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CIRCULAR DICHROISM STUDY OF PALLADIUM(II) COMPLEXES WITH SOME OPTICALLY ACTIVE POLYACIDS

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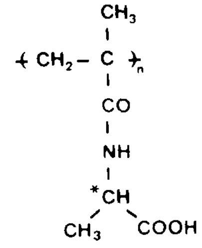
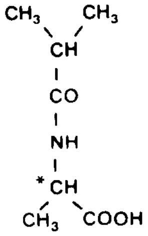
Abstract—The complexes formed between palladium(II) and a series of polymers and model molecules derived from alanine, aspartic acid and glutamic acid have been investigated by electronic absorption and circular dichroism. It has been concluded that 1 N and 2 N optically active species are formed with participation of the carboxylate and the amide group (five membered chelate ring). In most cases the 1 N complex is the major species, except for the polymer and model molecule derived from alanine where the 2 N complex can form at high pH. With the polymers, the complexes become optically inactive at high pH when the carboxylate–palladium bonds are hydrolyzed.

INTRODUCTION

Previous papers [1, 2] reported the study of copper(II) complexes of an optically active polyacid derived from alanine, poly (*N*-methacryloyl-L-alanine) (PNMA) (I).



(I) PNMA



(II) NIBA

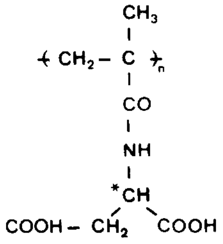
The complexing properties of the model molecule of PNMA, *N*-isobutyroyl-L-alanine (NIBA) (II), were also investigated in order to demonstrate the role of the macromolecular chain in the process of complex formation. It was shown that NIBA forms only a weak 1:1 ligand/metal complex through the carboxyl group.

On the contrary, PNMA forms a series of complexes depending on pH. Some of these complexes involve the deprotonation of the amide group with formation of 2:1 ligand–metal species between two side chains of the polymer (two metal–nitrogen bonds).

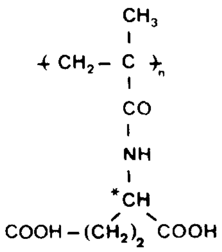
It is well known that the ability to deprotonate the amide group decreases in the following order:

Pd(II) > Cu(II) > Ni(II) > Co(II)

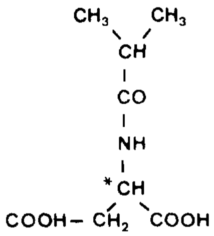
In peptides, for example, the amide is deprotonated by Pd(II) as early as pH 2.5 compared to pH 5 for Cu(II) [3]. Thus, it seemed interesting to investigate the palladium complexes of PNMA and polymers similar to PNMA. For this purpose, polymers derived from aspartic acid [poly(*N*-methacryloyl-L-aspartic acid) (PNMAS) (III)] and glutamic acid [poly(*N*-methacryloyl-L-glutamic acid) (PNMG) (IV)] were synthesized as well as the corresponding model molecules, *N*-isobutyroyl-L-aspartic acid (NIBAS) (V) and *N*-isobutyroyl-L-glutamic acid (NIBAG) (VI).



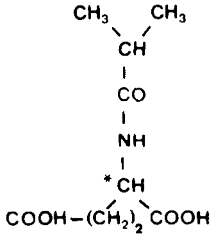
(III) PNMAS



(IV) PNMG



(V) NIBAS



(VI) NIBAG

The complexes formed by compounds **I** to **VI** with palladium(II) were studied by electronic absorption in the visible and u.v. range and by circular dichroism.

EXPERIMENTAL

Samples

N-methacryloyl-L-alanine was prepared from methacryloyl chloride and L-alanine according to the method of Kulkarni and Morawetz [4] (m.p. 130°C; $[\alpha]^{20}_{546}$ −41° in water). *N*-methacryloyl-L-aspartic acid (m.p. ~130°C dec.; $[\alpha]^{20}_{546}$ +1.1° in methanol) and *N*-methacryloyl-L-glutamic acid (m.p. 125°C; $[\alpha]^{20}_{546}$ −25.8 in water) were prepared in the same way using aspartic and glutamic acid respectively.

The model molecules (**II**, **V** and **VI**) were obtained from isobutyroyl chloride and the corresponding amino-acid [NIBA (**II**) m.p. 154°C; $[\alpha]^{20}_{546}$ −59° in water; NIBAS (**V**) m.p. 137°C; $[\alpha]^{20}_{546}$ −10.1° in water; NIBAG (**VI**) m.p. 121°C; $[\alpha]^{20}_{546}$ −23.4 in water). Monomers and model molecules were purified by recrystallization from ethyl acetate.

Polymers **I**, **III**, **IV** were obtained from the corresponding monomer by radical polymerization in dioxane initiated by AIBN, at 65°C PNMA (**I**) $[\alpha]^{20}_{546}$ −42° in water; PNMAS (**III**] $[\alpha]^{20}_{546}$ +4.1° in methanol; PNMG (**IV**) $[\alpha]^{20}_{546}$ −20.9 in water). Polymers were extensively dialyed against methanol and water and then recovered by freeze drying.

Compounds **I**–**VI** were also characterized by i.r. and NMR spectroscopies. They were also acid base titrated and some of them were found to contain significant amounts of water (2–5 wt %) even after freeze-drying. Thus, the samples were kept in a desiccator and the exact concentrations of stock solutions were determined by potentiometry. Potassium tetrachloropalladate K_2PdCl_4 was used for the preparation of palladium solutions.

METHODS

Absorption spectra were recorded at room temperature with a Cary 118 spectrophotometer. The molar extinction coefficient ϵ expressed in $l\ mol^{-1}\,cm^{-1}$ refers to palladium for $\lambda > 300$ nm and to the ligand for the u.v. range (200–300 nm). C.D. spectra were recorded at room temperature with a Jobin–Yvon Mark III dichrograph flushed with dry N_2. As for ϵ, the dichroïc signal $\Delta\epsilon$ refers to palladium or ligand depending on the wavelength range. Solutions with molar ratio R ([ligand]/[Pd]) ranging from 1 to 8 were investigated.

RESULTS AND DISCUSSION

Complexes of palladium are square planar with a D_{4h} symmetry. No apical interaction exists unlike copper for example [3, 5]. They exhibit *d–d* transitions due to the metal and charge transfer transitions between the ligand and the metal.

d–d Transitions are usually observed in the 300–500 nm range. Solutions of $PdCl_4^{2-}$ for example have absorption bands between 380 and 470 nm with low (100–250 $l\,mol^{-1}\,cm^{-1}$) ϵ values [6, 7]. The replacement of Cl^- by higher field ligands decreases the wavelength of the electronic transitions (increases the energy) with the following order of increasing field strength [8]:

$$Cl^- < H_2O, OH^- < COO^- < NH_2 < N\ \text{peptide} \quad (1)$$

d–d Transitions of palladium are often overlapped by intraligand and charge transfer transitions with much higher ϵ values.

Charge-transfer transitions in complexes of palladium are of high energy compared to those of nickel and copper and most of the corresponding wavelengths are in the inaccessible range ($\lambda < 190$ nm) [9, 10]. Only the lower field strength ligands such as Cl^-, H_2O, OH^- give charge transfer transitions with $\lambda > 200$ nm.

COMPLEXES OF Pd(II) WITH NIBA, NIBAG AND NIBAS

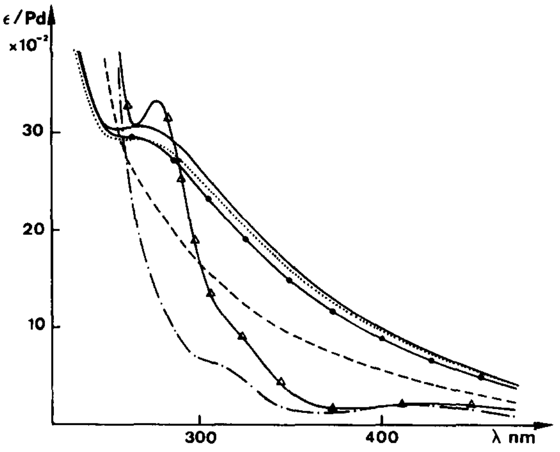


Fig. 1. Absorption spectra of NIBA–Pd ($R = 2$) as a function of pH (—△—) 2.25; (—·—) 4.08; (---) 5.09; (—●—) 6.2; (——) 9.7; (······) 12.2.

The absorption spectra of NIBA–Pd ($R = 2$) between pH 2 and 4 are close to that of $PdCl_4^{2-}$ with a band near 420 nm (ϵ = 180–220 $l\,mol^{-1}\,cm^{-1}$) attributed to the A transition ($d_{xy}\rightarrow d_x2 - {}_y2$) and a shoulder around 310 nm (ϵ = 500–1000 $l\cdot mol^{-1}\cdot cm^{-1}$) attributed to the E transition ($d_{xz,yz}\rightarrow d_x2_{-y}2$) (Fig. 1). Intense charge transfer transition bands appear at 280 nm (π $Cl^-\rightarrow 3d_x2_{-y}2$) and 237 nm ($\sigma$ $Cl^-\rightarrow d_x2_{-y}2$, not shown in Fig. 1). Upon increase of pH, the absorption due to the charge transfer transitions decreases and ϵ increases for the *d–d* transitions, indicating the exchange of Cl^- with higher field ligands. At high pH, only one large band is observed at 270 nm, overlapping all the transitions. Figure 2 shows the dichroïc spectra for $R = 1$. A low pH, the complex is optically active as soon as pH 4 is reached. The negative band at 390 nm and the positive one at 330 nm are typical of the A and E transitions of a 1 N complex (one nitrogen, one carboxylate) [11]. The shoulder at 315 nm indicates a small contribution of a 2 N complex (E transition) [5, 12–15]. As pH increases, the intensity of the two bands decreases and a red shift is observed indicating that the 1 N complex become predominant. A large weak positive band appears near 450 nm, attributed to a singlet triplet transition for *N*-methylalanine [12].

For a higher [ligand]/[metal] ratio ($R = 8$, Fig. 3), a large negative and a positive band are observed at 400 and 350 nm assigned to the A and E transitions

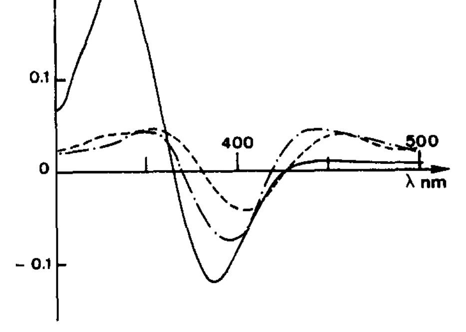


Fig. 2. C.D. spectra of NIBA–Pd ($R = 1$) vs pH: (——) 4.03; (---) 6.89; (—·—) 8.87.

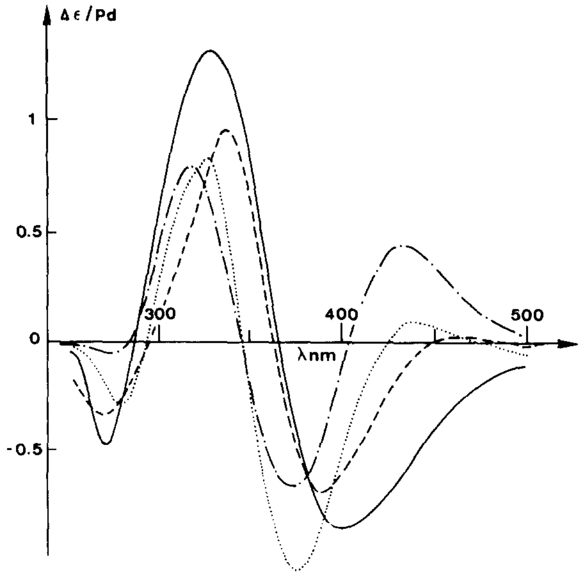
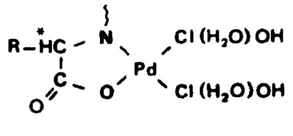
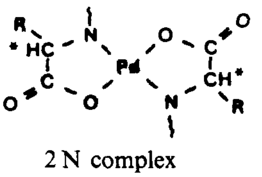


Fig. 3. C.D. spectra of NIBA–Pd ($R = 8$) as a function of pH: (——) 4.35; (—·—) 6.27; (······) 7.78; (---) 11.2.

of a 1 N complex. As pH increases (pH 6–7), the C.D. spectrum becomes typical of a 2 N complex which is favoured by the high R value [5, 9, 12, 16] ($\lambda = 375$ and 328 nm). At very high pH, a slight red shift is observed for the A and E transitions ($\lambda = 388$ and 337 nm). This may be attributed to the breaking of the Pd–COO bonding with replacement of COO^- by OH^- [3, 13, 17–20]. In this case, NIBA would act as a monodentate ligand and optical activity would result from a vicinal effect.

From the above results, we may assume that the following NIBA–Pd(II) complexes are present in the intermediate pH range:





1 N complex	2 N complex
R = $-CH_3$	NIBA
R = $-(CH_2)_2$–COOH	NIBAG
R = $-(CH_2)$–COOH	NIBAS

The 2 N complex is favoured with high R values.

Figure 4 gives the C.D. spectra of NIBAG–Pd(II) complexes at $R = 1$. The spectra are very complicated but the blue shift and increase of the 430 nm band between pH 3.9 and 6.9 suggest the replacement of Cl^- by H_2O and OH^- in a 1 N complex as for NIBL. Simultaneously the features of the spectra between 300 and 400 nm support the intermediate existence of a mixture of 1 N and 2 N complexes.

When the γ carboxyl group ionizes, strong electrostatic repulsions occur between the two carboxylate groups and the 2 N complex disappears. At high pH the C.D. spectrum is typical of a pure 1 N complex with a negative band at 390 nm (A transition) and a positive one at 340 nm (E transition).

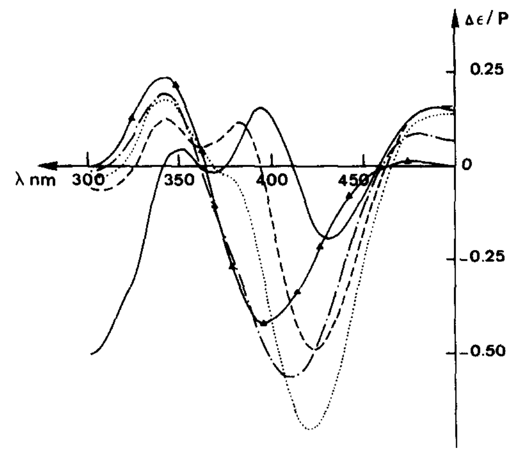
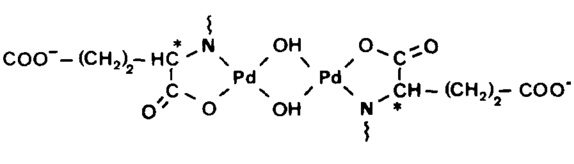


Fig. 4. C.D. spectra of NIBAG–Pd ($R = 1$) as a function of pH: (——) 3.9; (---) 5.9; (······) 6.9; (—·—) 8.9; (—▲—) 11.1.

The formation of a dimeric species is also likely to occur [21]:



Even at higher R values ($R = 2$ or 8) where the 2 N complex should be favoured, the spectra at high pH are typical of a 1 N complex.

In the NIBAS–Pd(II) system at $R = 8$ (Fig. 5), spectra at low pH are typical of a 1 N complex with a positive and negative bands at 390 and 330–350 nm. At higher pH the signs of these band is changed in relation with the ionization of the β carboxyl group which is close to the asymmetric carbon, but the wavelengths remain typical of the A and E transitions of a 1 N complex even for $R = 8$.

Thus, from the study of the complexes of NIBA, NIBAG and NIBAS with Pd(II), it may be concluded

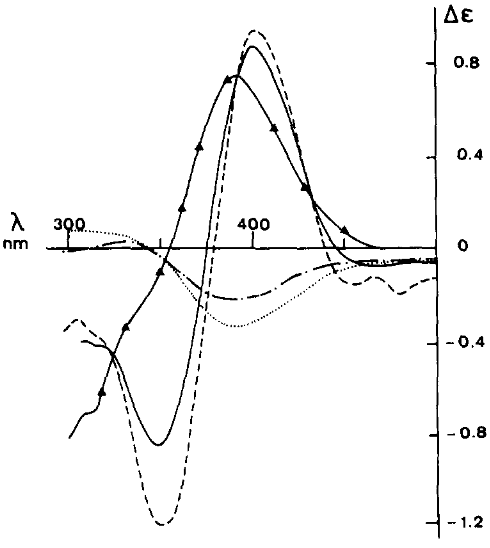


Fig. 5. C.D. spectra of NIBAS–Pd ($R = 8$) as a function of pH: (—▲—) 4; (——) 5.1; (---) 6.1; (······) 8.9; (—●—) 11.0.

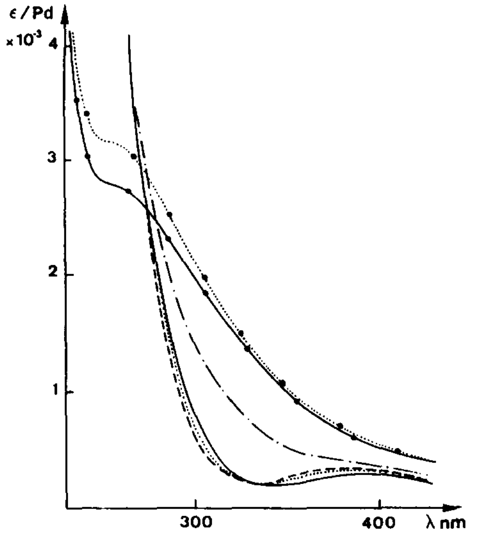


Fig. 6. Absorption spectra of PNMA–Pd ($R = 8$) as a function of pH (——) 3.18; (– – –) 3.85; (·····) 4.71; (—·—) 8.59; (··●··) 11.08; (—●—) 12.22.

that 1 N complexes are always formed even at high R values except for NIBA where a 2 N complex exists at high pH. For NIBAG and NIBAS, the non-existence of a 2 N complex may be ascribed to electrostatic repulsions between the γ or β carboxylates groups (the net charge of such a complex would be −4).

COMPLEXES OF Pd(II) WITH PNMA, PNMG AND PNMAS

In these systems, the absorption spectra between 200 and 400 nm for $R = 1$, 2 or 8 are very similar. Figure 6 (PNMA–Pd(II)) shows the same changes as for NIBA–Pd(II) (Fig. 1) on increasing the pH. The shoulder which appears near 270 nm with a high ε value may be assigned to the $OH^- \rightarrow Pd(II)$ charge transfer transition [22].

Figure 7 shows typical C.D. spectra of the PNMA–Pd(II) mixture ($R = 8$). As pH is raised, the negative band at 430 nm is replaced by a more intense negative band at 370 nm. These bands are ascribed to the A–E transitions of the 1 N and 2 N complexes. The A and E transitions are not well resolved, typical of *cis* complexes [16, 22, 23].

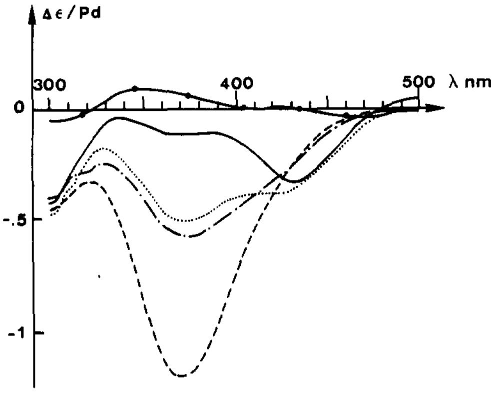


Fig. 7. C.D. spectra of PNMA–Pd ($R = 8$) as a function of pH: (——) 3.5; (······) 4.6; (– – –) 6.2; (—·—) 8.7; (—●—) 11.4.

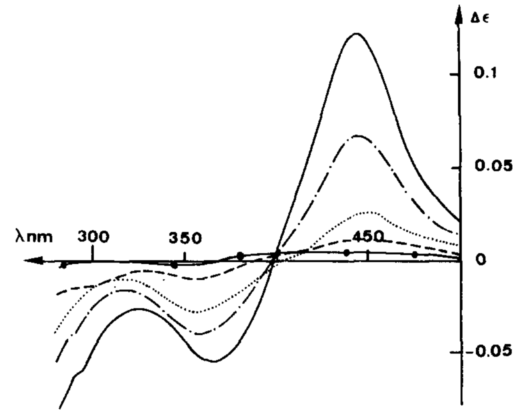
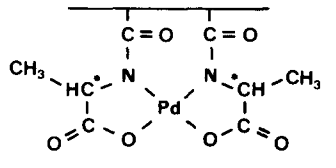
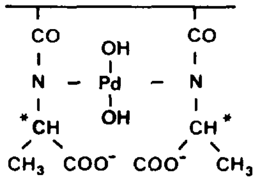


Fig. 8. C.D. spectra of PNMG–Pd ($R = 8$) as a function of pH (——) 4.3; (—·—) 6.0; (······) 7.1; (– – –) 9.5; (—●—) 11.0.



Above pH 6.2, the optical activity decreases and disappears above pH 10. This is related to the hydrolysis of the COO–Pd bonds. This effect was also observed for other palladium [24, 25] and copper(II) complexes.



In the PNMG–Pd(II) system ($R = 8$) (Fig. 8), both 1 N and 2 N complexes exist in the intermediate pH range and become optically inactive as pH increases. At pH about 6, the amount of 2 N complex ($\lambda = 365$ nm) is lower than in the PNMA–Pd(II) system, very probably because of the additional electrostatic repulsions between the γ carboxylate groups. Similar results were obtained for PNMG–Pd(II) at lower R values (1 and 2) and for PNMAS–Pd(II) at $R = 8$, 2 and 1.

From the study of the complexes of palladium with the three polymers and their model molecules, the following conclusions may be drawn.

(i) In all cases, optical activity appears at rather low pH (3–4) and results from the formation of five membered chelates involving the α carboxyl group and the nitrogen of the amide group (with copper no chelate is formed for model molecules [2]). This is caused by the strong ability of palladium to deprotonate the amide group.

(ii) With model molecules, the 1 N complex is always favoured except with NIBA in which electrostatic repulsions are less important and allow the formation of a 2 N complex at high pH.

(iii) With PNMA, the 2 N complex is favoured for the same reason. In addition the vicinity of two ligands on the polymer chain is also favourable and gives a 2 N *cis* complex. With PNMG and PNMAS, the formation of the 2 N complex is more difficult and a mixture of 1 N and 2 N is observed even at high *R* values which should favour the 2 N species.

(iv) A high pH, the complexes formed with the three polymers become optically inactive when the COO–Pd bonds are hydrolyzed.

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