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Interactions of Cysteinato-O-methylesterpalladium(II)-μ-dichloro-cysteinato-O-methylesterpalladium(II) with Nucleosides and AMP*

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The reactions of the binuclear complex Cysteinato-O-methylester–palladium(II)-μ-dichloro–cysteinato-O-methylester–palladium(II), {Pd(O-MeCys)Cl}$_2$, with nucleosides, Nucl, and adenosine-5′-monophosphate disodium, AMP-Na$_2$, have been studied in aqueous and dmso solutions. From dmso solutions, the monomeric complexes, {Pd(O-MeCys)(NuCl)Cl} were isolated and characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectra. In the case of Nucl = inosine (Ino) or guanosine (Guo) the complexes are transformed to {Pd(O-MeCys)(Nucl-H$^+$)}, when dissolved in water. The same complexes were formed by direct mixing of the reactants in water. In these latter complexes the exocyclic oxygen of the 6th position participates in the bonding with the metal, besides the N$_7$ of the purine ring, either in a chelate or a dimeric or polymeric O$_6$N$_7$ manner. The reaction with AMP-Na$_2$ in aqueous solution gave the product: {Pd(O-MeCys)(AMP)}Na. The results indicate that in this complex the nucleotide AMP coordinates to palladium through the N$_7$ atom of the purine ring and the phosphate group, most probably in a chelate form.

Introduction

The dimeric compounds {M(O-Mecys)Cl}$_2$, M is Pd or Pt and O-Mecys is the anion of the cysteine O-methylester, have been prepared in this laboratory [1], and the reactions of the platinum complex with nucleosides have been studied recently [2].

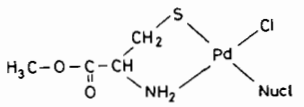
This paper describes the results of the interaction of nucleosides and AMP-Na$_2$ with the palladium dimer. These reactions are worthy of study, because it is interesting to compare the general reactivity of these two dimers with nucleosides. Similar reactions of dipeptide–Pd(II) complexes with nucleotides have been studied, mainly with ^{13}C NMR spectroscopy, by Kozłowski *et al.* [3–5].

Results and Discussion

The interaction of the dimeric complex, {Pd(O-Mecys)Cl}$_2$, with nucleosides in dmso solutions, is a straightforward breakdown of the two chloride bridges between the two palladium atoms with formation of the mononuclear complexes, {Pd(O-Mecys)(Nucl)}Cl according to the general equation:

$$\{Pd(O\text{-}Mecys)Cl\}_2 + 2Nucl \xrightarrow{dmso} 2\{Pd(O\text{-}Mecys)(Nucl)Cl\} \quad (1)$$

Due to the high *trans* influence of the sulfur atom, the chloride *trans* to it would be expected to be labilized and replaced by a nucleoside molecule in reaction (1), producing:



Structure (I)

The analytical results fit well with the proposed formulation (Table I).

The molar conductances of the complexes in DMF solution (Table I) indicate that they are not electrolytes in this solvent, in contrast with the analogous complexes of platinum, which were found to dissociate in this solvent [2]. On the other hand the complexes of the nucleosides with one ionizable N(1) imino proton (*i.e.* inosine and guanosine), attain high conductances when dissolved in water, and complexes of the type, {Pd(O-Mecys)(Nucl-H$^+$)}, were precipitated, with liberation of HCl, according to the equation:

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TABLE I. Analytical and Conductivity Data of the Complexes.[a]

Compound	%C	%H	%N	%Pd	Cl	Λ_M, Ω^{-1} cm^2 mol^{-1}	
						10^{-3} *M* in DMF	10^{-3} *M* in H_2O
Pd(O-Mecys)(Ino)Cl	30.50	3.77	12.50	19.20	6.34	7.5	120
	(30.88)	(3.68)	(12.87)	(19.56)	(6.52)		
Pd(O-Mecys)(Ino-H$^+$)	32.70	3.42	13.20	20.50			
	(33.10)	(3.74)	(13.74)	(20.96)			
Pd(O-Mecys)(Guo)Cl	30.28	3.90	15.50	19.50	6.60	8.0	115
	(30.04)	(3.76)	(15.02)	(19.03)	(6.35)		
Pd(O-Mecys)(Guo-H$^+$)	32.60	3.95	16.50	20.80			
	(32.14)	(3.83)	(16.07)	(20.36)			
Pd(O-Mecys)(Ado)Cl	30.50	3.52	15.60	19.10	6.32	6.5	
	(30.82)	(3.85)	(15.41)	(19.52)	(6.54)		
Pd(O-Mecys)(Cyd)Cl	30.40	3.80	10.40	20.90	7.02	7.0	9.0
	(30.05)	(4.05)	(10.79)	(20.50)	(6.84)		
{Pd(O-Mecys)(AMP)}Na	27.00	3.42	13.70	17.20			90
	(26.60)	(3.17)	(13.30)	(16.85)			

[a]The numbers in parentheses represent the calculated figures.

TABLE II. Characteristic IR Bands of the Complexes (cm^{-1}).[a]

Compound	ν_{NH_2}	$\nu_{C=O}$ acetyls	$\nu_{C=O}$ rings	δ_{NH_2}	$\nu_{C=C}$ $\nu_{C=N}$	ν–PO_3^{2-}	ν_{Pd-Cl}
{Pd(O-Mecys)(Ino)Cl}	3200–3400 vs,br	1740 s	1695 vs	1590 s	1500 m		333 m
					1540 m		
{Pd(O-Mecys)(Ino-H$^+$)}	3200–3400 vs,br	1738 s	1620 vs	1588 s	1500 m		
					1533 m		
{Pd(O-Mecys)(Guo)Cl}	3200–3400 vs,br	1739 s	1694 vs	1595 s	1500 m		330 m
					1537 m		
{Pd(O-Mecys)(Guo-H$^+$)}	3200–3400 vs,br	1740 s	1620 vs	1585 s	1500 m		
					1560 m		
{Pd(O-Mecys)(Ado)}Cl	3200–3400 vs,br	1737 s		1595 s	1500 m		332 m
					1570 m		
{Pd(O-Mecys)(Cyd)Cl}	3200–3400 vs,br	1738 s	1680 vs	1600 s	1500 m		330 m
					1550 m		
{Pd(O-Mecys)(AMP)}Na	3200–3400 vs,br	1735 s		1595 s		1160–1190 m,br	

[a]Measured on KBr disks: s = strong; m = medium; vs = very strong; br = broad.

$$\{Pd(O\text{-}Mecys)(NuCl)Cl\} \xrightarrow{H_2O} \{Pd(O\text{-}Mecys)(Nucl\text{-}H^+)\} + HCl \quad (2)$$

Reaction (2) is reversed in acidic solution and the complexes, {Pd(O-Mecys)(Nucl-H$^+$)}, were converted to the parent ones, {Pd(O-Mecys)(Nucl)Cl}, when dissolved in 0.5 *N* HCl. The complexes, {Pd(O-Mecys)(Nucl-H$^+$)} may also be prepared directly, by performing the reaction (1) in aqueous solutions:

$$\{Pd(O\text{-}Mecys)Cl\}_2 + 2Nucl \xrightarrow{H_2O} 2\{Pd(O\text{-}Mecys)(Nucl\text{-}H^+)\} + 2HCl \quad (3)$$

Reaction (3) may proceed in two main steps. First the chloride bridges may be broken down by the nucleosides, which then remain attached to the palladium with their N(7) atom (as will be shown below), and this is demonstrated by the formation of a transient clear yellow reaction mixture. In the second step the compounds {Pd(O-Mecys)(Nucl-

TABLE III. ^{1}H NMR Chemical Shifts of the Ligands and Complexes.

Compound	H(2)	H(5)	H(6)	H(8)	Solvent
Ino	8.11			8.22	dmso-d_6
{Pd(O-Mecys)(Ino)Cl}	8.20			8.69	dmso-d_6
{Pd(O-Mecys)(Ino-H$^+$)}	8.30			8.64	dmso-d_6
Guo				7.80	dmso-d_6
{Pd(O-Mecys)(Guo)Cl}				8.41	dmso-d_6
{Pd(O-Mecys)(Guo-H$^+$)}				8.36	dmso-d_6
Ado	7.95			8.17	dmso-d_6
{Pd(O-Mecys)(Ado)Cl}	8.08			8.70	dmso-d_6
Cyd		5.75, 5.66	7.78, 7.79		dmso-d_6
{Pd(O-Mecys)(Cyd)Cl}		6.18, 6.09	8.11, 8.20		dmso-d_6
AMP-Na_2	7.72			7.94	D_2O
{Pd(O-Mecys)(AMP)}Na	7.90			8.50	D_2O

H$^+$)} are very rapidly precipitated, and this may include the ionization of the N(1)-H imino proton, due to the considerable lowering of the pK_a of this proton when the nucleosides are coordinated to metals, and especially to Pd(II), through their N(7) atom [6, 9, 10]. There is accumulation, due to resonance, of a negative charge on the exocyclic O(6) atom, and nucleophilic substitution of the coordinated chloride by this negatively charged oxygen atom. This behavior is also in contrast with that of the analogous platinum complexes, where attempts to prepare complexes with the O(6) atom of the nucleosides participating in coordination resulted in the destruction of the parent compounds [2].

IR Spectra

Some characteristic IR bands of the complexes are given in Table II.

The ν(C=O) of the ligand (O-Mecys), shown at 1720 cm^{-1} in the initial complex, {Pd(O-Mecys)Cl}$_2$, moves to slightly higher frequencies (about 1730 cm^{-1}) in all the mixed ligand complexes isolated. The $\delta(NH_2)$ of the amino acid coordinated to palladium, which is shown at 1580 cm^{-1} in the initial complex, may be assigned to a band near 1600 cm^{-1}. The ν(C=O) of the exocyclic carbonyl oxygen of the nucleosides appears at almost constant frequency (1700 cm^{-1}) in the complexes Pd(O-Mecys)(Nucl)Cl and free ligands, thus excluding its participation in bonding with palladium [6–8]. On the other hand in the complexes {Pd(O-Mecys)(Nucl-H$^+$)} this band is shifted to lower frequencies by about 75 cm^{-1} and appears at about 1620 cm^{-1}. This lowering of the ν(C=O) frequency may be taken as a good indication of the O(6) keto oxygen involvement in bonding with the metals [8, 11–13]. The shift to lower frequencies of the ν(C=O) band upon ionization of the N(1)H imino proton in Ino and Guo indicates the loss of the double bond character of the C=O group [14, 15]. This is possibly more pronounced in the ionic sodium salt of guanosine (shift to 1595 cm^{-1}) [13] and less whenever the metal-oxygen bonding is more covalent, as in the case of Pt(II) and Pd(II) for example (shift to 1625 cm^{-1}) [6, 16]. Certainly, the double bond character of the C=O is also lowered when the oxygen interacts covalently with a metal, without ionization of the N(1)H imino proton [8a]. Oxygen involvement in bonding with metals, following deprotonation of the imino proton, has also been found in the crystal structure of *cis*-diamminoplatinum a-pyridone blue [17], where both O$^-$ and N atoms bridge two platinum atoms. Kistenmacher *et al.* [18] have also found an O–Ag(I) interaction in the crystal structure of (nitrato)(1-methylcytosine)silver(I). Recently Bau *et al.* showed the participation of the exocyclic O(6) in coordination in the crystal structure of a tetranuclear copper(II)–inosine monophosphate o-phenanthroline complex, when inosine acts as an O(6) N(7) bridging ligand with a Cu–O(6) distance of 1.956 Å [19]. Very recently Marzilli *et al.* have presented evidence for O(6) binding with metals, mainly from ^{13}C NMR spectra [20].

The parent dimeric complex, {Pd(O-Mecys)Cl}$_2$ shows a band at 312 cm^{-1} assigned to Pd–Cl–Pd stretching, which is displaced to about 330 cm^{-1} in the complexes {Pd(O-Mecys)(Nucl)Cl} and disappears in the complexes {Pd(O-Mecys)(Nucl-H$^+$)}.

In view of the above discussion, there must exist a strong O(6)–Pd interaction in the complexes {Pd(O-Mecys)(Nucl-H$^+$)} which may be formulated either as O(6)N(7) chelate monomers (II), or as dimers (III), or polymers (IV) with O(6)N(7) bridges:

TABLE IV. ^{13}C NMR Chemical Shifts of the Ligands and Complexes.

Compounds	O-Mecys H Carbons				Nucleoside Carbons								
	CH_2	CH	OCH_3	C=O	C_2	C_4	C_5	C_6	C_8	C_1'	C_2'	C_3'	C_4'	C_5'
O-Mecys H	38.1	52.5	54.1	169.0										
{Pd(O-Mecys)Cl}$_2$	32.3	63.0	53.0	170.0										
Ino					146.0	148.2	124.4	156.5	138.7	87.4	74.0	70.2	85.6	61.2
{Pd(O-Mecys)(Ino)Cl}	32.8	63.2	53.1	170.0	146.8	149.1	126.6	157.8	142.2	88.1	74.6	69.8	86.0	60.8
{Pd(O-Mecys)(Ino-H$^+$)}	32.7	63.3	53.2	170.1	150.2	149.0	126.8	165.6	142.1	88.0	74.5	69.9	85.8	60.6
Guo					153.6	151.3	116.6	156.7	135.6	86.3	73.7	70.3	85.1	61.7
{Pd(O-Mecys)(Guo)Cl}	32.9	63.4	53.2	169.8	154.7	152.4	118.6	158.0	138.9	87.6	74.0	69.8	85.6	61.1
{Pd(O-Mecys)(Guo-H$^+$)}	33.0	63.3	53.3	170.0	158.2	152.3	117.7	165.7	138.8	87.2	74.0	70.0	85.3	61.2
Ado					148.5	147.0	114.5	152.0	135.8	88.4	71.0	73.9	86.3	61.0
{Pd(O-Mecys)(Ado)Cl}	32.6	63.3	53.1	169.7	150.0	147.1	116.4	156.2	143.7	83.6	71.2	74.0	86.4	61.1
Cyd					152.9	163.7	99.6	148.6	–	90.8	74.6	69.8	83.8	61.3
{Pd(O-Mecys)(Cyd)Cl}	32.6	63.2	53.1	169.7	156.6	166.3	97.9	147.3		90.9	74.8	69.5	84.0	61.0
AMP-Na_2					153.0	149.0	119.0	155.5	140.5	87.7	71.0	75.2	84.7	65.1
{Pd(O-Mecys)(AMP)}Na	32.8	63.2	53.5	169.8	154.2	149.2	121.2	160.5	147.6	87.9	71.2	75.5	84.9	65.2

Structure (II)

Structure (III)

Structure (IV)

^1H NMR Spectra

Some characteristic ^1H NMR chemical shifts of the ligands and the complexes are given in Table III.

The ^1H NMR spectra of (O-Mecys) in the initial and final complexes are not well resolved in dmso-d_6 solutions. In the last complexes particularly the bands of O-Mecys are not shown clearly because they coincide with some of the nucleoside resonances. However, the ^1H NMR spectra are very useful in assigning the bonding sites of the nucleosides with Pd(II). The complexes Pd(O-Mecys)(Ino)Cl and Pd(O-Mecys)(Ino-H$^+$) in dmso-d_6 show two resonances at 8.69 and 8.20 ppm for the first and at 8.64 and 8.30 ppm for the second complex, assigned to H(8) and H(2) respectively. The downfield shift of the H(8) resonance (0.47 ppm for the first and 0.42 ppm for the second complex), may be taken as a good indication of the N(7) coordination of inosine with Pd(II), as in other similar cases [6, 8, 21]. The downfield shifts of the H(2) resonances (0.09 ppm for the first and 0.19 ppm for the second complex) are very small to account for any N(1)–Pd interaction. The complexes Pd(O-Mecys)(Guo)Cl and Pd(O-Mecys)(Guo-H$^+$) in dmso-d_6 show one resonance at 8.41 and 8.36 ppm respectively, assigned to H(8) and this again indicates N(7) coordination of guanosine to Pd(II) in both complexes. The complex Pd(O-Mecys)(Ado)Cl shows two resonances at 8.70 and 8.08 ppm, assigned to H(8) and H(2) respectively. This indicates that adenosine coordinates to Pd(II) in this complex only through its N(7) atom, in contrast with other cases where adenosine coordinates through both N(1) and N(7) atoms, forming dimeric or polymeric complexes [2, 21]. In the complex Pd(O-Mecys)(Cyd)Cl, the cytidine signals of H'(1) and H(5) became larger and the H(5) was shifted downfield to the greatest extent (Table III). This result is the same as that found for cytidine–platinum and cytidine–palladium complexes [6(b), 21, 22], and indicates that the N(3) of the pyrimidine ring is the ligation site.

^{13}C NMR Spectra

In order to gain more information about the structures of the complexes, and especially those of the deprotonized nucleosides, the ^{13}C NMR spectra of the ligands and complexes have been recorded in dmso-d_6 solutions and the chemical shifts are given in Table IV.

The assignments for the nucleosides [23, 24] and O-methylcysteinester [2] have already been made.

The chemical shift changes in the proton decoupled spectra confirm that the nucleoside binding sites were as suggested above.

In the complex [Pd(O-Mecys)(Ino)Cl], the downfield shifts observed for the C(5) and C(8) resonances (2.2 and 3.5 ppm respectively) are consistent with N(7) coordination, since these carbons are adjacent to this nitrogen. However, in the deprotonated complex, {Pd(O-Mecys)(Ino-H^+)}, the most dramatic change in the chemical shifts was observed for the C(6) (9.1 ppm downfield shift with respect to the free nucleoside), and this may be taken as an indication of O(6) participation in coordination with the palladium, besides the N(7). A relatively large downfield shift (4.2 ppm) was also observed for the C(2), but this is due to the ionization of the N(1)-H iminoproton [20]. The same sort of pattern was also observed in the ^{13}C NMR spectra of the guanosine complexes, suggesting N(7) coordination of the guanosine in the complex [Pd(O-Mecys)(Guo)Cl], and N(7) O(6) coordination in the complex [Pd(O-Mecys)(Guo-H^+)].

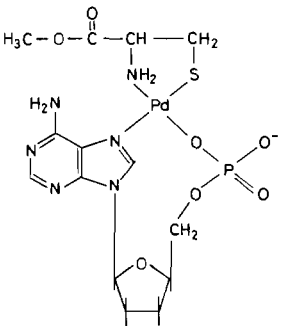
For the adenosine complex, the largest chemical shift differences occured at C(8) and C(5), 7.9 and 1.9 ppm downfield with respect to the uncomplexed adenosine, and this confirms coordination at N(7). In the cytidine complex, the downfield shift observed for the C(2) and C(4) resonances, in contrast to the upfield shifts of the C(5) and C(6) signals, confirms coordination through N(3).

Finally the reaction of the dimeric complex, {Pd-(O-MeCys)Cl}$_2$ with the nucleotide AMP-Na_2 has been studied in aqueous solutions. The complex isolated is free from chlorine, behaves as a 1:1 electrolyte in water and the analytical results fit well with the formulation {Pd(O-Mecys)(AMP)}Na (See Table I). The complex was also isolated as the tetramethylammonium salt. From the ^1H and ^{13}C NMR spectra of the complex (See Tables III and IV) it is suggested that only the N(7) atom of the purine ring is coordinated to palladium. On the other hand, IR and ^{31}P NMR spectra suggested simultaneous coordination through the phosphate group of the nucleotide.

The band at 1115 cm^{-1}, in the IR spectrum of AMP-Na_2 is attributed to the antisymmetric $-PO_3^{2-}$ vibration. Upon formation of the Pd-AMP complex, the $-PO_3^{2-}$ band is split, with a new band appearing as a doublet in the 1160–1190 range. The splitting of the degenerate $-PO_3^{2-}$ band is indicative of a lowering of the symmetry of the phosphate group and may be taken as direct evidence for palladium coordination to it [25, 26].

The ^{31}P NMR spectra also suggest the participation of the phosphate group in coordination to palladium. Thus the resonance of the $-PO_3^{2-}$ (pH = 8.80) appears as a singlet at −5.90 ppm relative to 85% phosphoric acid. This band is shifted to −7.00 ppm in the complex {Pd(O-Mecys)(AMP)}Na, while in the fully protonated group $-PO_3H_2$ (pH = 2) the same resonance appears at −11.00 ppm. This intermediate resonance value of the phosphate group may indicate its coordination to palladium.

Therefore, in the complex {Pd(O-Mecys)(AMP)}-Na, the nucleotide AMP acts as a bidentate ligand through its phosphate group and N(7) atom, most likely in a chelate form (Structure V):



Structure (V)

Experimental

The dimeric complex {Pd(O-Mecys)Cl}$_2$ was prepared according to the literature [1]. All other chemicals were obtained from Fluka A.G. The experimental techniques have been described previously [27].

Preparation of the Complexes {Pd(O-Mecys)(Nucl)-Cl} (Nucl = Ino, Guo, Ado, Cyd)

1 mmol of the dimeric complex {Pd(O-Mecys)-Cl}$_2$ and 2 mmol of the respective nucleoside were suspended in 3 ml dmso-d_6 and stirred at 37 °C until complete dissolution was effected. At this instant the ^1H NMR spectra indicated the presence of only one species in the solution and complexes were precipitated with excess isopropanol: ether (1:2). The yield was in the range of 85–90%.

Preparation of the Complexes {Pd(O-Mecys)(Nucl-H^+)} (Nucl = Ino, or Guo)

(a) 1 mmol of each of the complexes [Pd(O-Mecys)(Nucl)Cl] was suspended in 25 ml water and stirred for 2 hrs. The pH of the mixture was adjusted to about 5 with 0.5 *N* KOH and the precipitated complex was filtered, washed with water,

ethanol and ether and dried at 80 °C under vacuum. The yield was in the range 80–90%. (b) 1 mmol of the dimeric complex $\{Pd(O\text{-}Mecys)Cl\}_2$, and 2 mmol of the respective nucleoside were suspended in 100 ml water and stirred at 60 °C for 2 hrs. The pH of the mixture was adjusted to about 5 with 0.5 *N* KOH and the precipitated complex was filtered, washed with water, ethanol and ether and dried at 80 °C under vacuum. The yield was about 85%.

Preparation of the Complex {Pd(O-Mecys)(AMP)}Na

1 mmol of the dimeric complex $\{Pd(O\text{-}Mecys)Cl\}_2$ and 2 mmol of AMP-Na_2 were suspended in 10 ml water and stirred at 55 °C until complete dissolution occurred. The complex was then precipitated with excess ethanol, washed with 80% ethanol until free from chloride, then with absolute ethanol and ether, and dried at 60 °C under vacuum. The yield was about 50%.

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