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Organomercury alkoxides. Vibrational spectra and structure of MeHgOPh and PhHgOR (R = Ph, Me, Et)

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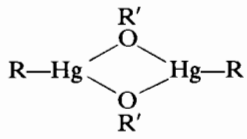
Abstract—Studies of RHgOPh (R = Me, Ph) by osmometry and Raman spectroscopy in dichloromethane, and by i.r. and Raman spectroscopy in the solid state, indicate monomeric structures in the solid state and solution with ν(Hg—O) near 600 cm^{-1}. The complexes PhHgOR (R = Me, Et) are dimeric in the solid state with ν(OHgO) modes in the region 500–430 cm^{-1}.

INTRODUCTION

From ebullioscopic measurements it has been shown that PhHgOMe is dimeric in boiling benzene [mol. wt (found)/mol. wt (calculated for monomer) 1.99], but other alkoxides are partially dissociated into monomers, e.g. PhHgOPh has mol. wt (found)/mol. wt (calculated for monomer) 1.31 [1]. A dimer is expected to have three-coordination for mercury(I) in contrast with the usual linear geometry in organomercury compounds [2, 3], e.g. related thiolates(II) [4, 5]. Assignment of mercury–oxygen mode(s) in vibrational spectra should allow differentiation between monomeric and dimeric structures as the dimeric structure is expected to have a centre of symmetry. Vibrational spectra of RHg^{II} alkoxides have not been assigned, although closely related $(MeHg)_2O$ [6], $(PhHg)_2O$ [7], and MeHgOH [8] have Hg–O modes in the range 675–511 cm^{-1}.



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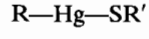

II

RESULTS AND DISCUSSION

Except for the phenoxides RHg^{II} alkoxides are extremely moisture sensitive, hydrolysing readily to the oxide, and although prepared with rigorous exclusion of air and moisture i.r. spectra indicate presence of a minor impurity of $(PhHg)_2O$. Thus, solution studies were restricted to RHgOPh (R = Me, Ph) with dichloromethane chosen as solvent as these complexes are sufficiently soluble at ambient temperature, and although dichloromethane has intense, polarized, Raman bands at 704 and 286 cm^{-1} [9] it is free of bands in the region expected for ν(Hg–O) modes.

RHgOPh (R = Me, Ph)

The complexes RHgOPh were found to be monomeric at 25°, and molecular weight studies of a mixture of PhHgOPh and Ph_3As gave no indication of complex formation (Table 1). Raman spectra of RHgOPh within the range bounded by CH_2Cl_2 bands at 704 and 286 cm^{-1} are similar to spectra of the solid complexes (Fig. 1), and i.r. and Raman spectra of the solids are very similar, indicating monomeric structures in the solid state also (Table 2). Spectra have been assigned by comparison with spectra of RHgSPh (R = Ph [5], Me), $(PhS)_2Hg$ [5], PhSH and $(PhS)_2$ [10], PhOH [11], Ph_2O [12], MeOPh [13], and a range of PhHg^{II} [5, 6, 14, 15] and MeHg^{II} [6, 8, 16, 17] compounds. Methylmercury(II) modes are clearly identified by band intensities which are similar in both MeHgSPh and MeHgOPh. The frequencies of X-sensitive modes can be estimated from PhOH and Ph_2O. Although Whiffen's notation for phenyl modes was devised for molecules of C_{2v} symmetry [18] it has been successfully applied to PhHg^{II} compounds of lower symmetry [15], e.g. PhHg^{II} acetate, and is used here for alkoxides. Recent assignments for PhHgCl are given in Table 2 to illustrate similarities in frequencies, relative intensities (particularly i.r. vs Raman), and depolarization ratios of PhHg^{II} modes.

For PhHgOPh the frequencies of the PhHg^{II} and OPh fundamentals are sufficiently different to enable assignment of modes for each group. However, there is some uncertainty in assignment of *t* and y X-sensitive OPh modes, assigned to bands at 535 and 509 cm^{-1} (i.r.), respectively, in MeHgOPh. For PhHgOPh there are two bands at 539 and 514 cm^{-1} which would appear to correspond to these modes, but both bands are associated with weak Raman bands and while this is characteristic of the y X-sensitive it is not expected for the *t* mode, e.g. in MeOPh [13] and PhOH [11] the *t* mode is an intense polarized band. The nearest band of this description in PhHgOPh is at 586 cm^{-1} ($\rho = 0.2$).

Assignment of RHg^{II} and OPh modes leaves two possible frequencies for a ν(Hg—O) mode in monomeric RHgOPh, at 629 and 590 cm^{-1} (i.r., R = Me) and 632, 583 cm^{-1} (i.r., R = Ph), and these

Table 1. Molecular weight data*

Complex	Conc(M)	Calc'd†	Found	Found/Calc'd
PhHgOPh	0.47×10^{-2}	371	361	0.97
MeHgOPh	0.33×10^{-2}	309	303	0.98
PhHgSPh	0.34×10^{-2}	387	399	1.03
MeHgSPh	0.39×10^{-2}	325	327	1.01
Ph_3As	0.62×10^{-2}	306	313	1.02
PhHgOPh + Ph_3As	0.66×10^{-2}	345‡	339	0.98

* In dichloromethane.
† Calculated for monomer.
‡ Calculated for equimolar mixture with absence of complex formation.

values are similar to those in $(MeHg)_2O$ (590, 570 cm^{-1} (i.r.) [6]) and $(PhHg)_2O$ (ν_{as} 675 cm^{-1} (i.r.) [7]). For a monomeric structure with point group C_s ν(Hg—O)(A') should appear in both i.r. and Raman spectra and be polarized. For MeHgOPh the band at 590 cm^{-1} (i.r.) is unlikely to be ν(Hg—O) as the Raman spectrum does not have a corresponding band and, consistent with assignment as ν(Hg—O) the band at 630 cm^{-1} (Raman, CH_2Cl_2) is polarized ($\rho = 0$). The analogous band for PhHgOPh, 632 cm^{-1} is also polarized ($\rho = 0$), as also is the band at 590 cm^{-1} (discussed above as a possible t mode).

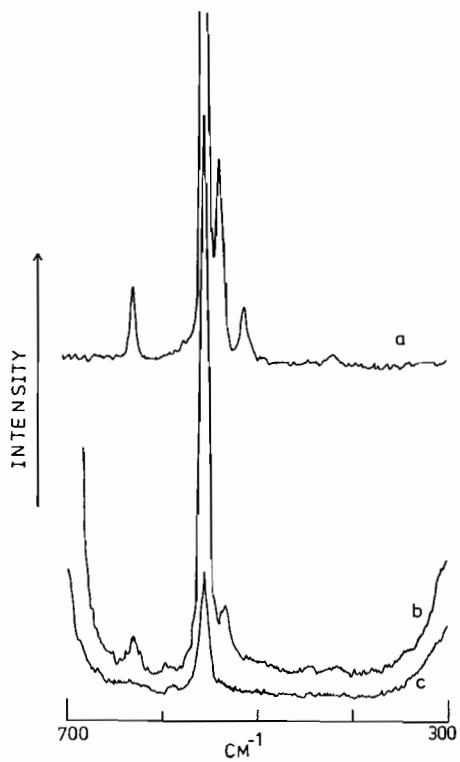

Fig. 1. Raman spectrum of MeHgOPh. (a) Solid. (b) In CH_2Cl_2, parallel polaroid. (c) In CH_2Cl_2, perpendicular polaroid.

Although assignment of ν(Hg—O) is not definite, but probably at *ca.* 630 cm^{-1}, the values possible are consistent with monomeric behaviour demonstrated by osmometry and comparison of solid state and solution spectra, and are thus of assistance in ascertaining whether other $PhHg^{II}$ alkoxides (studied in the solid state only) are monomeric or dimeric.

PhHgOR (R = Me, Et)

Spectra of these complexes were assigned by comparison with spectra of RHgOPh and other organomercury compounds, including analogous thiolates, together with reported spectra and assignments for ROH [19, 20], $(MeO)_2$ [21], $(MeS)_2$ [22], $(EtS)_2$ [22], Et_2O [23], H_3GeOMe [24], $Et_2Sn(OMe)_2$ [25], and $PhB(OMe)_2$ [26]. As found for PhHgOPh the frequencies of $PhHg^{II}$ modes are close to those reported by BARRACLOUGH *et al.* [14] and GOGGIN and MCEWAN [15], and relative intensities follow similar trends.

Unlike monomeric RHgOPh (R = Me, Ph) spectra do not have bands above 500 cm^{-1} that cannot be readily assigned as $PhHg^{II}$ or alkoxide modes (Table 3). Mercury–ligand stretching frequencies are sensitive to coordination number in the expected way [27], e.g. $Hg(SMe)_2$ (linear SHgS, with weak intermolecular interactions [28]) has ν_{as}(SHgS) 377, ν_s(SHgS) 297 cm^{-1} [29], much higher than $Hg(SBu^t)_2$ (tetrahedral HgS_4 polymer with bridging sulfur [30]) ν_{as}(SHgS) 172, ν_s(SHgS) 188 cm^{-1} [29], and consistent with dimer formation and coordination number three for mercury spectra of PhHgOR (R = Me, Ph) have bands in the region 430–500 cm^{-1} assigned as ν(OHgO) modes, well below ν(Hg—O) in monomeric RHgOPh (R = Me, Ph). Consistent with a centre of symmetry in PhHgOMe ν_{as}(OHgO) (502 cm^{-1}) is absent in Raman spectra and ν_s(OHgO) (446 cm^{-1}) is absent in i.r. spectra. For PhHgOEt most bands within the region 550–400 cm^{-1} are present in both i.r. and Raman spectra. However, the band at 485 cm^{-1} (i.r.) loses much of its intensity in the Raman

Table 2. Infrared and Raman spectral frequencies for RHgOPh and PhHgCl in the region 1000–200 cm^{-1}*

MeHgOPh		PhHgOPh		PhHgCl†		Assignment‡
i.r.	Raman	i.r.	Raman	i.r.	Raman	
994m	995vs	996m	997vs	998m	997s	p, ring (PhHg)
		991w				j,γ(CH)(PhHg)
		911vvw		910vw		i,γ(CH)(PhHg)
870m		862vw				i,γ(CH)(PhO)
					843vw	g,γ(CH)(PhHg)
842m	840w(b)					
827s	832w	837s	838w			r,X-sens(PhO)
		819m				
799s						Me rock
		799vw	800vw			583+223(?)
752vs	753w	754s	759w			f,γ(CH)(PhO)
722vvw		734s		727s, 723s		f,γ(CH)(PhHg)
693vs		695s		692s		v,ϕ(CC)(PhHg)
		685s				v,ϕ(CC)(PhO)
				675w(b)		
		668vw	668m [666m(p,0.05)]	664w	664m[666s(p)]	r,X-sens(PhHg)
629w	629w [630w(p,0)]	632m	635m [632m(p,0)]			ν(Hg-O)?
		618vvw	618w [617w(dp,0.84)]	615w	616vw[615w(dp)]	s,α(CCC)
590m						
		583s	586m [590m(p,0.2)]			t,X-sens(PhO)?
548vvw	555vs[557s(p,0.2)]					ν(Hg-C)
		539m	542vvw			270x2?
535m	539m [536w(p,0)]					y,X-sens(PhO)
509m	513w	514m	516vw			y,X-sens(PhO)
			486vvw		466vvw	
		450m		454ms		y,X-sens(PhHg)
	418vw	411vvw				w,ϕ(CC)
265w	266w	270m(b)	278vvw			u,X-sens(PhO)
		250m	250w(sh)		240vs[239vs(p)]	t,X-sens(PhHg)
229vw	234m	263m	237s			x,X-sens(PhO)
		223m	223m	221wm	225vw	u,X-sens(PhHg)

* Nujol mulls (i.r.) and solids (Raman), spectra in dichloromethane given in parentheses [ ] with ρ in parentheses ( ). Abbreviations: w, weak; m, medium; s, strong; v, very; b, broad. See Fig. 1 for spectra of MeHgOPh.

† From Reference [15]. BARRACLOUGH *et al.* [14] assign *j*, γ(CH) to a low intensity band at 986w (i.r. [6]) [987w (R[14])] and assign bands at 330vs (i.r. [6]) [317s (R[14])] and 220m (i.r. [6]) [238vs, 224w (R[14])] as predominantly ν(Hg–Cl) and ν(Hg–C), respectively. Spectra in tetrahydrofuran below 800 cm^{-1} given in parentheses [ ].

‡ Whiffen's notation [18], and major component.

spectrum, and the Raman band at 430 cm^{-1} is more intense than other bands in this region of the spectrum.

Thus, vibrational spectra of PhHgOR (R = Me, Et) are consistent with a dimeric structure in the solid state, as found for PhHgOMe in boiling benzene using ebullioscopy. However, RHgOPh (R = Me, Ph) are monomeric in dichloromethane at 25°C and in the solid state with ν(Hg—O) near 600 cm^{-1}, higher than for ν(OHgO) modes in dimeric PhHgOR (R = Me, Et) containing three-coordinate mercury (500–430 cm^{-1}). Analysis of the spectra does not exclude the presence of weak intermolecular Hg . . . O interactions, e.g. as occurs in phenyl(quinolin-8-olato)mercury(II) with Hg . . . O 3.33(4) Å [33].

EXPERIMENTAL

Materials

Phenylmercury(II) oxide was prepared by reported methods [1, 7], and used to prepare PhHgOR (R = Me, Et) [1]; PhHgOMe has i.r. absorption 1029 s(b) (lit. 1030 cm^{-1}), PhHgOEt 1088 m, 1044 s(b), 872 m (lit. 1090, 1050 and 880 cm^{-1}). The complex PhHgOPh [i.r. absorption 1258 vs(b), 837 s (lit. 1255 and 840 cm^{-1} [1])], MeHgOPh and MeHgSPh were prepared by reported methods [31, 32]. Dichloromethane was purified as described [34], and dimethyl- and diethylcarbonate (Fluka) were distilled and stored over molecular sieves.

Physical measurements

Molecular weights were determined in dichloromethane at 25°C with a Knauer vapour pressure osmometer. Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol

Table 3. Infrared and Raman spectral frequencies for PhHgOR (R = Me, Et) in the region 1000–200 cm^{-1}*

PhHgOMe		PhHgOEt		Assignment†
i.r.	Raman	i.r.	Raman	
998w	995vs	997m	999vs	p, ring
976vw		965vw		h,γ(CH)
912vvw		907vw	911ww(b)	i,γ(CH)
		872m	882vvw(b)	ν(C-c),ν(C-O),Me rock
		852w	852vvw(b)	CH_2 rock
731s }				
727s }		725vs		f,γ(CH)
702m		699s		v,δ(CC)
	663s		663m	r,X-sens
	617vw	618vw	618vw	s,α(CCC)
502w		485s(b)	489vw(b)	ν_{as}(OHgO)
476w	476m			2x244(?)
460w		453s	463vw(b)	y,X-sens
	446m	431w	430w(b)	ν_s(OHgO)
		409vw		w,φ(CC)
		268vw		
255vw }		255vw(sh)		
241vw }	244s	237w	245m(b)	t,X-sens
227w }	233m(sh)			
216w }		223w	214m	u,X-sens
		206w		x,X-sens

* Nujol mulls (i.r.) and solids (Raman). Abbreviations: w, weak; m, medium; s, strong; v, very; b, broad; sh, shoulder.

† WHIFFEN's notation [18], and major component.

and hexachlorobutadiene mulls, and far i.r. spectra (600–200 cm^{-1}, Nujol mulls, polyethylene plates), were recorded with a Perkin–Elmer 577 spectrometer. For moisture sensitive alkoxides mulls were prepared in a dry nitrogen glove bag with Nujol and hexachlorobutadiene dried over molecular sieves, and the sample compartment was purged with dry air. Raman spectra were measured with a Cary 82 laser Raman spectrometer over the range 1500–100 cm^{-1} using 514.5 nm excitation. All spectra were obtained at ambient temperature, and maximum errors are considered to be 4 cm^{-1} for both i.r. and Raman spectra.

Infrared spectra (4000–1000 cm^{-1})

MeHgOPh. 3064 w, 3010 w(sh) and 3004 w and 2990 w, 2922 w, 1588 vs and 1574 vs(sh), 1483 vs(sh) and 1475 vs, 1445 m, 1413 vw, 1384 vvw, 1333 vvw, 1277 s, 1246 vs(b), 1194 vw, 1190 m, 1175 w, 1169 vvw, 1163 m, 1144 vw, 1071 m, 1023 vw cm^{-1}.

PhHgOPh. 3038 w and 3025 w, 3008 w, 2988 w, 1590 s, 1576 m(b), 1488 s and 1479 s(b), 1434 m, 1330 vw, 1305 vw(sh) and 1283 s, 1258 vs(b), 1217 w, 1194 vw, 1184 vw, 1173 vw(sh) and 1168 w, 1148 w, 1075 w, 1064 vw, 1025 m cm^{-1}.

PhHgOMe. 2920 vw, 2899 w, 2860 vw, 2832 w, 2774 w, 1478 w, 1445 vw, 1432 m, 1382 vw (b), 1305 vw, 1263 w, 1158 vw(b), 1090 vw(vb), 1078 vw, 1066 vw, 1029 s(b), 1020 s cm^{-1}.

PhHgOEt. 3070 w and 3050 w, 2950 m, 2872 w and 2822 m, 2690 w, 1478 w(b), 1577 w, 1480 m, 1437 w(sh) and 1430 m, 1374 m, 1353 m, 1303 vw, 1251 m, 1192 vw, 1156 vw, 1088 m, 1044 s(b), 1020 m cm^{-1}.

Raman spectra (1600–1000 cm^{-1})

MeHgOPh. 1446 w, 1278 w, 1261 m, 1195 s, 1174 w, 1151 w, 1071 vw, 1028 s cm^{-1}.

PhHgOPh. 1480 w, 1446 vw, 1435 vvw, 1334 vw(b), 1307 vw, 1282 vw, 1258 s, 1196 w, 1164 w, 1150 w, 1084 w, 1030 s cm^{-1}.

PhHgOMe. 1480 w, 1258 vw, 1162 w, 1080 vw, 1035 vw, 1018 m cm^{-1}.

PhHgOEt. 1480 vw, 1444 vvw, 1430vvw, 1332 vvw, 1190 vw(b), 1157 w, 1080 w, 1025 m cm^{-1}.

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