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Coordination complexes of 2-thienyl- and 2-furyl-mercurials

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The reactions of di(2-thienyl)mercury, 2-thienylmercury chloride and 2-furylmercury chloride with a variety of nitrogen- and phosphorus-containing ligands have been studied. The presence of the electron-withdrawing heteroatoms results in these mercurials being stronger acceptors than the corresponding phenylmercury compounds. The complexes have been characterized by elemental analysis, melting points, infrared, and ^{199}Hg NMR spectroscopy. 2,9-Dimethyl- and 3,4,7,8-tetramethylphenanthroline form 1:1 chelate complexes, as does 1,2-bis(diphenylphosphino)ethane, whereas ethylenediamine and 2,2′-bipyridyl do not form complexes. Though non-chelating ligands such as 2,4′- and 4,4′-bipyridyl do not form complexes, bis(diphenylphosphino)methane forms 1:2 complexes in which the ligand bridges two mercury atoms. Monodentate ligands, such as triphenylphosphine, cause disproportionation of the organomercury chloride. 2-Thienylmercury chloride forms a 4:1 complex with 4,4′-dipyridyl disulfide in which it is believed that a molecule of the organomercurial is coordinated to both of the nitrogen and both of the sulfur atoms.

KEYWORDS: organomercury; complexes; ligands; coordination; 2-thienyl; 2-furyl; ^{199}Hg NMR; IR

INTRODUCTION

Organomercury compounds have found an impressive range of applications, e.g. as pesticides, fungicides, algicides, bactericides, antiseptics, diuretics and herbicides.[1] In addition, their ability to accommodate all functional groups and their remarkable chemical and thermal stability have made organomercury compounds particularly attractive as synthetic intermediates.[2] The most significant of the synthetic applications include (i) the solvomercuration–demercuration of alkenes,[2] (ii) the use of α-halomethymercury compounds as carbene transfer reagents[3] and (iii) the stereospecific dimerization of organomercury halides via transmetallation reactions.[4] The effectiveness of organomercurials in many of the above roles is influenced by the acidity of the mercury atom and its attendant ability to accept electron density from donor systems. Certainly, the activity and toxicological properties of organomercury compounds are dependent upon the extent and nature of interaction with bases.[5,6] For example, the effectiveness of 2,3-dimercaptopropan-1-ol (British anti-Lewisite; BAL) in treating organomercury poisoning is dependent upon the acceptor properties of the mercury compounds and upon their ability to react with the available sulfur atom of BAL.[7,8]

The ability of 2-coordinate mercury(II) to form complexes is very dependent upon the nature of the groups attached to mercury. Thus, whereas mercury(II) halides form a wide range of adducts with monodentate and polydentate ligands,[9,10] no complexes have been isolated for mercury dialkyls. The relative electronegativities of mercury and the adjoining groups, together with the resulting influence upon the formal charge on mercury, play an important role in complex formation. Thus, the inability of mercury dialkyls to form stable complexes may be a reflection of the similar electronegativities of alkyl groups and mercury (*ca* 2.3 and 1.9 respectively), hence resulting in low formal charge on mercury. Replacement of alkyl by more electronegative groups enhances stable complex formation. Certainly, the replacement of one of the organic groups attached to mercury to form organomercury halides (RHgX) increases the acceptor

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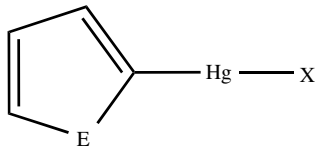
character of mercury, and complexes, particularly of nitrogenous bases, have been isolated for a range of R and X.[11–17] Substitution in R_2Hg by electron-withdrawing substituents in R also increases the formal charge on mercury, thereby enhancing the formation of stable addition compounds. Thus, bis(trinitromethyl)mercury,[18] bis(fluoroalkyl)mercurials[19,20] and bis(trichlorovinyl)mercury[21] form a wide range of isolable complexes in contrast to the dialkylmercurials themselves. Similarly, whereas Ph_2Hg only gives rise to weak complexes of the type Ph_2Hg2L(L = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 2,4,7,9- tetramethyl-1,10-phenanthroline),[22,23] the Lewis acidity of mercury is enhanced by the use of fluorinated (and, therefore, electron-withdrawing) substituents, and important coordination chemistry of such fluorinated aryl mercurials has been reported.[24–34] The structures and coordination chemistry of organomercurials have been very well reviewed.[35–37]

The dissociation constants of 2-furan carboxylic acid (pK_a = 3.15) and 2-thienylcarboxylic acid (pK_a = 3.48) compared with benzoic acid (pK_a = 4.19)[38] indicate that the furyl and thienyl groups are more electronegative than the phenyl group due to the presence of the heteroatom. Indeed, we have previously shown that R_2Hg(R = 2-thienyl, 2-furyl) do form isolable complexes,[39] and herein we expand on these studies and report the coordination chemistry of 2-furylmercury chloride, 2-thienylmercury chloride and di(2-thienyl)mercury (Fig. 1) with a variety of monodentate and bidentate nitrogen and phosphorus donors.



where E = O or S

Figure 1. 2-Thienylmercury(II) chloride (E = S, X = Cl), 2-furylmercury(II) chloride (E = O, X = Cl) and di(2-thienyl)-mercury(II) (E = S, X = 2-thienyl).

MATERIALS AND METHODS

The ligands were commercially available from Aldrich and were used without further purification. The organomercurials, 2-furylmercury(II) chloride (m.p. 149–151 °C, lit. 151 °C[40]) and 2-thienylmercury(II) chloride (m.p. 185–187 °C, lit. 183 °C[40]) were prepared by the mercuration of furan and thiophene respectively. Di-2-thienylmercury (m.p. 199–200 °C,

Table 1. Quantities of reactants, analytical data, ^{199}Hg NMR chemical shifts (δ) and physical properties of products

Complex[a]	Mass RHgX/g (mmol)	Mass ligand/g (mmol)	Analyses/%[b] C	H	N	$\delta(^{199}Hg)$/ppm	M.p./°C	Appearance
T_2Hg tmp	0.61	0.39	48.05	3.62	4.52	−1430	180–210	Colourless prism
	(1.66)	(1.65)	(47.79)	(3.67)	(4.64)			
$(T_2Hg)_2$ dppm	0.37	0.38	44.01	2.93	—	−1110	110–112	White powder
	(1.00)	(1.00)	(44.04)	(3.06)				
THgCl dmp	0.59	0.40	40.43	2.74	5.10	−797	159–163	White powder
	(1.85)	(1.84)	(40.90)	(2.87)	(5.31)			
THgCl tmp	0.57	0.42	42.58	3.18	4.81	−1090	220–221	White powder
	(1.78)	(1.77)	(43.24)	(3.45)	(5.04)			
$(THgCl)_2$ dppm	0.90	0.54	40.07	2.83	—	−678	210–212	White powder
	(2.82)	(1.41)	(39.13)	(2.76)				
THgCl dppe	0.44	0.55	50.43	3.66	—	−910	165–167	White powder
	(1.38)	(1.38)	(50.20)	(3.79)				
$(THgCl)_4$ pySSpy	0.64	0.44	21.86	1.36	1.69	Insoluble	175–180	Yellow powder
	(2.00)	(2.00)	(20.85)	(1.34)	(1.87)			
FHgCl dmp	0.31	0.22	40.76	2.92	5.45	−2285	190–192	White needles
	(1.03)	(1.00)	(42.27)	(2.96)	(5.47)			
FHgCl tmp	0.31	0.24	44.53	3.55	5.19	−2452	233–235	White needles
	(1.03)	(1.00)	(44.24)	(3.87)	(5.33)			
$(FHgCl)_2$ dppm	0.30	0.31	40.33	2.87	—	−2118	256–260	White powder
	(1.00)	(1.00)	(40.00)	(2.85)				

[a] T = 2-thienyl; F = 2-furyl; tmp = 3,4,7,8-tetramethyl-1,10-phenanthroline; dppm = bis(diphenylphosphino) methane; dmp = 2,9-dimethyl-1,10-phenanthroline; dppe = 1,2-bis(diphenylphosphino)ethane; pySSpy = 2,2′-dipyridyl disulfide.
[b] Theoretical values in parentheses.

lit. 198–200 °C[40]) was prepared by symmetrization of 2-thienylmercury chloride with sodium iodide in acetone.

Microanalyses were carried out by Medac Limited at Brunel University. Melting points were carried out using an Electrothermal melting point apparatus and are uncorrected. The FTIR spectra of the ligands, organomercurials and complexes were obtained as KBr discs in the range 4000–600 cm^{-1} with an ATI Mattson Genesis Series FTIR spectrometer. Identical spectra were obtained as Nujol mulls but were not as well resolved. ^{199}Hg NMR studies were carried out using a Bruker AC500 FTNMR instrument operating at 71.635 MHz at room temperature. All spectra were recorded in dimethylformamide-d_7 and chemical shifts are given in parts per million and referenced to mercury(II) perchlorate standard (1 M $Hg(ClO_4)_2$ in 1 M $DClO_4$; $\delta = -2250$ ppm).[41]

The ligand, dissolved in the minimum amount of ethanol, was added to a hot solution of the organomercurial, also in ethanol (*ca* 50 cm^3). The resulting solution was left to cool in ice to crystallization and the product was then filtered off under suction and dried *in vacuo*. The quantities of materials used, appearance, melting points, ^{199}Hg chemical shifts and analytical data are reported in Table 1.

RESULTS AND DISCUSSION

The reactions of 2-furyl- and 2-thienyl-mercury chloride with a variety of nitrogen and phosphorus donors in ethanolic solutions produced a number of stable complexes (Table 1), showing that they were better acceptors than phenylmercury chloride[42] due to the presence of the heteroatoms. Both dmp and tmp formed 1 : 1 chelate complexes, as previously shown for $(C_2Cl_3)_2Hg$ tmp,[43] with both mercurials. Although we previously reported[39] that di(2-thienyl)mercury did not form an isolable complex with tmp, though it did with dmp, we have now shown that such a complex can be isolated (Table 1). However, the acceptor character of these mercurials is somewhat limited, as no complexes could be isolated with some other chelating ligands, such as ethylenediamine or 2,2′-bipyridyl. Organomercurials tend to preserve approximate linearity on coordination,[24,43,44] and so the ligands interact largely with p-orbitals on the metal. Thus, 1,10-phenanthroline and its substituted derivatives form isolable complexes with organomercurials, as these ligands are planar molecules. In contrast, 2,2′-bipyridyl does not form complexes with the organomercurials studied herein. This is due to twisting of the rings to minimize interaction

Table 2. IR bands (KBr discs) 4000–600 cm^{-1}

T_2Hg	3100w, 1410m, 1330w, 1220s, 1090w, 1050w, 970m, 850s, 720w, 700s
THgCl	3100w, 1400s, 1330m, 1218vs, 1082m, 1050w, 965m, 850vs, 833s, 705vs, 692m
FHgCl	3120w, 1445s, 1350m, 1200m, 1140vs, 1090m, 1050m, 995s, 915w, 890s, 755vs, 740vs
Dppm	3095w, 1590m, 1490s, 1440vs, 1395m, 1362w, 1310w, 1185w, 1092m, 1030m, 1000m, 900m, 793m, 742vs, 720w, 695vs
Dppe	3455s, 3090w, 1950m, 1590w, 1491s, 1440vs, 1337w, 1309w, 1160m, 1100m, 1083m, 1071m, 1026m, 750m, 738s, 725vs, 693vs
Dmp	3500m, 1678s, 1625s, 1602s, 1563m, 1510vs, 1440w, 1420w, 1370s, 1214w, 1143w, 1030w, 860vs, 790m, 760m, 738s
Tmp	3400w, 1620m, 1580m, 1528vs, 1435vs, 1397m, 1272m, 1240m, 1200s, 1020w, 950m, 915w, 860m, 835s, 738vs, 714w
PySSpy	3413m, 1619s, 1569vs, 1477s, 1407s, 1319w, 1284w, 1214w, 1118vs, 1064m, 806s, 701m, 620m, 528m
T_2Hg tmp	2950w, 1620m, 1582m, 1528vs, 1438vs, 1390m, 1325m, 1271m, 1240s, 1208vs, 1190m, 1080m, 1020m, 730s, 702vs, 690vs, 1000m, 955s, 921m, 879s, 850vs, 822vs
$(T_2Hg)_2$ dppm	3050w, 1484m, 1434vs, 1311w, 1187m, 1160m, 1099s, 995m, 840m, 786m, 740s, 690vs
THgCl dmp	3500w, 1620m, 1600s, 1566m, 1512vs, 1440m, 1390s, 1380s, 1224m, 1208s, 1150s, 1038m, 862vs, 843s, 775s, 726s, 685vs
THgCl tmp	3500w, 2750m, 1620m, 1585m, 1530s, 1440s, 1390s, 1270w, 1240m, 1205m, 925m, 878m, 820s, 720vs, 700vs, 690vs
$(THgCl)_2$ dppm	3095w, 1497m, 1445vs, 1403m, 1350w, 1325w, 1220m, 1100vs, 1033w, 1002m, 965m, 845m, 790s, 738s, 700vs, 684vs
THgCl dppe	3500w, 3100w, 1492m, 1442vs, 1402m, 1326w, 1220m, 1101m, 1082m, 1070m, 1031m, 1080m, 962m, 841vs, 723vs, 698vs, 690vs
$(THgCl)_4$ pySSpy	3448w, 1619m, 1577vs, 1542w, 1477m, 1411m, 1315w, 1214m, 1110m, 1060s, 1010m, 813s, 705s
FHgCl dmp	2910w, 1622w, 1606m, 1573w, 1514vs, 1456s, 1383m, 1374m, 1230m, 1152m, 1055m, 997s, 883s, 860vs, 763m, 738s, 720s
FHgCl tmp	2950w, 1628m, 1600m, 1538s, 1446s, 1391s, 1278w, 1250m, 1206w, 1181w, 1016w, 922m, 877s, 855w, 810s, 712vs
$(FHgCl)_2$ dppm	1492s, 1442vs, 1202w, 1166w, 1104s, 1021w, 1000m, 785m, 738vs, 718s, 688vs

of the 3,3′ hydrogen atoms, resulting in poor overlap of mercury–ligand orbitals. With other bidentate ligands, such as 2,4′- and 4,4′-bipyridyl, where the positions of the donor atoms preclude chelation, no complex could be isolated, though we had isolated complexes of these ligands with trichlorovinylmercurials.[17,45] With 4,4′-dipyridyldisulfide, 2-thienylmercury chloride formed an unusual 1 : 4 complex in which it is believed that the organomercurial is coordinated to both of the nitrogen and both of the sulfur atoms of the ligand. Unfortunately, we were unable to grow sufficiently good crystals of this complex for X-ray analysis.

Whereas triphenylphosphine caused disproportionation of the organomercury chlorides, resulting in the formation of $(Ph_3P)_2HgCl_2$, both dppm and dppe formed isolable complexes. All three mercurials formed complexes of the type $(RHgR')_2$ dppm (R = R′ = 2-thienyl; R = 2-thienyl, 2-furyl, R′ = Cl), because of the steric strain that would result from chelation, in which the ligand bridges two mercury atoms. Such a structure has been confirmed crystallographically for $((C_6F_5)_2Hg)_2(Ph_2AsCH_2AsPh_2)$,[24] in which the geometry around mercury consists of one arsenic atom and two C_6F_5 groups in a T-shaped formation with a C–Hg–C angle of 173°. Preliminary studies of the phosphine analogue have confirmed a similar arrangement, yet again illustrating the weak coordination characteristics of organomercurials and their preference for approximately linear coordination around mercury. In contrast, dppe formed 1 : 1 complexes, which are doubtless chelated.

The ^{199}Hg NMR chemical shifts are shown in Table 1. They lie in the range −678 to −1430 ppm for the 2-thienyl complexes, with larger chemical shifts (−2118 to −2452 ppm) for the 2-furyl complexes, thus reflecting the greater electron-withdrawing effect of oxygen compared with sulfur. The IR spectra of the complexes (Table 2) appeared as the spectrum of the ligand superimposed on the spectrum of the organomercurial, with only minor shifts in some of the ligand absorption frequencies, indicating only weak bonding between mercury and the ligands. Thus, although these heterocyclic mercurials form more complexes than their phenylmercury analogues due to the presence of the electron-withdrawing heteroatom, these are still of a very weak nature

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