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COORDINATION COMPLEXES OF DI-2-THIENYLMERCURY AND DI-2-FURYLMERCURY

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Summary

The reaction of di-2-furylmercury and its sulphur analogue with some monodentate and bidentate nitrogen, phosphorus and sulphur bases has been studied. Both organomercurials are relatively weak electron acceptors, the thienyl compound being weaker than the furyl compound, and only four complexes, $(C_4H_3X)_2Hg$ L (X = O, L = phen, tmp; X = O, S, L = dmp) * have been isolated. These represent the first reported examples of complexes formed by heterocyclic organomercury compounds, and their infrared, ^1H NMR and mass spectra have been examined as well as their thermal behaviour.

Introduction

Because the electronegativities of alkyl groups and mercury have similar values (ca. 2.3 and 1.9 respectively on the Pauling scale) [1], the formal charge on mercury will be low, preventing strong coordinative mercury-ligand bonds being formed. Consequently, complexes of dialkylmercury compounds have not been isolated, contrasting sharply with mercury(II) halide systems, for which many complexes have been obtained [2]. For diphenylmercury, because the electronegativity of the phenyl group is greater (3.0) [1], complexes of the type Ph_2Hg 2L (L = phen, dmp and 2,4,7,9-tetramethyl-1,10-phenanthroline) * have been reported, though these complexes dissociate in solution [3,4]. An X-ray diffraction study of the diphenylmercury complexes formed by the methyl-substituted phenanthroline ligands did not unequivocally establish the role of the ligands since the structure could not be refined owing to disorder, but it is believed that interaction is only weak [5], as is the case in CCl_3HgCl phen [6].

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* phen, tmp and dmp represent abbreviations for 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline, respectively.

On the basis of oscillometric titrations, it has been suggested that diphenylmercury forms complexes with some neutral unidentate ligands in benzene solution [7], but no complexes have been isolated other than those mentioned above [3,4,8]. Dialkynylmercury compounds, $(RC{\equiv}C)_2Hg$, ($R = CH_3$, $ClCH_2$, $BrCH_2$, C_6H_5) also form isolable complexes with both phen and dmp [9,10].

Substitution in R_2Hg by electron withdrawing substituents in R increases the formal charge on mercury, thereby enhancing the formation of complexes, so that bis(trinitromethyl)mercury [11], bis(fluoroalkyl)mercury compounds [12,13], and bis(pentafluorophenyl)mercury [14—17] form a wide range of isolable complexes and recently five complexes of bis(trichlorovinyl)mercury have been obtained [18].

As yet, the coordination chemistry of heterocyclic organomercury compounds has not been investigated. The dissociation constants of 2-furancarboxylic acid (pK_a 3.15 at 25° C in aqueous solution) and 2-thienylcarboxylic acid (pK_a 3.48) when compared to that of benzoic acid (pK_a 4.19) [19] suggest that the furyl and thienyl groups are more electronegative than the phenyl group, and thus di-2-furylmercury and di-2-thienylmercury should have a greater tendency for complex formation than diphenylmercury. Herein, we report the results of our study of the coordination chemistry of these two heterocyclic organomercury compounds.

Results and Discussion

Replacement of sulphur in the hetero rings of di-2-thienylmercury by the more electronegative oxygen atom enhances the acceptor character of the organomercury compound, so that di-2-furylmercury forms isolable complexes with phen, dmp and tmp whereas the former forms an isolable complex only with dmp. These complexes, which represent the first reported examples of complexes formed by heterocyclic organomercurials, are no doubt basically tetrahedral, with the planar ligand ring system and the planar oxygen and sulphur containing rings approximately at right angles to minimise steric interference. Neither of the organomercury compounds formed isolable complexes with 2,2'-bipyridyl, 1,2-bis(diphenylphosphino)ethane, triphenylphosphine or 2,5-dithiahexane.

Evidently phen is too weak a donor to complex with the weak acceptor, di-2-thienylmercury, but the inductive effect of the methyl groups on the carbon atoms adjacent to the nitrogen atoms in dmp enhances the donor character of the nitrogens sufficiently to allow complex formation. It is of interest to note that when the methyl groups are situated further away from the nitrogen atoms as in tmp, complex formation with di-2-thienylmercury was not observed. ^{35}Cl NQR studies [18] of complexes of $(C_2Cl_3)_2Hg$ have shown that there is a greater degree of charge transfer to mercury from dmp than from tmp, since the resonance due to the α-chlorine atoms are at significantly lower frequencies in the dmp complex.

Support for the greater donor strength of dmp compared to tmp towards di-2-furylmercury comes from a study of the ^1H NMR spectra of the complexes. The NMR spectra of all four complexes isolated showed a small upfield shift of the bands due to the organomercury moiety, corresponding to increased shielding of these protons on complexation. The resonances due to the ligands showed only very small downfield shifts on complexation, indicating the weak nature of the complexes formed, the dmp complex showed the largest downfield shift, indicating strongest complex formation.

In view of the number of complexes formed, di-2-furylmercury would seem to be a stronger acceptor than both $(C_6H_5)_2Hg$ [3,4] and $(C_6Cl_5)_2Hg$ [20] but weaker than $(C_6F_5)_2Hg$, [14—17] $(C_2Cl_3)_2Hg$ [18] and $(C(NO_2)_3)_2Hg$ [11]. Di-2-thienylmercury is only a very weak acceptor, but in the view of the uncertainty about the nature of the $(C_6H_5)_2Hg$-phenanthroline complexes [5], it is difficult to draw any firm conclusions about the relative strengths of $(C_6H_5)_2Hg$ and $(C_4H_3S)_2Hg$ as acceptors, although we were unable to isolate a complex of $(C_6H_5)_2Hg$ from an equimolar mixture of the mercury compound and phen in ethanol.

All four complexes dissociated in a mass spectrometer even at low bombarding voltage (20 eV), so that the spectra obtained were similar to those of the uncoordinated mercury compound, in that the ion of highest molecular mass corresponded to RHg^+. Mass spectral features of some heterocyclic organomercury compounds will be reported elsewhere.

Comparison of the infrared spectra of the complexes with those of the free organomercury compounds allowed frequencies attributable to the organomercury moiety to be distinguished from those of the neutral ligand. Strong absorptions of the free mercury compounds at 692, 702, 833, 840 cm^{-1} for $(C_4H_3S)_2Hg$ and at 722, 740, 890, 1002 cm^{-1} for $(C_4H_3O)_2Hg$ are shifted to lower frequencies on complexation, as expected for metal-ligand modes on increase in coordination number. The shifts are greater for the dmp and tmp complexes than for the phen complex, because of the inductive effect of the methyl groups. Most of the bands associated with the phenanthroline ligands in the 1350—1620 cm^{-1} region are displaced to higher frequencies on coordination.

The DTA trace of $(C_4H_3O)_2Hg$ phen showed only one feature, a fairly large endotherm at 145°C, corresponding to fusion of the complex (visual m.p. 148°C). Comparison with the TG trace showed that mass loss of the complex commenced at this temperature, and continued up to about 260°C, mass loss occurring in one smooth step with no indication of any involatile intermediate being formed. As both ligand and mercury compound vaporise in this same temperature range, it is likely that the endotherm at 145°C corresponds to either vaporisation of the complex or dissociation followed by vaporisation. The dmp complex of $(C_4H_3O)_2Hg$ behaved in a somewhat similar manner, except that two endotherms were observed, the first at 222°C corresponding to fusion of the complex (visual m.p. 220°C) and the second at 250°C. Mass loss was observed over the range 150—260°C in a single smooth step. As both ligand and mercury compound vaporise within this temperature range, the second endotherm must correspond to either vaporisation of the complex or to dissociation and vaporisation.

The tmp complex behaves quite differently. The DTA trace showed a small endotherm at 201°C corresponding to fusion of the complex (visual m.p. 199—202°C) followed by a much larger endotherm at 206°C corresponding to vaporisation of $(C_4H_3O)_2Hg$ from the complex, as the TG trace shows mass loss from 150°C with an inflexion at 220°C corresponding to loss of 56.4% (calcd.:

58.7%) of the initial mass. The second step, 220—310° C, corresponds to loss of ligand (found 43.6%; calcd.: 41.3%) as evidence by the TG trace of the ligand itself. The discrepancy between experimental and theoretical values is due to overlap of the two processes.

Di-2-thienylmercury-dmp shows a smooth step on its TG trace from 160—280° C corresponding to total mass loss, while the DTA trace showed an endotherm at 190° C corresponding to fusion of $(C_4H_3S)_2Hg$ (visual m.p. 198° C) and a second of approximately equal size at 240° C corresponding to fusion of the complex (visual m.p. 240° C).

Experimental

Microanalyses were carried out by the Oxford Microanalytical Laboratories of Dr. F.B. Strauss. Mass spectra were recorded using an AEI MS30 mass spectrometer at a bombarding voltage of 20 eV and a source temperature of 200° C. Samples were injected via the direct insertion probe. ^{1}H NMR spectra were recorded as solutions in deuterochloroform, using a Jeol C-60 HL high resolution spectrometer. Thermal measurements were recorded using a DuPont Model 900 thermal analyser. Samples were heated at a rate of 5° min^{-1} under a flow of nitrogen of 50 cm^3 min^{-1}. Infrared spectra (4000—625 cm^{-1}) were recorded as KBr discs using a Unicam SP200 spectrometer.

Reagents

Di-2-thienylmercury (m.p. 199° C, lit. [21]198—199°C) and di-2-furylmercury (m.p. 114° C, lit. [22] 114° C) were prepared as previously described [23]. The ligands were commercially available and were used without further purification.

Preparation of complexes

Di-2-furylmercury-1,10-phenanthroline. 1,10-Phenanthroline monohydrate (0.20 g, 1.0 mmol) in ethanol (10 cm^3) was added to a warm solution of di-2-furylmercury (0.33 g, 1.0 mmol) in ethanol (10 cm^3). The resulting clear solution was evaporated by warming to about half volume, and cooling gave shiny white plates, which were filtered off and dried in vacuo. m.p. 148° C (dec). [Found: C, 46.75; H, 2.89; N, 5.30. $C_{20}H_{14}HgN_2O_2$ calcd.: C, 46.64; H, 2.75; N, 5.44%]. Infrared absorptions: 1628w, 1596w, 1571w, 1515m, 1502w, 1552w, 1427vs, 1408w, 1362w, 1348w, 1312w, 1267w, 1218w, 1200m, 1136m, 1095m, 1074m, 1051w, 994s, 944w, 880m, 875mw (sh), 848m, 830s, 802w, 792w, 785w, 757m, 728s, 718s, 698m, 680w cm^{-1}.

Di-2-furylmercury-2,9-dimethyl-1,10-phenanthroline. 2,9-Dimethyl-1,10-phenanthroline hemihydrate (0.22 g, 1.0 mmol) in ethanol (10 cm^3) was added to a warm solution of di-2-furylmercury (0.33 g, 1.0 mmol) in ethanol (10 cm^3) About half of the solvent was evaporated by warming and, on cooling, white needles were deposited. These were filtered off and dried in vacuo. m.p. 220°C (dec.). [Found: C, 47.7; H, 3.31; N, 5.03. $C_{22}H_{18}HgN_2O_2$ calcd.: C, 48.69; H, 3.35; N, 5.16%]. Infrared absorptions: 1625w, 1600s, 1560m, 1515m(sh), 1504vs, 1452s, 1440m(sh), 1430m, 1409mw, 1375s, 1360ms, 1310w, 1284w, 1242w, 1225w, 1208w, 1197ms, 1146s, 1134s, 1108w, 1090w, 1047w, 1022w, 988vs, 970w, 920w, 880s, 875m(sh), 848vs, 802m, 788mw, 778mw, 747m, 730vs, 720s(sh), 670w cm^{-1}.

Di-2-furylmercury-3,4,7,8-tetramethyl-1,10-phenanthroline. The ligand (0.23 g, 1.0 mmol) in ethanol (5 cm^3) was added to a warm solution of di-2-furylmercury (0.33 g, 1.0 mmol) in ethanol (5 cm^3). The white needles which formed on cooling were filtered off and dried in vacuo. m.p. 199—202°C (dec). [Found: C, 50.48; H, 3.79; N, 4.82. $C_{24}H_{22}HgN_2O_2$ calcd.: C, 50.51; H, 3.89; N, 4.91%]. Infrared absorptions: 1620w, 1580w, 1520s, 1450m, 1430s, 1382m, 1388w, 1312w, 1270w, 1240mw, 1199m, 1172w, 1137m, 1075w, 1069w, 989vs, 962w, 940w, 910w, 879s, 863m, 846w, 810mw, 800m, 718vs, 710vs cm^{-1}.

Di-2-thienylmercury-2,9-dimethyl-1,10-phenanthroline. The ligand (0.07 g, 0.30 mmol) in ethanol (5 cm^3) was added to a hot solution of di-2-thienylmercury (0.11 g, 0.30 mmol) in ethanol (30 cm^3). The white needles which formed on cooling were filtered off and dried in vacuo. m.p. 240°C (dec). [Found: C, 45.15; H, 3.23; N, 4.67. $C_{22}H_{18}N_2S_2Hg$ calcd.: C, 45.97; H, 3.16; N, 4.87%]. Infrared absorptions: 1628w, 1601m, 1563w, 1510s, 1480w, 1472w, 1465w, 1450m, 1430w, 1400m, 1379mw, 1365mw, 1325w, 1287w, 1245w, 1222m, 1208m, 1148m, 1120w, 1110w, 1094w, 1083w, 1073w, 1055w, 1040w, 976w, 944w, 920w, 890w, 846s, 833s, 811m, 774w, 745m, 730m, 719ms, 698s, 687vs, 670w cm^{-1}.

Attempted preparation of other complexes

Di-2-furylmercury. Equimolar mixtures of the mercury compound and ligand (2,2'-bipyridyl, 1,2-bis(diphenylphosphino)ethane, triphenylphosphine, 2,5-dithiahexane) in ethanol and the mercury compound and 2,2'-bipyridyl in hexane were evaporated to crystallisation. In every case, crystallisation of either the ligand or the mercury compound occurred, and these were identified by their melting points and infrared spectra.

Di-2-thienylmercury. Equimolar mixtures of the mercury compound and ligand (phen, tmp, 1,2-bis(diphenylphosphino)ethane, triphenylphosphine, 2,5-dithiahexane) in ethanol were evaporated to crystallisation. In every case, crystallisation of either the ligand or the mercury compound occurred, and these were identified by their melting points and infrared spectra.

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