Journal of Organometallic Chemistry, 159 (1978) 9—14

THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

XXX *. BASE ADDUCTS OF MERCURY(II) CYANIDE

D.P. GRADDON and J. MONDAL
School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033 (Australia)
(Received April 11th, 1978)

Summary

Thermodynamic data, obtained by calorimetric titration in acetonitrile solution, are reported for the reaction of mercury(II) cyanide with sixteen nitrogenous bases. As a Lewis acid $Hg(CN)_2$ is comparable to $Hg(CCl_3)_2$ and forms moderately stable, 3-coordinate adducts with unidentate N-bases in solution. Much more stable adducts are formed with bidentate bases and there is much less steric resistance to the formation of chelate, 4-coordinate adducts than is shown by $Hg(CCl_3)_2$.

Introduction

Mercury(II) cyanide has a simple molecular structure with linear, N≡C—Hg—C≡N, molecules [1]. It has been shown to react with a variety of Lewis bases giving addition compounds in which the coordination number of the mercury is increased. Preliminary crystal structure data have been reported for the 1/1 thiourea adduct, $(NH_2)_2CS \cdot Hg(CN)_2$ [2] and also the methanol solvate, $CH_3OH \cdot Hg(CN)_2$ [3], but the only such compound for which a complete crystal structure has been reported is the adduct with tetrahydrofuran, $4\ C_4H_8O \cdot 5\ Hg(CN)_2$ [4]; this compound, however, is a solvate rather than a true adduct, since the mercury atoms have only long contacts with O or N atoms of neighbouring molecules in addition to the two short Hg—C bonds.

Adducts with O-donors are generally of low stability but have been isolated with one or two molecules of dioxan [5], the latter adduct being rapidly decomposed on exposure. An adduct with hexamethylphosphoramide, $Hg(CN)_2(hmpa)_2$, has also been isolated and found to dissociate partially in benzene solution [6]

---

* For Part XXIX see ref. 27.

and a similar O-bonded dimethylsulphoxide adduct, $Hg(CN)_2(dmso)_2$, is extensively dissociated in tetrahydrofuran [7].

Much more stable addition compounds are formed by N-donors. Simple aliphatic amines form 2/1 adducts in the homologous series $(RNH_2)_2Hg(CN)_2$ [8] and the piperidine adduct $(pip)_2Hg(CN)_2$ [9]. Bases with two nitrogen atoms, however, form only 1/1 adducts and are presumably chelate, giving the mercury a coordination number of four; the adduct with *N,N,N′,N′*-tetramethyl-1,2-diaminoethane, $(tmed)Hg(CN)_2$, has been shown to dissolve undissociated in tetrahydrofuran [7] and that with diethylenetriamine, $(dien)Hg(CN)_2$, to be a non-electrolyte in dimethylsulphoxide solution [10]. Heterocyclic bases also form stable addition compounds. Those which have been isolated include $Hg(CN)_2$(3-cyanopyridine)$_2$, which is completely dissociated in tetrahydrofuran [7] and several 1/1 adducts with quinoline derivatives, which are only slightly dissociated in ethanol and are thus thought to contain 3-coordinate mercury [11]. The 1/1 adducts obtained with 2,2′-bipyridine and 1,10-phenanthroline (bipy and phen) have infrared spectra which indicate chelate bases and hence 4-coordinate mercury [12] and a 1/1 adduct with 2,9-dimethyl-1,10-phenanthroline has also been isolated [13]. Addition compounds have also been isolated with phosphines, for example $(Ph_3P)_2Hg(CN)_2$ [12] and some 1/1 adducts with diphosphines and diarsines in which the bases are bidentate [14].

A recent review [15] shows that there have been only a few studies of equilibria involving the reaction of mercury(II) cyanide with Lewis bases in solution. Some pH-metric studies have been made of the reactions of amines with $Hg(CN)_2$ in aqueous solution [16] but the reactions are complex. The only studies made in other solvents appear to be those of Izatt et al. on the reaction of $Hg(CN)_2$ with thiourea in water/ethanol [17] or water/formamide [18] mixtures. These both show successive formation of $(tu)Hg(CN)_2$ and $(tu)_2Hg(CN)_2$ (tu = thiourea) and complete thermodynamic data are reported for varying solvent compositions.

The present paper reports thermodynamic data, obtained by calorimetric titration in acetonitrile solution, for the formation of 1/1 adducts of $Hg(CN)_2$ with a wide variety of N-donors, including uni- and bi-dentate heterocyclic bases, primary and secondary amines and uni- and bi-dentate tertiary amines.

Results and discussion

Complete thermodynamic data are shown in Table 1 for the formation of 1/1 adducts with all the sixteen bases studied. No evidence was found for further addition of base in any system and under these conditions it is clear that the maximum coordination number of the mercury is three in adducts with unidentate bases.

Simple heterocyclic bases form 1/1 adducts of low stability with moderate enthalpies of formation. Substitution of pyridine by CH_3 in the 4-position increases adduct stability without observable change in the enthalpy of reaction, but the very small increase in enthalpy required to produce such a small change in adduct stability would be below the limits of measurement of our technique and the increased stability can be seen as a typical inductive effect. Substitution at the 2-position leads to a distinct decrease in the enthalpy of adduct forma-

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF BASES WITH $Hg(CN)_2$ IN ACETONITRILE SOLUTION AT 30°C. Range of concentrations of $Hg(CN)_2$ in mmol l^{-1}, K in l mol^{-1}, ΔG° and ΔH° in kJ mol^{-1}, ΔS° in J K^{-1} mol^{-1}

Base	[Hg]	K	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
pyridine	6.0—10.0	5.3 ± 0.3	36.6 ± 0.5	4.2 ± 0.2	107 ± 2
4-mepy	4.0—6.0	10.9 ± 0.4	36.6 ± 0.7	6.0 ± 0.2	101 ± 3
2-mepy	4.0—8.0	2.9 ± 0.2	24.9 ± 0.2	2.7 ± 0.3	73 ± 2
bipy	4.0—6.0	175 ± 10	19.7 ± 0.4	13.0 ± 0.2	22 ± 2
phen	3.0—5.0	$>10^4$	28.6 ± 0.4		
$BuNH_2$	2.0—3.5	59 ± 7	55.2 ± 1.4	10.3 ± 0.4	148 ± 6
$CxNH_2$ [a]	2.0—3.5	51 ± 7	54.9 ± 1.3	9.9 ± 0.4	149 ± 6
Et_2NH	3.5—4.5	48 ± 4	31.0 ± 0.3	9.7 ± 0.3	70 ± 2
piperidine	2.0—5.0	86 ± 8	51.5 ± 2.7	11.2 ± 0.3	133 ± 10
Et_3N	5.3—7.5	14.0 ± 0.5	21.2 ± 1.1	6.7 ± 0.2	49 ± 4
Me-piperazine	1.6—2.3	102 ± 13	37.8 ± 1.3	11.7 ± 0.4	86 ± 6
Me_2piperazine	2.0—3.0	18 ± 3	38.2 ± 2.1	7.3 ± 0.5	102 ± 9
dmed [b]	0.9—1.3	$>10^4$	55.5 ± 0.5		
tmed [c]	4.0—6.0	$>10^4$	50.8 ± 1.6		
tmpd [d]	1.2—2.9	3900 ± 800	38.7 ± 0.4	20.8 ± 0.5	59 ± 3
tmbd [e]	1.5—2.5	134 ± 7	30.4 ± 1.1	12.4 ± 0.2	59 ± 4

[a] Cyclohexylamine. [b] *N,N'*-Dimethyl-1,2-diaminoethane. [c] *N,N,N',N'*-Tetramethyl-1,2-diaminoethane. [d] *N,N,N',N'*-Tetramethyl-1,3-diaminopropane. [e] *N,N,N',N'*-Tetramethyl-1,4-diaminobutane.

tion and in adduct stability, presumably due to the steric effect of the 2-methyl group.

The bidentate bases, 2,2'-bipyridine and 1,10-phenanthroline, form much more stable adducts, particularly the latter; this must be seen as a chelate effect indicating 4-coordinate mercury, but most interestingly is accompanied by a decrease in the enthalpy of adduct formation. Such decreases accompanied by increased adduct stabilities are also observed in adducts of bipyridine with mercury(II) halides [19] and may be attributed either to weakening of the Hg—N bonds because of misfitting of the bidentate base with the large mercury atom or to an opposing enthalpy change arising from the bending of the linear X—Hg—X molecule.

Because of the possibility that hydrogen displacement might take place when NH bases react with mercury compounds, conductivity studies were made of the reaction of $Hg(CN)_2$ with cyclohexylamine and NMR studies of that with piperidine. In the first case no evidence was found of ionic species and in the second the N—H peak of piperidine could still be observed even in the presence of a large excess of $Hg(CN)_2$. It may be concluded that hydrogen displacement does not occur and that the reactions observed calorimetrically are simple addition reactions.

Primary aliphatic amines form more stable adducts than heterocyclic bases with $Hg(CN)_2$ and the adducts have considerably larger enthalpies of formation. The secondary and tertiary amines, Et_2NH and Et_3N, form less stable adducts and so little heat was produced in the reaction with Bu_3N that measurements of K and ΔH could not be made. Adduct stability is increased by including the N-atom in a ring, piperidine giving a much more stable adduct

TABLE 2

STABILITIES (K in l mol^{-1}) AND ENTHALPIES OF FORMATION (kJ mol^{-1}) OF 1/1 ADDUCTS OF MERCURY(II) COMPOUNDS WITH SELECTED BASES IN SOLUTION AT 30°C

Compound		Solvent	py		4 mepy		bipy		phen		tmed	
			$-\Delta H$	K	$-\Delta H$	K	$-\Delta H$	K	$-\Delta H$	K	$-\Delta H$	K
PhMgBr	[21]	benz			30	2			20	800	26	210
$Hg(C_6F_5)_2$	[22]	benz	12	2	13	5	17	14	47	2300	29	23
$Hg(CN)_2$		MeCN	36	5	36	11	20	175	28	$>10^4$	51	$>10^4$
$Hg(CCl_3)_2$	[23]	benz	37	11	38	14	31	449	42	$>10^4$	50	73
$Hg(SCN)_2$	[24]	MeCN	42	69	45	118	41	$>10^4$	51	$>10^4$	64	$>10^4$
HgI_2	[19,20]	benz	64	132	68	266	49	4300	71	$>10^4$	96	$>10^4$

than Et_2NH and with increased enthalpy of formation. An increased enthalpy of formation is also observed with dimethylpiperazine compared to Et_3N, though the very small increase in adduct stability shows that this potentially bidentate base is only unidentate and chelation does not occur. Comparisons with *N*-methylpiperazine indicate that when this base forms an adduct with $Hg(CN)_2$ it does so by coordination of the secondary nitrogen atom rather than the tertiary.

The data for open chain bases with two donor N atoms give some evidence for the effect of chelate ring size on adduct stability: the amines with N—C_2—N chains give 1/1 adducts of very high stability indicating that they are chelate with 4-coordinate mercury and the increased enthalpies of formation also support this. These larger enthalpies of reaction also show that there is little loss of enthalpy associated with the mercury becoming 4-coordinate, so that the unusually low enthalpies of formation of adducts with bipyridine and phenanthroline must derive from specific misfitting of these bases with the large mercury atom and not simply from the bending of the NC—Hg—CN unit.

Increasing the chelate ring size to six by using a N—C_3—N chain leads to a distinct reduction in both the enthalpy of adduct formation and adduct stability and data for the formation of the adduct with *N,N,N′,N′*-tetramethyl-1,4-diaminobutane, which would give a 7-membered chelate ring, suggest that either this base is unidentate or the formation of a 7-membered ring adds little to adduct stability.

While $Hg(CN)_2$ is commonly referred to as a "pseudohalide", it may also be regarded as a highly substituted organomercury compound, comparable to $Hg(CCl_3)_2$ or $Hg(C_6F_5)_2$ and it is interesting to compare data for the formation of adducts of a series of bases with different mercury compounds. Table 2 collects data for the enthalpies of formation and stabilities of adducts with five bases. Because of the differing solubilities of the original mercury compounds, some of these data have been obtained in benzene solution and some in acetonitrile, but the change of solvent can be expected to produce only minor effects [25].

It can be seen that with most bases the enthalpies of adduct formation and adduct stabilities both increase in the order: $RHgX << Hg(C_6F_5)_2 < Hg(CN)_2 < Hg(CCl_3)_2 < Hg(SCN)_2 < HgX_2$ (where X = Cl, Br or I), corresponding to increasing electronegativity of the groups bound to the mercury atom. One very interesting feature apparent from this comparison is the abnormally low stabilities (but not enthalpies of formation) of adducts of tmed with $Hg(CCl_3)_2$ and $Hg(C_6F_5)_2$. This must be due to steric interference between the alkyl substituents on the tertiary N atoms and the bulky CCl_3 or C_6F_5 groups; this effect is completely absent in $Hg(CN)_2$, in which the linear $C{\equiv}N$ groups have minimal steric effect.

Experimental

Mercury cyanide, 2,2′-bipyridine and 1,10-phenanthroline hydrate were purified by crystallisation from ethanol. Liquid bases were purified by redistillation, under reduced pressure where necessary, and stored over anhydrous potassium carbonate. Acetonitrile for use as solvent was redistilled and dried and stored over anhydrous sodium sulphate. Water was removed from solutions of phenanthroline by azeotropic distillation before making up to volume.

Calorimetric titrations were carried out on a LKB 8700 titration calorimeter by the technique previously described [26]. Briefly, a solution of the base in acetonitrile was titrated into 100 ml of a solution of mercury(II) cyanide in acetonitrile and the heat change recorded after each incremental addition, 10—15 additions being made to complete the titration. The enthalpy was obtained from the extrapolated, integrated heat of reaction; equilibrium constants, K, were then calculated at each point in the titration and the enthalpy refined iteratively to give constant values of K throughout the titration. Data in Table 1 are the average of at least three titrations over the given range of concentrations of mercury cyanide. Uncertainties in ΔH° are mean deviations; those for K are the sum of the mean deviations and the average standard deviation in individual titrations; uncertainties in ΔG° and ΔS° are derived. The technique used gives most satisfactory results when $10 < K < 1000$ l mol^{-1}; when $K < 1$ it is no longer possible to evaluate K or ΔH° and when $K > 10^4$ it is no longer possible to evaluate K, but ΔH° is known with increased precision.

Acknowledgment

We are grateful to the Australian Research Grants Committee for supporting this work. One of us (J.M.) acknowledges a Colombo Plan fellowship.

References

1 R.C. Seccombe and C.H.L. Kennard, J. Organometal. Chem., 18 (1969) 243.
2 M.P. Rodriguez, M. Cubero, A. Lopez-Castro and C. Moreno-Bajo, Nature, 206 (1965) 392.
3 J.C. Monier and M. Griffon, C.R. Acad. Sci. Paris, 250 (1960) 4011.
4 M. Frey and M. Ladesert, Acta Cryst., B, 27 (1971) 2119.
5 H. Rheinboldt, A. Luyken and H. Schmittmann, J. Prakt. Chem., 149 (1937) 30.
6 J.L. Vidal and G.E. Ryschkewitsch, J. Inorg. Nucl. Chem., 38 (1976) 1933.
7 S.C. Jain and R. Rivest, Inorg. Chim. Acta, 3 (1969) 552.
8 K.N. Mikhalevich, S.M. Galetskaya and V.V. Skopenko, Ukr. Khim. Zhur., 37 (1971) 289.
9 I.S. Ahuja and K.S. Rao, Indian J. Chem., 13 (1975) 413.
10 G. Cova, D. Galizzioli, D. Giusto and F. Morazzoni, Inorg. Chim. Acta, 6 (1972) 343.
11 I.S. Ahuja and K.S. Rao, J. Inorg. Nucl. Chem., 37 (1975) 586.
12 S.C. Jain and R. Rivest, Inorg. Chim. Acta, 4 (1970) 291.
13 M.C. Esquivel, A.S. Macias and L.B. Reventos, Anal de Quim., 71 (1975) 831.
14 S.C. Jain, J. Inorg. Nucl. Chem., 35 (1973) 413.
15 L.G. Hepler and G. Olofsson, Chem. Rev., 75 (1975) 585.
16 E. Porzsolt, M.T. Beck and A. Bitto, Inorg. Chim. Acta, 19 (1976) 173.
17 R.M. Izatt, D. Eatough and J.J. Christensen, J. Phys. Chem., 72 (1968) 2720.
18 R.M. Izatt, C.H. Bartholomew, C.E. Morgan, D.J. Eatough and J.J. Christensen, Thermochim. Acta, 2 (1971) 313.
19 Y. Farhangi and D.P. Graddon, Aust. J. Chem., 27 (1974) 2103.
20 Y. Farhangi and D.P. Graddon, Aust. J. Chem., 26 (1973) 983.
21 D.P. Graddon and J. Mondal, J. Organometal. Chem., 107 (1976) 1.
22 Y. Farhangi and D.P. Graddon, J. Organometal. Chem., 71 (1974) 17.
23 D.P. Graddon and J. Mondal, J. Organometal. Chem., 132 (1977) 1.
24 Y. Farhangi and D.P. Graddon, Aust. J. Chem., 29 (1976) 2405.
25 L.T. Ang and D.P. Graddon, J. Inorg. Nucl. Chem., 38 (1976) 2279.
26 D.P. Graddon and K.B. Heng, Aust. J. Chem., 24 (1971) 1781.
27 D.P. Graddon and I.A. Siddiqi, Aust. J. Chem., 30 (1977) 2133.