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THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

X*. BASE ADDUCTS OF BIS(PENTAFLUOROPHENYL)MERCURY(II)

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Summary

Thermodynamic data are reported for the formation in benzene solution at 30° of 1/1 adducts of $Hg(C_6F_5)_2$ with pyridine ($-\Delta H^0$ 11.8 kJ/mole, K 2.1 l/mole), 4-methylpyridine (12.6, 4.7), 2,2′-bipyridine (17.2, 14.0), 1,10-phenanthroline (47.4, 2300), 1,2-diaminoethane (43.5, 386), *N,N*′-tetramethyl-1,2-diamino-ethane (29.5, 23.5), -propane (34.8, 4.2) and -butane (28.8, 13.1). The diamines probably all behave as bidentates, but in the bipyridine adduct the Hg—N bonds are unusually weak. This can be explained if $Hg(C_6F_5)_2$ remains linear in the adducts and newly formed Hg—N bonds involve only *p*-orbitals on the mercury atom.

Introduction

Thermodynamic data have recently been reported [1] for the reaction of bis(pentafluorophenyl)mercury(II) with pyridine and 2,2′-bipyridine in benzene and carbon tetrachloride solutions. This paper reports thermodynamic data for the reaction of this compound with a wider range of bases in benzene solution; the work is part of a more extensive study of the thermodynamics of reactions in which metal complexes behave as Lewis acids, with consequent increase in the coordination number of the metal atom. The work with bis(pentafluorophenyl)mercury(II) has been carried out to confirm qualitative observations made on the relative stabilities of adducts of this compound with various bases [2] and to obtain information about the behaviour of a mercury compound expected to show more A-type [3] behaviour than the previously studied [4] mercury(II) halides.

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* For Part IX see ref. 15.

TABLE 1

EQUILIBRIUM CONSTANT AND ENTHALPY OF REACTION $Hg(C_6F_5)_2 + B = Hg(C_6F_5)_2B$. Individual titrations in benzene solution at 30°. Uncertainties in K are standard deviations.

Base, B	$[Hg(C_6F_5)_2]$ (mole/l)	Max % reaction	K (l/mole)	$-\Delta H^0$ (kJ/mole)
Pyridine	0.00214	62	2.40 ± 0.10	14.5
	0.00322	60	1.95 ± 0.10	10.9
	0.00687	60	1.90 ± 0.15	10.0
4-Methylpyridine	0.00564	75	5.57 ± 0.09	12.4
	0.01438	67	3.83 ± 0.06	12.9
2,2′-Bipyridine	0.00309	54	13.30 ± 0.20	17.2
	0.00626	57	15.30 ± 0.13	17.3
	0.00936	35	13.40 ± 0.15	17.1
1,10-Phenanthroline	0.00196	73	3.2×10^3	46.9
	0.00573	54	1.7×10^3	48.6
	0.01111	29	2.0×10^3	46.8
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	0.00199	42	24.36 ± 0.18	32.4
	0.00445	37	20.89 ± 0.63	28.1
	0.00706	65	25.15 ± 0.38	28.1
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	0.00396	32	4.11 ± 0.10	36.0
	0.00768	33	4.21 ± 0.01	33.3
$(CH_3)_2N(CH_2)_4N(CH_3)_2$	0.00127	56	14.99 ± 0.51	30.0
	0.00258	40	13.84 ± 0.51	28.2
	0.00486	51	10.49 ± 0.65	28.2
$H_2N(CH_2)_2NH_2$	0.00202	90	382 ± 9	43.8
	0.00414	89	390 ± 10	43.2

Experimental

Materials

Bis(pentafluorophenyl)mercury(II) was prepared and purified by the previously reported method [2]. Benzene for use as solvent was purified by freezing, followed by distillation, and dried over calcium hydride. Pyridine was heated under reflux with solid potassium permanganate before redistillation; 4-methylpyridine was redistilled. Tetramethyldiaminoethane, tetramethyldiaminopropane and tetramethyldiaminobutane were obtained from the Aldrich Chemical Co. All the liquid bases were dried over anhydrous potassium carbonate. 2,2′-bipyridine and 1,10-phenanthroline hemihydrate were purified by crystallisation from ethanol; the water of hydration was removed from benzene solutions of 1,10-phenanthroline by azeotropic distillation before making up to volume.

Calorimetry

Equilibrium constants and enthalpies of adduct formation were determined by calorimetric titration in a LKB 8700-2 titration calorimeter. Details of the technique used, including precautions necessary to maintain reproducible heats of dilution of the bases in benzene by appropriate drying methods, and the method of calculation have been reported previously [5]. Briefly, 100 ml of a benzene solution of the metal compound in the concentration range $1\text{-}20 \times 10^{-3}$ M was placed in the titration vessel and allowed to reach equilibrium in the thermostat, in which the titrant was also pre-equilibrated. The base or a solution of base in benzene was then added in 10-15 aliquots and the heat of reaction (Q) determined after each addition, after correcting for the heat of dilution of the

TABLE 2

THERMODYNAMIC DATA FOR REACTION $Hg(C_6F_5)_2 + B = Hg(C_6F_5)_2B$ IN BENZENE SOLUTION AT 30°.

Uncertainties are mean deviations from the averages of different titrations.

Base, B	K (l/mole)	$-\Delta G^0$ (kJ/mole)	$-\Delta H^0$ (kJ/mole)	$-\Delta S^0$ (J/K/mole)
Pyridine	2.1 ± 0.2	1.8 ± 0.3	11.8 ± 1.8	33 ± 5
4-Methylpyridine	4.7 ± 0.9	3.8 ± 0.5	12.6 ± 0.3	29 ± 3
2,2′-Bipyridine	14.0 ± 0.8	6.7 ± 0.2	17.2 ± 0.1	36 ± 2
1,10-Phenanthroline	$2.3 \pm 0.6 \times 10^3$	19.4 ± 0.7	47.4 ± 0.8	93 ± 4
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	23.5 ± 1.8	7.9 ± 0.3	29.5 ± 3.0	71 ± 6
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	4.2 ± 0.1	3.6 ± 0.1	34.8 ± 1.2	102 ± 5
$(CH_3)_2N(CH_2)_4N(CH_3)_2$	13.1 ± 1.8	6.4 ± 0.4	28.8 ± 0.8	74 ± 2
$H_2N(CH_2)_2NH_2$	386 ± 14	15.0 ± 0.1	43.5 ± 0.3	94 ± 2

titrant. The enthalpy of the reaction was obtained from the extrapolated, integrated heat of reaction (Q_∞); equilibrium constants (K) were calculated at each step in the titration and the value of Q_∞ refined to give the most consistent values of K. In all cases this required the assumption of 1/1 stoichiometry, but the titration was repeated with different metal concentrations to provide a further check on this. Values of K and ΔH^0 obtained in individual titrations are given in Table 1.

The uncertainties given for K in Table 1 are standard deviations of the 10-15 values of K in each titration. Reproducibility of K from one titration to another is not so good, but with values of $K < 100$ is usually within ± 10%, the spread of values becoming rather wider with large values of K, the limit of measurement being about 10^5. Reproducibility of ΔH^0 is typically within ± 5% when $10 < K < 1000$, becoming rather more precise at high values of K and rather less for lower values of K. Average values of the thermodynamic data for each system are shown in Table 2, where uncertainties given are the mean deviations from different titrations. While some very small mean deviations are no doubt fortuitious, consideration of other experimental uncertainties leads to an expected reliability of about ±10% in ΔH^0 and ± 1 kJ/mole in ΔG^0. It is not profitable to discuss differences smaller than this.

Discussion

The results for 2,2′-bipyridine are identical with those of Puhl and Henneike [1]. The formation constant for the pyridine adduct, corrected to 25°, is $K = 2.27$ compared with their value of $K = 2.1$, as good agreement as could be expected. However, the enthalpy of formation of the pyridine adduct, $-\Delta H^0 = 11.8$ kJ/mole, is smaller than their value of 18.1 kJ/mole, though the discrepancy is not very large. Data for formation of the 4-methylpyridine adduct were obtained to provide a check on the data for pyridine, since it has been found in many similar systems [6—10] that 4-methylpyridine forms rather more stable adducts with a slightly more negative enthalpy of formation. The value of $-\Delta H^0 = 12.6$ kJ/mole thus supports our value of 11.8 for pyridine. Our formation constant data are also consistent with formation constants calculated from Canty and Deacon's molecular weight data [2]. The molecular weight data give $K = 11$ for 2,2′-bipyridine and $K = 2340$ for 1,10-phenanthroline at 25°, compared with our values of 14 and 2300 at 30°; considering the uncertainties in the molecular weight determinations such agreement is quite astonishingly good. Molecular weight data for the ethylene diamine complex reveal no dissociation in benzene, but the data in chloroform give the ethylene diamine adduct a stability in between that of the bipyridine and phenanthroline adducts, as observed in the calorimetric work.

The very small difference in the enthalpies of formation of the adducts with pyridine and 2,2′-bipyridine may indicate that the bipyridine is unidentate, but if this were so a decreased adduct stability would be expected due to the *ortho* effect [7—10] of the uncoordinated pyridyl ring; in fact the bipyridine adduct is considerably more stable, suggesting that there is a chelate effect and hence that both nitrogen atoms are coordinated. The most likely explanation of all the data seems to be that the bipyridine is bidentate but the Hg—N bonds are unusually weak.

The contrast of bipyridine with 1,10-phenanthroline is dramatic: the large enthalpy of formation and much greater stability of the phenanthroline adduct show that both nitrogen atoms are coordinated and the Hg—N bonds are much stronger even than in the pyridine adduct. While it is usual for phenanthroline complexes to be a little more stable than those of bipyridine [11], it is quite unusual for the difference to be so marked as in this instance.

Crystal structures of several adducts of this type have been determined [12,13] and in each case the linear structure of the mercury(II)—aryl is retained in the adduct, presumably with *sp* bonds at the mercury atom, so that the orbitals available for further coordination are *p* orbitals in the plane normal to the C—Hg—C axis. The coordinated 1,10-phenanthroline molecule should be planar and could be expected to give good overlap between the donor orbitals on the N atoms and these *p* orbitals. A coordinated bipyridine molecule, however, must be twisted to avoid clashing of the 6,6′-H atoms and this leads to the donor electrons on the nitrogen atoms being directed well away from the mercury atom, so that only poor overlap can be expected with consequently weak Hg—N bonds. A similar twist can be expected in the coordinated diamines, but in this case because the orbitals on the N atoms are sp^3-hybridized the donor orbitals still overlap well with the mercury *p* orbitals and strong Hg—N bonds can be expected.

The usually large endothermic heats of dilution of aliphatic amines in benzene make it impossible to carry out satisfactory calorimetric titrations except when adduct formation constants are very large or there is a large enthalpy of reaction and the titration can be done with a high concentration of the metal complex. Attempts to titrate tributylamine with bis(pentafluorophenyl)mercury(II) were unsuccessful, but the experimental conditions were such that it could only be concluded that the product $K \cdot \Delta H$ was less than about 150 kJ·l/mole^2. Successful titrations were, however, carried out with potentially bidentate amines: ethylenediamine, tetramethylethylenediamine and tetramethyl-1,3-diaminopropane and -1,4-diaminobutane. The comparatively large negative enthalpies of adduct formation show that all these bases are probably bidentate with relatively strong Hg—N bonds. The much lower adduct formation constants observed with the tertiary bases than with ethylene diamine are probably due to steric interference between the methyl groups and the pentafluorophenyl groups;

molecular models of the adducts show that such interference is likely.

The high stability of the phenanthroline adduct, together with the reported crystal structures of adducts of substituted phenanthrolines with diphenylmercury [12], led us to attempt calorimetric titrations of diphenylmercury with 1,10-phenanthroline, but no heat change could be detected, indicating that, even with this base, the adduct of diphenylmercury is very unstable. We also failed to detect any heat change when bis(pentafluorophenyl)mercury(II) was titrated with tributylphosphine or 1,2-bis-diphenylphosphinoethane, showing that the phosphine adducts are of low stability, though they can be isolated as solids and the crystal structure has been determined of the adduct with methyldiphenylarsine [13]. This provides a marked contrast with mercury(II) halides, which form more stable adducts with phosphines than with nitrogenous bases [4] and reveals the more "A-type" or "harder" [14] behaviour of the bis(pentafluorophenyl) compound. Despite this, attempts to obtain data for adduct formation with tetrahydrofurane as a typical O-donor were unsuccessful, either K or ΔH or both being very small.

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