was passed slowly into the osmometer through an airtight inlet. The results did not differ significantly from those obtained under normal conditions. Stability constants of R_2HgL complexes were calculated using the expression $K = 2 - i/(i - 1)^2 c$ wehere i = calculated molecular weight of R_2HgL/observed molecular weight, and c is the initial concentration of the complex. X-ray photoelectron spectra of pelletised samples were recorded using Al K_α 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(polyfluorophenyl)mercurials, R_2Hg ($R = C_6F_5$, p-HC_6F_4, p-$MeOC_6F_4$, or o-HC_6F_4), were prepared by reported mercuration and symmetrization reactions, and were characterized by melting points and infrared spectra.[11,25,26] 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.[27,28]

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.[11,4]

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°) and bis(2,3,4,5-tetrafluorophenyl)mercury (0.32 mmol) in hexane were mixed. On cooling, the title compound was precipitated (yield, 60%), m. p. 120 °C.

Anal. $C_{30}H_{17}F_8HgOP$ (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, 714s, and 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. $C_{30}H_{17}F_8HgOP$ (777.02) calc'd: C 46.4; H 2.2; F 19.6%
found: C 46.2; H 2.2; F 19.2%

Infrared absorption: 3035w, 1595w, 1490sh, 1485s, 1455s, 1450s, 1420w, 1350m, 1220w(br), 1195w(br), 1185w, 1165m, 1154m, 1120m, 1090w, 1075w, 1025w, 995w, 905s, 890w, 850m, 745w, 725s, 705sh, 700m, and 695s cm^{-1}.

Similar attempts to isolate $(p\text{-}MeOC_6F_4)_2HgOPPh_3$ 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.

$(C_6F_5)_2Hgbpy$

Calc'd: mol. wt., 691. Found: mol. wt. (in benzene): 370 (1.11%), 367 (1.28%), 380 (1.75%), 376 (1.85%); (in CCl_4): 425 (0.654%), 429 (0.703%), 446 (0.773%).

$(p\text{-}HC_6F_4)_2Hgbpy$

Calc'd: mol. wt., 655. Found: mol. wt. (in benzene): 344 (1.48%), 347 (1.71%), 351 (1.72%), 348 (1.84%). The compound was insoluble in carbon tetrachloride.

$(o\text{-}HC_6F_4)_2Hgbpy$

Calc'd: mol. wt., 655. Found: mol. wt. (in benzene): 342 (1.60%), 342 (1.61%), 340 (1.75%), (in CCl_4): 365 (0.460%), 353 (0.659%).

$(p\text{-}MeOC_6F_4)_2Hgbpy$

Calc'd: mol. wt., 715. Found: mol. wt. (in benzene): 375 (1.54%), 380 (1.56%), 352 (1.84%); (in CCl_4): 393 (0.442%), 385 (0.552%), 390 (0.613%).

$(C_6F_5)_2HgOPPh_3$

Calc'd: mol. wt., 813. Found: mol. wt. (in benzene): 454 (1.21%), 493 (1.98%), 470 (2.01%), 480 (2.83%); (in benzene under N_2): 458 (1.20%), 460 (1.29%); (in CCl_4): 542 (0.525%), 557 (0.591%), 553 (0.648%).

$(p\text{-}HC_6F_4)_2HgOPPh_3$

Calc'd: mol. wt., 777. Found: mol. wt. (in benzene): 419 (1.49%), 428 (1.66%), 428 (1.85%); 427 (1.85%); (in CCl_4): 479 (0.645%), 476 (0.648%), 490 (0.804%).

$(o\text{-}HC_6F_4)_2HgOPPh_3$

Calc'd: mol. wt. 777. 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%), 560 (0.569%).

$(p\text{-}MeOC_6F_4)_2HgOPPh_3$

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 (0.626%).

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SAŽETAK

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

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Konstante stabilnosti dobivene mjerenjem molekulske težine kompleksa R_2Hgbpy (bpy = 2,2′-bipiridil) u tetraklormetanu i benzenu na 25 °C smanjuje se u nizu R = $C_6F_5 > p\text{-}HC_6F_4 \simeq p\text{-}MeOC_6F_4 \geq o\text{-}HC_6F_4$, a za $R_2HgOPPh_3$, u nizu R = $o\text{-}HC_6F_4 > C_6F_5 > p\text{-}HC_6F_4 \simeq p\text{-}MeOC_6F_4$ s većim vrijednostima u tetraklormetanu. Neočekivano veća stabilnost $(o\text{-}HC_6F_4)_2HgOPPh_3$ prema onoj $(C_6H_5)_2HgOPPh_3$ u vezi je sa strukturama tih merkurijala. Rendgenska fotoelektronska spektroskopija pokazuje da se akceptorska svojstva živinih spojeva smanjuju u nizu $HgCl_2 > (C_6F_5)_2Hg \simeq (p\text{-}HC_6F_4)_2Hg \simeq (o\text{-}HC_6F_4)_2Hg > (p\text{-}MeOC_6F_4)_2Hg > (C_6Cl_5)_2Hg \geq Ph_2Hg \geq Hg$. Slične studije spojeva RHgX pokazuju da ima razloga za pretpostavku o aditivnosti elektrofilnih efekata različitih grupa R i X na 4f-energiju vezanja žive.