CHAPTER VI :

PALLADIUM(II) COMPLEXES OF 1-AMIDINO-O-ALKYLUREAS

We describe in this chapter a filter paper chromatographic study of bis(1-amidino-O-methylurea) palladium(II) chloride. This study has led to the characterisation of hitherto unknown dichloromono(1-amidino-O-methylurea) palladium(II) as also a few other 1-amidino-O-alkylurea complexes of its type. The results of this study being quite distinct this study is included in a new chapter outside chapter V.

Experimental :

1-amidino-O-alkylurea sulphate compounds were prepared following Dutta and Râonly[301]. Bis(1-amidino-O-alkylurea) palladium(II) chloride complexes were obtained by slight modification (discussed under 'Results and Discussion') of the original procedure described by Dutta, Sengupta and Sur[227].

Dichloro mono(1-amidino-O-methyl/ethylurea) palladium(II) :

Method A : Palladium chloride (0.44 g) and lithium chloride (0.5g) were refluxed in methanol (or ethanol, 20 ml). The brown red solution was filtered and to the filtrate solid dicyandiamide (0.21 g) was added ($PdCl_2$:dicyandiamide in 1:1 mole ratio) and refluxed for 12-14 hours. Crops of a light orange coloured compound separated from time to time and were collected, washed with appropriate cold alcohol and dried in air (Table 6.1).

<u>Method B</u> : 1-amidino-O-methylurea sulphate[301] (0.55 g) in 10 ml water was converted to the hydrochloride by treatment with barium chloride (0.4 g in 5 ml water). The hydrochloride solution was made acidic (pH 3) with dilute HCl. This solution was added drop by drop to lithium chloropalladite (0.5 g lithiumchloride and 0.5g palladium chloride in 50 ml water) with stirring when light orange crystalline precipitate of $\underline{/}$ Pd(AMUH)Cl$_2$ $\underline{7}$ separated. Similar procedures were adopted for the other 1-amidino-O-alkyl-urea complexes (Table 6.1).

<u>$\underline{/}$ Pd(AMUH)$_2$ $\underline{7}$ $\underline{/}$ PdCl$_4$ $\underline{7}$:</u>
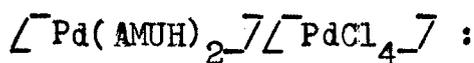
0.1g PdCl$_2$ and 0.1g lithium chloride were heated with 20 ml water, filtered and the filtrate was added to $\underline{/}$ Pd(AMUH)$_2$ $\underline{7}$ Cl$_2$ (in 10 ml water)[227] at pH 6.5, when a dirty orange red granular precipitate separated. This was cooled, filtered and then washed with cold water and finally with rectified spirit (Table 6.1).

<u>$\underline{/}$ Pd(py)$_2$ Cl$_2$ $\underline{7}$:</u>
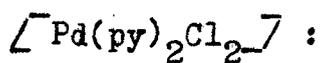
This was prepared by refluxing PdCl$_2$ with pyridine in xylene[302]. Its solubility being limited the sample was dissolved in the developer solvent prior to putting the spot.

<u>Chromatographic studies</u> :

The following developers were used :

Developer I : 70ml 0.5M KCl + 30 ml (1:1) pyridine.

The other developers (total volume 100 ml) were prepared in such a way that the concentration of KCl always remained constant (0.1M) but pyridine varied.

Developer II : 0.75 g KCl + 95 ml water + 5 ml pyridine
"   III : 0.75 g KCl + 90 ml water + 10ml pyridine
"   IV : 0.75 g KCl + 85 ml water + 15ml pyridine
"   V : 0.75 g KCl + 80 ml water + 20ml pyridine
"   VI : 0.75 g KCl + 75 ml water + 25ml pyridine
"   VII : 0.75 g KCl + 50 ml water + 50ml pyridine

The complexes were spotted as aqueous solution and were detected by spraying acidified (HCl) solution of rubeanic acid when an orange yellow spot developed. The R_f values (Table 6.2) are reproducible to within $\pm$ 0.02 R_f units.

Palladium was estimated by igniting the complexes to metallic palladium. Nitrogen was determined by combustion and chloride as silver chloride. Equivalent weight was determined by standard procedure[247].

The infrared spectra upto 650 cm^{-1} were run as KBr pellets at CDRI, Lucknow and upto 250 cm^{-1} at the Ohio State University, Columbus.

Table 6.1. Dichloro mono(1-amidino-O-alkylurea) palladium(II) complexes.

Method of synthesis	Alcohol	Complex	Analysis							
			Palladium		Nitrogen		Chloride		Water of cryst.	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
A	CH_3OH	$\angle Pd(AMUH)Cl_2\underline{}7$	36.8	36.5	19.3	19.1	23.7	24.1	-	-
B	CH_3OH	$\angle Pd(AMUH)Cl_2\underline{}7$	36.8	36.5	19.5	19.1	23.8	24.1	-	-
A	C_2H_5OH	$\angle Pd(AEUH)Cl_2\underline{}7$	35.3	34.9	18.4	18.2	23.0	23.1	-	-
B	C_2H_5OH	$\angle Pd(AEUH)Cl_2\underline{}7$	34.6	34.9	18.5	18.2	22.9	23.1	-	-
B	$n-C_3H_7OH$	$\angle Pd(AP^nUH)Cl_2\underline{}7$	33.7	33.4	17.8	17.4	22.1	22.1	-	-
B	$iso-C_4H_9OH$	$\angle Pd(AB^iUH)Cl_2\underline{}70.5H_2O$	31.4	31.1	16.5	16.3	20.6	20.6	2.6	2.6
-	-	$\angle Pd(AMUH)_2\underline{}7\angle PdCl_4\underline{}7 \; 3H_2O$	34.0	33.4	17.0	17.4	-	-	8.2	8.4

Table 6.2. Conductance, equivalent weight and R_f values of

$\angle^-Pd(AAUH)Cl_2\angle^7$.

Complex	Molar conductance in water ($mhos\ cm^2\ mole^{-1}$) at $25^\circ C$	Equivalent weight*		R_f (70ml 0.5M KCl + 30ml 1:1 pyridine).
		Found	Calcd.	
$\angle^-Pd(AMUH)Cl_2\angle^7$	204	152	146	0.86
$\angle^-Pd(AEUH)Cl_2\angle^7$	214	159	153	0.88
$\angle^-Pd(AP^nUH)Cl_2\angle^7$	211	166	160	0.89
$\angle^-Pd(AB^iUH)Cl_2\angle^7$	170	-	-	0.85

* Two equivalents of acid per molecule of complex were liberated.

Results and Discussion :

The present study was aimed at finding the best chromatographic developer for the identification of bis(1-amidino-0-alkylurea) palladium(II) complexes. These complexes were originally obtained by Dutta and coworkers by interaction of aqueous sodium chloropalladite and aqueous 1-amidino-0-alkylurea sulphate[227]. Following this reported prescription for 1-amidino-0-methylurea complex (with the only modification of using lithium chloropalladite instead of sodium chloropalladite) we obtained a light orange yellow precipitate instead of the reported pale cream coloured precipitate of bis(1-amidino-0-methylurea) palladium(II) sulphate. This orange yellow precipitate

on treatment with aqueous barium chloride gave a soluble fraction from which we could isolate pale cream coloured bis(1-amidino-0-methylurea) palladium(II) chloride as reported by Dutta and co-workers[227]. Significantly an orange coloured sparingly soluble product still remained with the barium sulphate, which was repeatedly extracted with water and then crystallised. Filter paper chromatography of the pale cream coloured bis(1-amidino-0-methylurea) palladium(II) chloride in aqueous KCl-pyridine developer (70 ml 0.5M KCl + 30ml 1:1 pyridine, Fig.6.1) provided two spots - the one with higher R_f (0.86) was small in size and was of lower intensity than the other with lower R_f (0.51) and of slightly bigger size. This result was rather unusual since bis(biguanide) palladium(II) chloride had provided in the same developer a distinct single spot (Chapter IV). This unusual chromatographic behaviour led us to conjecture the following possible equilibrium:

$$\angle Pd(AMUH)_2 \overline{7}Cl_2 \rightleftharpoons \angle Pd(AMUH)Cl_2 \overline{7} + AMUH \qquad \dots \quad (1)$$
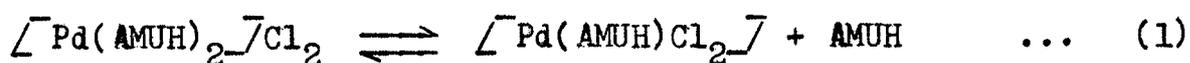
In support of this hypothesis we were happily surprised to see that the orange yellow sparingly soluble product that we mentioned above gave a single spot having the same R_f as the higher one of the two spots shown by $\angle Pd(AMUH)_2 \overline{7}Cl_2$ (Fig. 6.1). An analysis of the orange yellow sparingly soluble product was then completed and it turned out to be $\angle Pd(AMUH)Cl_2 \overline{7}$. Large concentration of chloride ion present in the developer possibly facilitated the shifting of the equilibrium (1) towards the mono(1-amidino-0-alkylurea) derivative. We wish to comment that
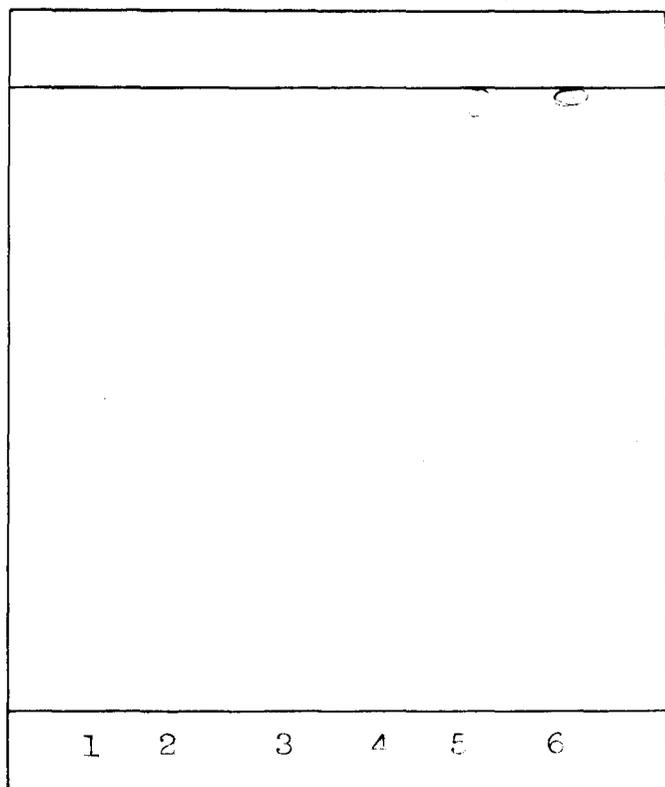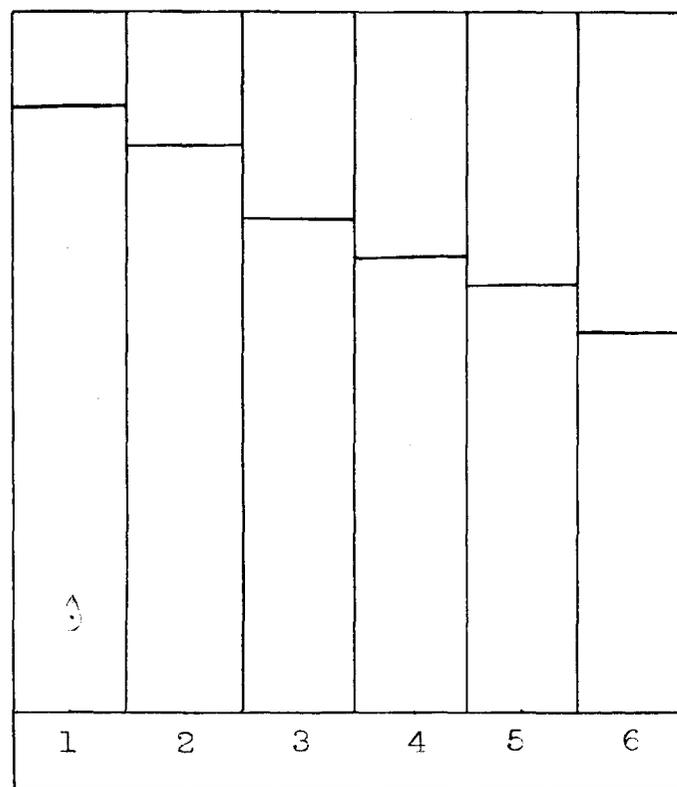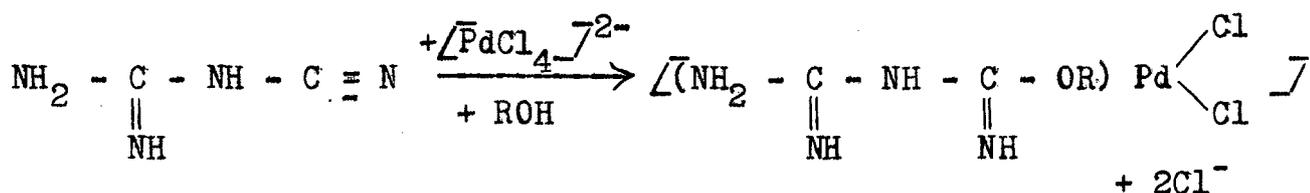
Fig. 6.1.

Fig. 6.2.

Fig.6.1. Chromatograms of $\angle Pd(AMUH)_2\angle7Cl_2$, $\angle Pd(AMUH)Cl_2\angle7$, $\angle Pd(py)_2Cl_2\angle7$ and $Li_2\angle PdCl_4\angle7$ in 70ml 0.5M KCl + 30ml 1:1 pyridine. 1 — $\angle Pd(AMUH)_2\angle7Cl_2$; 2 — $\angle Pd(AMUH)Cl_2\angle7$via fractional crystallisation of the product obtained by treating orange coloured $\angle Pd(AMUH)_2\angle7SO_4$ with $BaCl_2$ as described in reference (see text); 3 — $\angle Pd(AMUH)Cl_2\angle7$obtained by palladium(II) catalysed addition of methanol to dicyandiamide (Method A in experimental); 4 — $\angle Pd(AMUH)Cl_2\angle7$ obtained by $Li_2\angle PdCl_3\angle7$(1 mole) and AMUH.HCl (1 mole) at pH 3.0 (Method B in experimental); 5 — $\angle Pd(py)_2Cl_2\angle7$; 6 — $Li_2\angle PdCl_4\angle7$.

Fig.6.2. Chromatograms of $\angle Pd(AMUH)_2\angle7Cl_2$ in different developers (1,2,3,4,5,6) : Total volume 100ml; KCl concentration 0.1M; pyridine varying : 1 — 5ml; 2 — 10ml; 3 — 15ml; 4 — 20ml; 5 — 25ml; 6 — 50ml.

the synthesis of $\angle$ Pd(AMUH)$_2$_$\mathcal{7}$Cl$_2$ is better accomplished on

the addition of a few drops of ammonia to the solution of 1-

amidino-O-alkylurea sulphate prior to the addition of the

chloropalladite.. Under this condition pale cream coloured

precipitate of $\angle$Pd(AMUH)$_2$_$\mathcal{7}$SO$_4$ appears in good quantity with

very little of the orange yellow sparingly soluble staff. It

is quite likely that ammonia was used in the original synthesis,

mention of which was omitted through oversight. It is indeed a

fact that all sparingly soluble bis(biguanide) metal(II) sulp-

hates and bis(1-amidino-O-alkylurea) metal $\angle$ copper(II),

nickel(II)_$\mathcal{7}$ sulphates are obtained in slightly ammoniacal

medium[221]. During reaction of $\angle$PdCl$_4$_$\mathcal{7}^{2-}$ and AMUH.HCl (or

AMUH.$\frac{1}{2}$ H$_2$SO$_4$) acid is liberated, which leads to the formation

of $\angle$Pd(AMUH)Cl$_2$_$\mathcal{7}$ to some extent. Addition of few drops of ammo-

nia obviates the formation of $\angle$Pd(AMUH)Cl$_2$_$\mathcal{7}$. It was also

verified that the spot with higher R$_f$ was not due to tetrachloro

palladite or due to $\angle$Pd(py)$_2$Cl$_2$_$\mathcal{7}$, both of which gave R$_f$ almost

close to the solvent front (Fig. 6.1). This is what one would

expect on consideration of charge[116,300]. That bis(biguanide)

palladium(II) chloride provides a single spot under the same

condition is likely to be associated with its higher stability

towards dissociation than the corresponding bis(1-amidino-O-

methylurea) complex, as have been verified for copper(II) and

nickel(II) systems of the two ligands[221,226,274,303].

Having thus obtained a clue to the possible existence of

hitherto unknown $\angle$Pd(AMUH)Cl$_2$_$\mathcal{7}$ it now became our obligation

to develop a straight⊃forward.. synthesis for this complex. We have developed two such routes for the purpose. The first method (A) is via palladium(II) promoted addition of alcohol to dicyandiamide. It is now well established that metal ion promoted addition of alcohol to dicyandiamide leads to the synthesis of 1-amidino-0-alkylurea complexes. So far copper(II) and to a limited extent nickel(II) have been found suitable for such reactions[223,243,244,255,304]. The present study now shows that palladium(II) also can initiate this alcohol addition :

$$NH_2 - \underset{\underset{NH}{\|}}{C} - NH - C \equiv N \xrightarrow[+ ROH]{+ \underline{/}PdCl_4\underline{/}^{2-}} \underline{/}(NH_2 - \underset{\underset{NH}{\|}}{C} - NH - \underset{\underset{NH}{\|}}{C} - OR) Pd\underset{Cl}{\overset{Cl}{<}} \underline{/}$$
$$+ 2Cl^-$$

No reaction occurs between dicyandiamide and alcohol in the absence of palladium(II). In fact dicyandiamide can be recovered in over 95% yield even after 50 hours reflux in alcohols.

The second method (B) involves the reaction of $\underline{/}PdCl_4\underline{/}^{2-}$ and 1-amidino-0-alkylurea chloride in 1:1 ratio in the presence of excess chloride ions at pH 3.0. Of these two methods, however, the second method (B) gives better yield. That both these methods of synthesis provided the same complex was revealed by the fact that both these preparations gave a single spot with the same R_f (e.g. $\underline{/}$Pd(AMUH)Cl_2$\underline{/}$, R_f = 0.86 in 70 ml 0.5M KCl + 30 ml 1:1 pyridine developer, Fig. 6.1). That palladium(II) does promote addition of alcohol to dicyandiamide giving 1-amidino-0-alkylurea

is shown by an inspection of the infra red spectrum of $/^-$Pd(AMUH)Cl$_2^-/$. There is no typical split nitrile (C $\equiv$ N) band due to dicyandiamide[304] at 2176 and 2222 cm^{-1}, instead a characteristic C - O - R (R = CH$_3$) stretch appears at 1205 cm^{-1} [305]. The spectra of $/^-$Pd(AMUH)Cl$_2^-/$and $/^-$Pd(AEUH)Cl$_2^-/$ also show bands at 325 cm^{-1} (unsplit) and at 312 and 325 cm^{-1} respectively which can be assigned to Pd-Cl stretch. The corresponding Pd-Cl stretch in the compound $/^-$Pd(dipy)Cl$_2^-/$ appears[306] at 354 and 343 cm^{-1}. The Pd-N stretch appears at 490 cm^{-1} for both complexes[308]. It is an established fact that AMUH is an N - N bidentate donor[244,309].

Complexes of the empirical composition $/^-$Pd(AAUH) Cl$_2^-/$ are expected to give nonelectrolytic conductance values. Interestingly in aqueous solution at 0.0005M dilution the complexes register bi-univalent electrolyte values (Table 6.2). This indicates that the complexes are rapidly aquated. That indeed this happens is also substantiated by our being able to determine the equivalent weights of the complexes via passage through a H-form cation exchanger column (Table 6.2). We were unable to find a suitable solvent where the complexes would dissolve without solvolysis. Furthermore if $/^-$Pd(AMUH)Cl$_2^-/$ behaved as a nonelectrolyte during a chromatographic run we would naturally expect an R_f value almost close to the solvent front. In reality $/^-$Pd(AMUH)Cl$_2^-/$ is possibly being chromatographed as one of $/^-$Pd(AMUH)(py)Cl$^-/$Cl, $/^-$Pd(AMUH)(py)$_2^-/$Cl$_2$ etc. in aqueous KCl-pyridine developer thus explaining its R_f being lower than

that of a nonelectrolyte $\sqrt{}Pd(py)_2Cl_2\_7$ or an anion like
$\sqrt{}Pd\ Cl_4\_7^{2-}$. For a soft acid like palladium(II), partial or
total replacement of chloride groups by pyridine is not unreaso-
nable. Unfortunately a suitable non coordinating developer
could not be found for further chromatographic investigation.

A complex of the composition $\sqrt{}Pd(AMUH)Cl_2\_7$ can also be
written as an ionic isomer $\sqrt{}Pd(AMUH)_2\_7\sqrt{}Pd\ Cl_4\_7$. This latter
complex was independently prepared (vide experimental) and it
turned out that properties of $\sqrt{}Pd(AMUH)_2\_7\sqrt{}Pd\ Cl_4\_7$ are much
different from these of $\sqrt{}Pd(AMUH)Cl_2\_7$. $\sqrt{}Pd(AMUH)_2\_7\sqrt{}Pd\ Cl_4\_7$
is extremely insoluble in water so much so that we could not
even run its chromatogram.

Effect of KCl/pyridine :

Like our previous studies (Chapter IV) here also as the
concentration of KCl or pyridine increases.the R_f values of the
complexes also increases. But pronounced effect is observed in
the case of pyridine than with KCl solution. The chromatographic
behaviour of $\sqrt{}Pd(AMUH)_2\_7Cl_2$ in various developers of varying
concentration of pyridine (keeping the KCl concentration constant)
have been studied. These studies revealed that as the concentra-
tion of pyridine increases (KCl concentration constant), for a
fixed time (4 hours) of chromatographic run the solvent front
moves to lesser and lesser height (Fig. 6.2). During these runs
the R_f of the upper spot increases gradually (from 0.76 to 0.87)

and attain a steady value while that of the lower spot increases
sharply from 0.20 till the two spots fuse together to give an
over all R_f value 0.85 (Fig. 6.2).

It is interesting to note that recently Banerjea and
Banerjee[298,310] have observed during kinetic experiments that a
large concentration of chloride ion and a low pH lead to disso-
ciation of bis(biguanide) palladium(II) chloride, $[Pd(BigH)_2]Cl_2$,
to dichloromono(biguanide) palladium(II), $[Pd(BigH)Cl_2]$. This
latter compound was synthesised and characterised. Biguanides
and 1-amidino-O-alkylureas being close in their behaviour as
coordinating ligands[221,244] it is no wonder that dichloromono-
(1-amidino-O-alkylurea) palladium(II) complexes should also
exist. Indeed they do.