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Π-ARENE COMPLEXES OF THE MAIN GROUP ELEMENTS. II.(a) COMPLEXES OF CADMIUM(II) AND ZINC(II)(b)

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Summary

π-Arene complexes of cadmium(II) and zinc(II) have been prepared from the first time. The 1:1 complexes $Cd(AsF_6)_2$·Arene(Arene=hexaethyl- or hexamethylbenzene, pentamethylbenzene, durene, p-xylene or benzene), $Cd(SbF_6)_2$·Arene(Arene = hexamethylbenzene, toluene or benzene) and $Zn(SbF_6)_2$·Arene(Arene = hexamethylbenzene or pentamethylbenzene) are synthesized from the strong acid salt and arene in liquid sulfur dioxide. ^1H and ^{13}C NMR spectra are consistent with localized bonding of the arene to the metal cation. Exchange-averaged ^{13}C chemical shifts for the systems $Cd(AsF_6)_2$–arene–SO_2 confirm the 1:1 stoichiometry in solution and suggest that the stabilities of the complexes are in the approximate range 0.48–2.1 M^{-1} for the series benzene-hexamethylbenzene. For the system $Cd(AsF_6)_2$–C_6Me_6–SO_2, a detailed ^{113}Cd NMR study is consistent with the solution stoichiometry and stability determined from ^{13}C NMR. In general, complexation to an arene produces deshielding of the ^{113}Cd resonance of $Cd(AsF_6)_2$.

Introduction

A combination of the weak-donor solvent sulfur dioxide and the poorly-coordinating hexafluoroarsenate(V) anion has proved useful previously in the isolation and solution study of solvolytically-sensitive π-arene complexes of the mercurous ion [1]. In the present work we show that the same or very similar combinations of solvent and counter-ion allow the preparation and solution characterization of the hitherto unknown

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(a) Ref. 1 is considered to be Part I of this series.

(b) No reprints available.

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π-arene complexes of divalent cadmium and zinc. Prior to our study the only evidence for species of this type concerns the cadmium complexes: benzene and the xylenes are retarded selectively when CdF_2-Al_2O_3 is used as the stationary phase in a gas-solid chromatographic column [2].

In a preliminary communication [3] we suggested that the exchange-averaged ^{13}C NMR spectra of the 1:1 cadmium- and zinc-arene complexes were best interpreted in terms of localized bonding of the aromatic molecule to the metal cation, similar to that occurring in the well-known copper(I) and silver(I) analogues. Our completed study lends further weight to this suggestion, and also includes an assessment of the stabilities of some of the cadmium complexes from ^{13}C and ^{113}Cd NMR data.

Results and Discussion

Preparation of the Complexes

The complexes were prepared by mixing SO_2 solutions of the components, the arene being in excess:

$$M(EF_6)_2 + \text{Arene} \xrightarrow{SO_2} M(EF_6)_2\cdot\text{Arene}$$

(M = Cd or Zn, E = Sb; or M = Cd, E = As)

Removal of all volatiles from solutions containing excess arene yielded the 1:1 complexes of $Cd(AsF_6)_2$ with hexaethyl- and hexamethyl-benzenes, pentamethylbenzene, durene, *p*-xylene, and benzene, of $Cd(SbF_6)_2$ with hexamethylbenzene, toluene, and benzene, and of $Zn(SbF_6)_2$ with hexamethyl- and pentamethyl-benzenes. Because of their relatively poor solubilities, the zinc complexes could also be isolated readily by filtration of saturated solutions. All of the zinc and cadmium complexes were decomposed rapidly by traces of water or organic donor solvents.

Low solubility precluded a detailed study of the zinc complexes in solution but $Cd(AsF_6)_2$ and $Cd(SbF_6)_2$ and arene complexes derived from these are very soluble in SO_2, and the latter were thus characterized readily in solution by NMR*.

In SO_2 solution the complexes were often coloured, even when the isolated complexes (see Table 4) were not, so that some form of specific solvation is indicated. (The colours of the complexes and (parenthesized) the corresponding free arenes in SO_2 are: $Zn(SbF_6)_2\cdot C_6Me_6$,

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*At ambient probe temperautre (305 or 308 K) the complexes decompose in SO_2 solution in a matter of hours, so that the fact spectral acquisition allowed by high concentration is essential.

red (bright yellow), $Zn(SbF_6)_2 \cdot C_6HMe_5$, red (bright yellow); $Cd(AsF_6)_2 \cdot C_6Et_6$, red (bright yellow), $Cd(As(Sb)F_6)_2 \cdot C_6Me_6$, red (bright yellow); $Cd(AsF_6)_2 \cdot C_6HMe_5$, deep orange (yellow); $Cd(AsF_6)_2 \cdot C_6H_2Me_4$, orange (yellow); $Cd(AsF_6)_2 \cdot C_6H_3Me_3$, amber (pale yellow); $Cd(AsF_6)_2 \cdot C_6H_4Me_2$, amber (colourless); $Cd(As(Sb)F_6)_2 \cdot C_6H_5Me$, pale yellow (colourless); $Cd(As(Sb)F_6)_2 \cdot C_6H_6$, very pale yellow (colourless).) Unbound arenes form charge transfer complexes with SO_2 [4], and probably the complexed arenes are involved in a similar interaction.

^{1}H NMR Spectra

The proton spectra of both the Cd(II) and the Zn(II) complexes of benzene or alkylated benzenes exhibit small but reproducible downfield shifts of the aromatic and aliphatic resonances, relative to those of the free arene. For example in a 0.2 m solution of $Cd(Durene)_2(AsF_6)_2$ at ambient probe temperature, both the aromatic and methyl signals are shifted by ca. 0.1 p.p.m. The complexes must be extensively dissociated in solution (see below) but the direction of the exchange-averaged complexation shift is informative, for silver(I)-arene complexes show similar small downfield shifts [5,6], whereas aromatic protons of arenes bound to a transition metal in an η^6-manner are normally shielded. Thus the cadmium and zinc complexes are unlikely to have an η^6 structure, and more localized bonding is indicated.

^{13}C NMR Spectra

As shown by the representative ^{13}C NMR data in Table 1, shifts, relative to the free arene, are observed in arene solutions containing either $Cd(AsF_6)_2$ or $Zn(SbF_6)_2$. In no case could separate signals be observed for free and bound arenes, either at 308 K or (for the more soluble cadmium complexes) at ca. 203 K. However, as shown below, the variation of the observed exchange-averaged ^{13}C shift, $\Delta\delta_c (=\delta_c^{obsd} - \delta_c^{free\ arene})$ with reactant ratio and concentration provides information on the stoichiometry and stability of the complexes formed, while for the less symmetrical arenes, the magnitude and direction of the complexation shifts give structural information.

^{113}Cd NMR Spectra

In principle, ^{113}Cd NMR data should provide a useful complement to the ^{13}C NMR data. This expectation is based on the known high sensitivity of the cadmium chemical shift to the environment of the nuclide, and in particular to the degree of substitution in dialkylcadmiums [8]. (Typical cadmium alkyls display a range of ca. 150 p.p.m. [8].) In practice, the interpretation of the ^{113}Cd shifts for arene: $Cd(AsF_6)_2$ mixtures in SO_2 is complicated: the shift of

Table 1. ^{13}C Chemical Shifts, $\Delta\delta_c$, Induced in Some Aromatic Substrates by $Cd(AsF_6)_2$, $Zn(SbF_6)_2$ and $AgAsF_6$ in SO_2 Solution$^{(a,b)}$

Substrate	Metal Cation	Arene:Salt Ratio	$\Delta\delta_c$(p.p.m.)^c						
			C_1	C_2	C_3	C_4	C_5	C_6	CH_3
Hexamethylbenzene	Cd^{2+}	2.5^d	[0.79]	[0.79]	[0.79]	[0.79]	[0.79]	[0.79]	0.13
	Zn^{2+}	2.5^d	[0.72]	[0.72]	[0.72]	[0.72]	[0.72]	[0.72]	0.18
	Cd^{2+}	2	[1.59]	[1.59]	[1.59]	[1.59]	[1.59]	[1.59]	0.41
	Ag^+	2	[-0.83]	[-0.83]	[-0.83]	[-0.83]	[-0.83]	[-0.83]	0.56
	Cd^{2+}	1	[2.56]	[2.56]	[2.56]	[2.56]	[2.56]	[2.56]	0.68
Pentamethylbenzene	Cd^{2+}	2.5	[2.21]	[2.26]	[3.51]	[2.26]	[2.21]	-4.72	0.31
1,2,4,5-Tetramethylbenzene	Cd^{2+}	2.5	[1.57]	[1.57]	-0.61	[1.57]	[1.57]	-0.01	0.10
	Zn^{2+}	2.5^d	[0.33]	[0.33]	-0.11	[0.33]	[0.33]	-0.11	0.04
	Cd^{2+}	2	[2.15]	[2.15]	-0.64	[2.15]	[2.15]	-0.64	0.26
	Ag^+	2	[1.19]	[1.19]	-6.26	[1.19]	[1.19]	-6.26	0.28
	Cd^{2+}	1	[3.68]	[3.68]	-1.29	[3.68]	[3.68]	-1.29	0.33
1,3,5-Trimethylbenzene	Cd^{2+}	2	[2.63]	-0.23	[2.63]	-0.23	[2.63]	-0.23	0.39
	Ag^+	2	[1.90]	-3.89	[1.90]	-3.89	[1.90]	-3.89	0.36
	Cd^{2+}	1	[4.06]	-0.54	[4.06]	-0.54	[4.06]	-0.54	0.51
1,2-Dimethylbenzene	Cd^{2+}	5	[1.82]	[1.82]	0.61	-0.74	-0.74	0.61	0.20
	Ag^+	5	[2.22]	[2.22]	-1.39	-4.01	-4.01	-1.39	0.20
1,3-Dimethylbenzene	Cd^{2+}	5	[1.55]	1.14	[1.55]	-0.16	-0.57	-0.16	0.16
	Ag^+	5	[1.75]	0.67	[1.75]	-2.46	-4.33	-2.46	0.08
1,4-Dimethylbenzene	Cd^{2+}	2	[2.39]	0.36	0.36	[2.39]	0.36	0.36	0.25
	Ag^+	2	[2.46]	-3.31	-3.31	[2.46]	-3.31	-3.31	0.08
	Cd^{2+}	1	[3.43]	0.38	0.38	[3.43]	0.38	0.38	0.31
Toluene	Cd^{2+}	5	[1.11]	0.55	0.22	-0.32	0.22	0.55	0.11
	Ag^+	5	[2.10]	-0.36	-1.98	-2.78	-1.98	-0.36	0.08
	Cd^{2+}	2	[1.80]	0.85	0.25	-0.65	0.25	0.85	0.13
	Cd^{2+}	1	[3.67]	1.75	0.52	-1.31	0.52	1.75	0.35
Benzene	Cd^{2+}	2.5	0.29	0.29	0.29	0.29	0.29	0.29	
	Zn^{2+}	2.5^d	0.08	0.08	0.08	0.08	0.08	0.08	
	Cd^{2+}	1	0.82	0.82	0.82	0.82	0.82	0.82	
1-Trifluoromethylbenzene	Cd^{2+}	2.5	not observed	0.04	0.06	0.06	0.06	0.04	
1,4-Dichlorobenzene	Cd^{2+}	2.5	[0.10]	0.06	0.06	[0.10]	0.06	0.06	
Naphthalene	Cd^{2+e}	2.5	0.43	0.23	0.23	0.43			

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[a] $\Delta\delta_c = \delta_c^{obsd} - \delta_c^{free\ arene}$; the chemical shifts of the free arenes are given in Ref. 1; arene concentration = 0.52m except where noted; $^{13}C-\{^1H\}$ spectra were measured at 305-308 K (See Experimental).

[b] Data for $AgAsF_6$ complexes from Ref. 1; other authors [7] have reported similar data for different solvents.

[c] Estimated error due to spectral measurement ± 0.06 p.p.m. or less; square brackets denote substituted carbons.

[d] [Arene] ≃ 0.17m.

[e] $\Delta\delta_c^{C_9} = 0.30$ p.p.m.

$Cd(AsF_6)_2$ is appreciably concentration dependent (Fig. 1a)* and the shifts of arene-complexed Cd^{2+} probably are also. In addition, general medium effects on both bound and free $Cd(AsF_6)_2$ shifts, arising from the mere presence of uncomplexed arene in solution, may be significant (c.f. Ref. 8).

Ignoring medium effects, and assuming identical concentration dependences for free and arene-bound $Cd(AsF_6)_2$ we find that complexation by arenes always produces downfield shifts of the cadmium resonance, as shown by the data in Table 2, but there are no obvious trends in the exchange-averaged ^{113}Cd complexation shifts. The system C_6Me_6–$Cd(AsF_6)_2$ has been studied in detail by ^{113}Cd NMR (Fig. 1 a and b) to obtain corroboration of the stoichiometry and stability of $Cd(C_6Me_6)^{2+}$ (see below).

Solution Stoichiometries and Stabilities of Typical Arene Complexes of Cadmium(II)

The variation of $\Delta\delta_c$ with [arene]/[$Cd(AsF_6)_2$] has been studied in detail for the arenes hexamethylbenzene (HMB), durene, mesitylene, *p*-xylene, toluene and benzene. Figure 2a and b shows the variation for the aryl carbon nuclei of HMB and benzene, respectively. Similar curves are found for the various different carbon nuclei of the other

Table 2. ^{113}Cd Chemical Shifts, $\Delta\delta_{Cd}$, Induced in $Cd(AsF_6)_2$ by Some Arenes[a]

Arene	$\Delta\delta_{Cd}$(p.p.m.)
Hexamethylbenzene[b]	27
Mesitylene	41
o-Xylene	89
m-Xylene	62
p-Xylene	41
Toluene	42
Benzene	25

[a] $\Delta\delta_{Cd} = \delta_{Cd}^{obsd} - \delta_{Cd}^{free\ Cd(AsF_6)_2,\ same\ concn.}$; Arene/$Cd(AsF_6)_2$ = 5 and [Arene] = 0.52m in arene-containing solutions.

[b] See text for a more detailed study with HMB.

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*Such concentration dependence is well known for other salts of cadmium in water [8,9].

substrates also. In all cases the monotonic change in $\Delta\delta_c$ with change in [arene]/[$Cd(AsF_6)_2$] is satisfactorily interpreted in terms of the formation of a 1:1 complex* in the labile equilibrium:

$$Cd^{2+} + \text{arene} \rightleftarrows Cd(\text{arene})^{2+}$$

The observed values of $\Delta\delta_c$ can be analyzed statistically using the program LISA [10], to yield the stability constants and bound shifts† shown in Table 3. (Data leading to very small bound shifts, < 40 Hz at 25.2 MHz, are not included in Table 3: in all cases they are consistent with 1:1 complex formation but, because of the small range, the fits are generally poorer.)

The calculated stability constants fall in the range 0.10–2.1 M^{-1}, very much smaller than those for $Hg_2(\text{arene})^{2+}$ [1] or $Hg(\text{arene})^{2+}$ [11] under the same conditions, but comparable to those measured for silver(I)-arene complexes in water [12]. (We are in the process of estimating the stabilities of the Ag^+ complexes in SO_2.) The very symmetrical arenes, HMB and benzene, each give a single value for K_1, of course. For the less symmetrical methylated benzenes, a range of values for K_1 are calculated, as was also found for the mercurous-arene complexes [1, 13]. In part, at least, the spread

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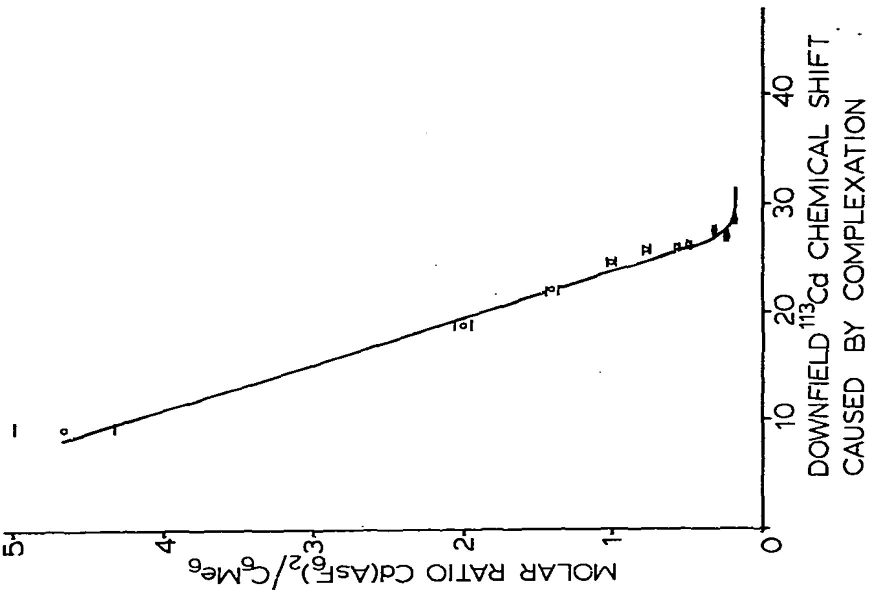
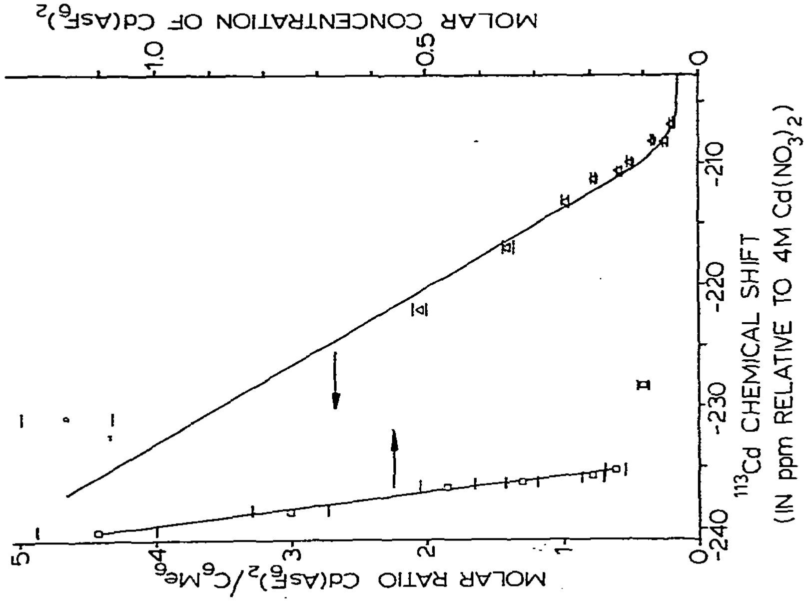
*For the system HMB-$Cd(AsF_6)_2$ a Job's plot based on the visible spectrum was consistent with 1:1 complex formation also.

†The bound shift is the value $\Delta\delta_c$ would take if the arene was present entirely as that complex.

Figure 1. (a) Right ordinate: concentration dependence of the ^{113}Cd chemical shift of $Cd(AsF_6)_2$ in liquid SO_2, showing linear dependence at higher concentrations. (Experimental data, □). Left ordinate: variation of ^{113}Cd chemical shift with $Cd(AsF_6)_2/C_6Me_6$ for the system $Cd(AsF_6)_2$-C_6Me_6-SO_2. (Experimental data: Δ([C_6Me_6] = 0.52m), O([C_6Me_6] = 0.17m); theoretical fit: solid line (K_1 = 0.54 M^{-1}, $\Delta\delta_{Cd}$ for $Cd(C_6Me_6)^{2+}$ = 169 p.p.m., σ/bound shift = 1.4)).

Figure 1. (b) Incremental ^{113}Cd chemical shifts for the system $Cd(AsF_6)_2$-C_6Me_6-SO_2 after correction for concentration dependence assuming the shifts of free and complexed $Cd(AsF_6)_2$ have the same dependence. (Corrected experimental data: O ; best theoretical fit: solid line (K_1 = 0.49 M^{-1}, $\Delta\delta_{Cd}$ for $Cd(C_6Me_6)^{2+}$ = 118 p.p.m., σ/bound shift = 0.7)).


MOLAR RATIO Cd(AsF$_6$)$_2$/C$_6$Me$_6$
0
1
2
3
4
5
DOWNFIELD ^{113}Cd CHEMICAL SHIFT
CAUSED BY COMPLEXATION
10
20
30
40


MOLAR CONCENTRATION OF Cd(AsF$_6$)$_2$
0
0.5
1.0
MOLAR RATIO Cd(AsF$_6$)$_2$/C$_6$Me$_6$
0
1
2
3
4
5
^{113}Cd CHEMICAL SHIFT
(IN ppm RELATIVE TO 4M Cd(NO$_3$)$_2$)
-240
-230
-220
-210

must reflect experimental error (as indicated by $|10^2\sigma/\text{bound shift}|$). In addition, localized bonding to the less-symmetrical arenes (see below) means that for these substrates the K's are calculated from shifts which may be a time-average for a rapidly equilibrating mixture of several isomers with different populations. There is no reason to believe that all carbons will be sensitive to complexation in all isomers, so, of a spread, the largest value of K_1 should be the best indicator of the minimum extent of complexation. Thus for the series benzene to HMB, K_1 may range from at least 0.48 to 2.1 M^{-1}.

The uncorrected data from a ^{113}Cd NMR chemical shift titration of $Cd(AsF_6)_2$ with HMB (Fig. 1a) gives $K_1 = 0.54\ M^{-1}$ and a bound ^{113}Cd shift of 169 p.p.m., with $10^2\sigma/\text{bound shift} = 1.4$. Making an approximate correction for concentration effects (Fig. 1b) gives $K_1 = 0.49\ M^{-1}$ and a bound shift of 118 p.p.m., with $10^2\sigma/\text{bound shift} = 0.7$. The complications referred to earlier make these values approximate but the data are quite consistent with formation of a 1:1 complex only, confirm the order of magnitude of K_1 for $Cd(HMB)^{2+}$, and show that binding of arenes to cadmium produces large changes in the shielding of the cadmium nucleus.

The Structure of the Cadmium(II)- and Zinc(II)-Arene Complexes from the ^{13}C NMR Complexation Shifts

In Part I [1] it was pointed out that if related methylated benzenes are considered as substrates, the incremental ^{13}C chemical shifts produced by complexation to Ag^+ differ markedly from the shifts produced by η^6 coordination to a transition metal. Shielding of all aromatic carbon nuclei is observed for the transition metal complexes, whereas, over

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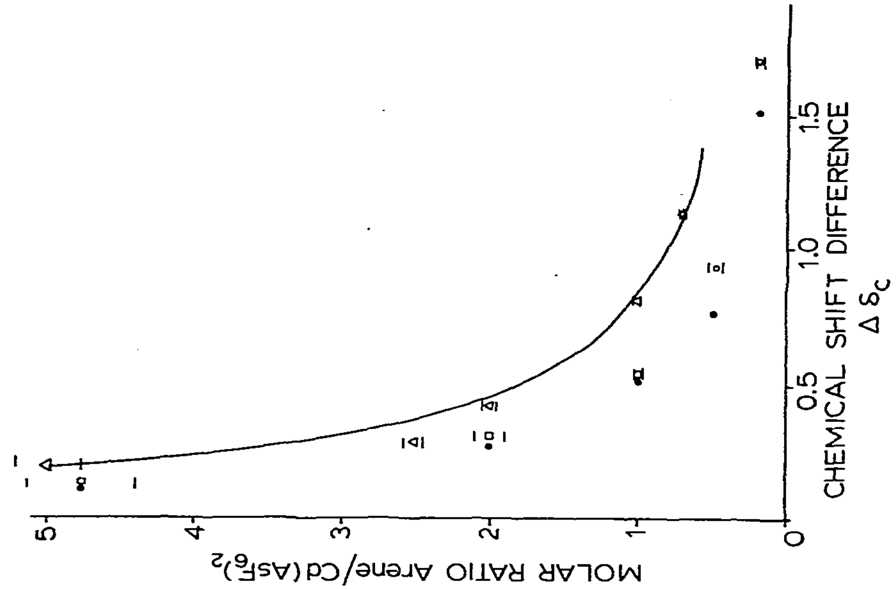
Figure 2. (a) Incremental ^{13}C chemical shifts of the aryl carbons of C_6Me_6 in the system C_6Me_6-$Cd(AsF_6)_2$-SO_2. (Experimental data: Δ($[C_6Me_6]$ = 0.52m), ○ ($[C_6Me_6]$ = 0.17m); best theoretical fit: ●, and (for $[C_6Me_6]$ = 0.52m) solid line ($K_1 = 2.09\ M^{-1}$, $\Delta\delta_C$ for $Cd(C_6Me_6)^{2+}$ = 6.01 p.p.m., σ/bound shift = 1.4)).

Figure 2. (b) Incremental ^{13}C chemical shifts of C_6H_6 in the system C_6H_6-$Cd(AsF_6)_2$-SO_2. (Experimental data: Δ($[C_6H_6]$ = 0.52m), □ ($[C_6H_6]$ = 0.26m), ○ ($[C_6H_6]$ = 0.17m)); best theoretical fit: ●, and (for $[C_6H_6]$ = 0.52m) solid line ($K_1 = 0.48\ M^{-1}$, $\Delta\delta_C$ for $Cd(C_6H_6)^{2+}$ = 4.48 p.p.m., σ/bound shift = 2.6)).


MOLAR RATIO Arene/Cd(AsF$_6$)$_2$
0
1
2
3
4
5
CHEMICAL SHIFT DIFFERENCE
$\Delta\delta_c$
0.5
1.0
1.5

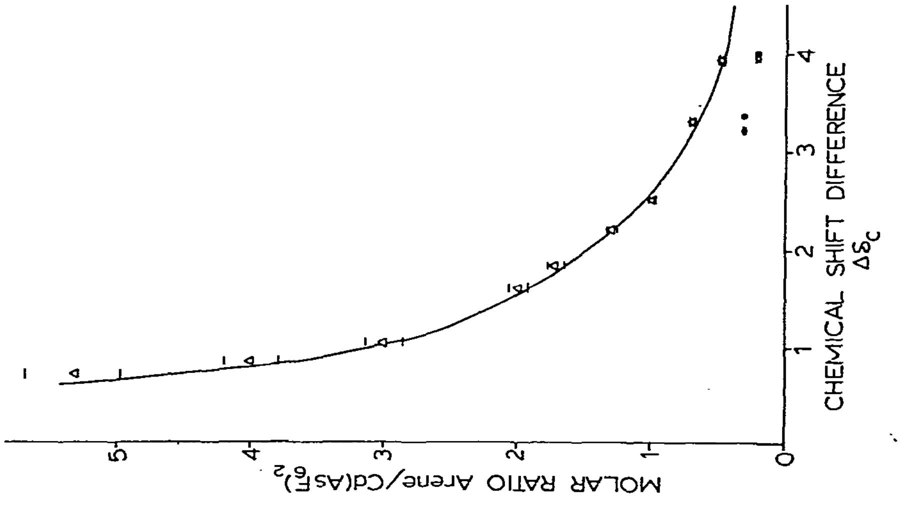

MOLAR RATIO Arene/Cd(AsF$_6$)$_2$
0
1
2
3
4
5
CHEMICAL SHIFT DIFFERENCE
$\Delta\delta_c$
1
2
3
4

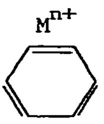
Table 3 . Bound shifts and formation constants for some Arene Complexes of Cadmium(II) in SO_2 [(a)]

Arene	^{13}C Resonance	$K_1(M^{-1})$ (b)	Bound Shift (b) (Hz)	$\lvert 10^2\sigma/\text{bound shift}\rvert$ (b)
Hexamethylbenzene	C_{1-6}	2.09	151.6	1.4
	C_{Me}	1.92	40.1	2.3
1,2,4,5-Tetramethylbenzene (Durene)	$C_{1,2,4,5}$	1.40	263.0	2.1
	$C_{3,6}$	0.54	-139.8	1.2
1,3,5-Trimethylbenzene (Mesitylene)	$C_{1,3,5}$	0.49	556.9	1.8
1,4-Dimethylbenzene (p-Xylene)	$C_{1,4}$	0.48	490.2	1.5
Methylbenzene (Toluene)	C_1	0.37	603.2	1.2
	$C_{2,6}$	0.48	238.4	1.5
	C_4	0.10	-611.0	0.5
	C_{Me}	0.23	82.9	1.5
Benzene	C_{1-6}	0.48	113.0	2.6

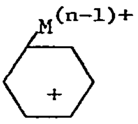
(a) At 305-308 K (see Experimental).
(b) For method of calculation, see text.

the whole series of hydrocarbons, some shielding and some deshielding of the aromatic carbon nuclei is observed for the silver complexes. Hence it was argued that the observation of both positive and negative complexation shifts for complexes of $C_6H_6Me_{6-x}$ with another metal cation is good empirical evidence for silver-like, i.e. localized, bonding in those arene complexes.

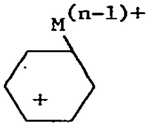
The likely contributing structures in the event of localized bonding are



a



b



c

To account for upfield and downfield complexation shifts it was suggested in the earlier work that structure **a** was most important, so that the net value of $\Delta\delta$ at the binding site should be in the direction found for olefin complexes of the same cation while downfield complexation shifts should occur remote from the binding site. Recent ^{13}C NMR data on mercuric-arene complexes [11, 14] are inconsistent with this "olefinic" model: both positive and negative values $\Delta\delta_c$ are observed for the aryl carbons, whereas $\Delta\delta_c$ is positive for mercuric-olefin complexes [15]. These new data do not invalidate the empirical use of the complexation shifts, but do suggest that localized coordination to an arene produces mainly the effect of partial quaternization at the binding site, as in structures **b** and **c**.

As both positive and negative ^{13}C complexation shifts are observed for zinc(II)- and cadmium(II)-arene complexes (Table 2) we conclude that both zinc(II) and cadmium(II) bind to arenes in a localized manner. The downfield ^1H complexation shifts (see above), also support the occurrence of similar structures for the arene complexes of the Group IB and IIB elements.

Mercurous-arene complexes are thought to have localized bonding, like silver(I), and are of considerable stability in SO_2 [1, 13]. An approximately constant weighted-average aryl carbon complexation shift, $\Delta\delta_c^{ave}$ $(= \frac{1}{6}\sum_i \Delta\delta_{c,i}$, with the summation over all aromatic carbon nuclei), is found for a range of these Hg_2^{2+} complexes, and is thought to reflect a near constancy of the shifts induced when Hg_2^{2+} perturbs the arene by localized coordination. Interestingly, for the cadmium complexes reported here, $\Delta\delta_c^{ave}$ is not a constant for constant concentration and reactant ratio but shows a uniform increase with the number of methyl substituents: when arene/Cd^{2+} = 2, $\Delta\delta_c^{ave}$ = 1.59, 1.22, 1.20, 0.57 and 0.43 p.p.m., and when arene/Cd^{2+} = 1, $\Delta\delta_c^{ave}$ = 2.56, 2.02, 1.76, 1.40, 1.15 and 0.82 p.p.m., for arene = HMB, durene, mesitylene, *p*-xylene, toluene, and benzene, respectively. The most plausible explanation for this variation is a gradation in the stabilities of the weakly-formed cadmium complexes, the HMB complex being formed to the greatest extent, the benzene complex to the least extent (c.f. Table 3).

Experimental

Materials

Sulphur dioxide (Matheson Anhydrous Grade) was stored in the gas phase over Linde 3A Molecular Sieves at least 12 h. before use. All arenes were obtained commercially; solids were purified by sublimation and liquids by distillation from calcium hydride under a dry nitrogen atmosphere. Cadmium fluoride (Alfa Ultrapure Grade), zinc fluoride (PCR Anhydrous Grade) and arsenic pentafluoride (PCR) were used without further purification. Antimony pentafluoride (PCR) was purified by double distillation under a dry nitrogen atmosphere.

General Preparative Procedure

All of the products are exceedingly moisture-sensitive. Reactions were carried out in baked out (140°C) glass vessels as previously described [1], and all manipulations of solid reagents and liquid SbF_5 were performed in a nitrogen-filled glove box, the atmosphere of which was circulated through liquid nitrogen traps. SbF_5 was dispensed from an all-glass syringe. Liquid arenes were added outside the glove box either by syringe using standard N_2-vacuum line techniques or *in vacuo* from a calibrated Teflon and glass vacuum line. AsF_5 was added from the calibrated vacuum line.

Preparation of Zinc(II) Hexafluoroantimonate, Cadmium(II) Hexafluoroantimonate and -arsenate, and the Attempted Preparation of Zinc(II) Hexafluoroarsenate

$Zn(SbF_6)_2$ was obtained by the reaction of ZnF_2 with a slightly greater than stoichiometric amount of SbF_5 in liquid SO_2 at room temperature in a sealed glass H-tube of a type described previously [17]. The reaction mixture was stirred for one week before extracting the soluble from the insoluble material (the latter being unreacted ZnF_2 and/or $ZnF(SbF_6)$. The colourless zinc salt was separated from $SbF_5.SO_2$ by recrystallization from liquid SO_2. *Anal*. Calcd. for $F_{12}Sb_2Zn$: Sb 45.36, Zn 12.18; found: Sb 45.13, Zn 11.99.

$Cd(SbF_6)_2$ was prepared in essentially the same manner as $Zn(SbF_6)_2$, but the reaction was much faster (<1 h.), and the higher solubility of the salt in SO_2 necessitated removal of $SbF_5.SO_2$ by heating (*ca*. 323 K) and pumping *in vacuo*. *Anal*. Calcd. for $CdF_{12}Sb_2$: Cd 19.25, Sb 41.70; found: Cd 19.28, Sb 42.02.

$Cd(AsF_6)_2$ was prepared in a manner analogous to the SbF_6^- salt. Volatiles were removed *in vacuo* at room temperature. *Anal*. Calcd.

Table 4. Analytical Data and Infrared Spectra for (a) $Cd(AsF_6)_2$.Arene, (b) $Cd(SbF_6)_2$.Arene, and (c) $Zn(SbF_6)_2$.Arene

Arene	Colour	Found and (parenthesized) calculated Analysis (%) Cd	C	H	Infrared Spectra (4000-500 cm^{-1})$^{(a)}$
(a)					
Hexaethylbenzene	yellow	15.4±0.3 (15.26)	29.09 (29.35)	4.01 (4.10)	3000w, 2930w, 2880w, 1445m, 1390m, 1280m, 1060m, 995vw, 790m.
Hexamethylbenzene	cream	17.4±0.2 (17.23)	21.96 (22.09)	2.76 (2.79)	2970m, 2940sh, 2880m, 1485m, 1395w, 1150w, 1100w, 1055s, 1050m, 975w, 830m.
Pentamethylbenzene	pale orange	17.6±0.6 (17.60)	20.88 (20.69)	3.71 (2.53)	2950w, 1550m, 1465s, 1440s, 1390s, 1280m, 1210w, 1060w, 1030w, 1010w, 995w, 900sh, 880m.
1,2,4,5-Tetramethyl-benzene	cream	18.4±0.4 (18.00)	19.08 (19.23)	2.37 (2.26)	2930vw, 1550vw, 1485s, 1460s, 1445s, 1395s, 1290w, 1250m, 1205w, 1030m, 1025sh, 1005m, 935w, 910sh, 895s, 865w.
1,4-dimethylbenzene	colourless	19.0±0.2 (18.85)	15.76 (16.11)	1.72 (1.69)	1500s, 1450w, 1385m, 1225w, 1195m, 1115m, 1105sh, 1050w, 955w, 900m, 885w, 835s, 790m.
Benzene	colourless	19.3±0.3 (19.78)	12.38 (12.68)	1.07 (1.07)	3070vw, 1470s, 1180vw, 1030m, 1020w, 980m, 910m.
(b)					
Hexamethylbenzene	cream	15.3±0.3 (15.06)			
Toluene	off-white	16.5±0.3 (16.72)			
Benzene	colourless	17.3±0.4 (16.98)			
(c)					
Hexamethylbenzene	red		20.47 (20.61)	2.70 (2.60)	2930vw, 1430w, 1285vw, 1180s, 1080s, 970vw, 795vw.
Pentamethylbenzene	red		19.03 (19.28)	2.47 (2.35)	3000w, 2920w, 2865w, 1470m, 1440m, 1385m, 1330w, 1320w, 1275w, 1190w, 1145w, 1075w, 1010w, 860vw.

(a) Nujol/Fluorolube Oil mull spectra; anion bands omitted.

for As_2CdF_{12}: As 30.56, Cd 22.93, found: As 30.29, Cd 22.93.

An attempt to prepare $Zn(AsF_6)_2$ in the same way as $Cd(AsF_6)_2$ was unsuccessful. ZnF_2 dissolves in AsF_5/SO_2 solutions, but the soluble product slowly loses volatiles in vacuo leaving, eventually, ZnF_2. Attempts to prepare $Cu(AsF_6)_2$ [18] have given similar results.

Preparation of Arene Complexes

Analytical data and infrared spectra for the complexes isolated are given in Table 4. All of the complexes had 1:1 stoichiometry.

$Zn(SbF_6)_2 \cdot C_6Me_6$ and $Zn(SbF_6)_2 \cdot C_6HMe_5$ were prepared by reaction of excess arene with $Zn(SbF_6)_2$ in SO_2 in a sealed H-tube (see above) at room temperature, filtration, removal of the solvent from the filtrate by cold trap techniques, and finally, removal of all volatiles from the solid product (318 K, 10^{-2} mm). A durene-containing product may be prepared similarly, but slowly loses durene on prolonged heating and pumping: the 1:1 stoichiometry reported earlier [3] appears to have been fortuitous. Similarly, the benzene was lost readily from a $Zn(SbF_6)_2$-benzene mixture, with or without SO_2 as solvent. Naphthalene and biphenyl are decomposed rapidly by contact with $Zn(SbF_6)_2$ in SO_2 solution at room temperature.

Basically the same technique successful for the isolation of the two zinc complexes was used for all the cadmium complexes, except that SO_2 was removed by lyophilization to avoid the evident decomposition which otherwise occurred. Attempts to isolate a mesitylene complex gave only a thick oily material, while the starting cadmium salts were recovered from attempts to prepare complexes of naphthalene, p-dichlorobenzene and benzotrifluoride. (Significantly, rather small ^{13}C NMR complexation shifts of these three substrates were observed (Table 1)).

Infrared Spectra

Nujol and Fluorolube Oil mull spectra were recorded over the range 4000–500 cm^{-1} using a Perkin-Elmer 621 Grating Infrared Spectrophotometer. Silver chloride windows were used.

^1H NMR Spectra

Proton spectra were measured at the ambient probe temperature of a Varian T-60 Spectrometer. Samples of complexes and of free arenes (for comparison) were prepared in sealed 5 mm o.d. medium-walled NMR tubes, and were referenced by sample interchange with a sample of TMS in SO_2.

Fourier Transform ^{13}C and ^{113}Cd NMR Spectra

$^{13}C-\{^1H\}$NMR spectra were measured at 25.2 MHz using either an XL-100-15 Spectrometer System (ambient probe temp. = 305 K) or an

XL-100-12 Spectrometer System (ambient probe temp. = 308 K) equipped with the Gyrocode Observe Accessory. Insignificant error should result from the slightly different probe temperatures. ^{113}Cd NMR spectra were measured at 22.2 MHz using the XL-100-12 Spectrometer. With the XL-100-15 an 8 K transform was used and with the XL-100-12 a 32 K transform.

Samples were prepared in sealed 10 mm o.d. hand-made medium-walled Pyrex tubes and the tubes were mounted coaxially in a 12 mm o.d. precision NMR tube as described earlier [1].

For ambient probe temperature ^{13}C measurements the external lock/reference substance was D_2O/dioxane as used previously. For low temperature measurements, $(CD_3)_2CO$ was used as an external reference and lock. Typical FT parameters used in obtaining spectra were: flip angle 20° (10 μs), sweep width 5000 Hz, acquisition time 2 sec., and repetition rate 19 min^{-1}. Under these conditions, 0.52 m arene samples gave acceptable spectra in from 1000 (for the more symmetrical arenes) to 20,000 (for pentamethylbenzene and toluene) transients.

D_2O was used as the lock substance for ^{113}Cd NMR spectra, the spectra being referenced by sample interchange with a 4M aq. $Cd(NO_3)_2$ solution. The 5:1 arene: $Cd(AsF_6)_2$ (0.1m in Cd) gave acceptable spectra in <u>ca</u>. 10,000 transients using a 15° flip angle (12 μs), sweep width of 10,000 Hz, an acquisition time of 1.6 sec. and a 10 min^{-1} repetition rate. The reference signal was visible with a single 90° pulse.

For both ^{13}C and ^{113}Cd NMR, increasing frequency is reported as increasing chemical shift, δ.

Analysis of ^{13}C and ^{113}Cd NMR Chemical Shift Titration Curves

The volume of each sample (which was initially prepared by weight) was determined from the weight of an equal volume of liquid sulfur dioxide.

The exchange-averaged shifts were analyzed as previously [1, 12] using the program LISA [9].

Elemental Analyses

Carbon, hydrogen, arsenic, antimony, zinc, and some cadmium microanalyses were performed by the Analytische Laboratorien, Elbach, West Germany. In addition, some cadmium analyses were carried out by atomic absorption using a Varian Techtron Model 1200 A.A. Spectrometer.

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