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π-ALLYLPALLADIUM(II) COMPLEXES OF AMINO ACIDS

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SUMMARY

Novel π-allylpalladium(II) complexes with amino acid anions as bidentate chelating ligands were prepared, characterized and investigated by means of IR, NMR and X-ray diffraction techniques. Single crystal X-ray analysis of (π-2-methylallyl)(glycinato)palladium(II) has been carried out: Cu–K_α radiation, monoclinic, space group $P2_1/c$, $a=12.03(1)$, $b=12.85(1)$, $c=10.86(1)$ Å, $\beta=103°50'(10')$, $Z=8$. The only relevant difference between the two independent molecules in the unit cell was found in the conformation of the glycinato moiety which appears twisted in one molecule and essentially planar in the other.

INTRODUCTION

Several examples of π-allyl complexes of palladium(II) and nickel(II) with bidentate chelating agents have been reported in the literature in recent years[1]. The reaction of bridged $(\pi\text{-allyl–M–X})_2$ complexes with the anion of a bidentate chelating agent may result in monomeric products as in the case of acetylacetonato[2] and Schiff bases[3] complexes or of bridged dimeric products such as $(\pi\text{-allyl–M–carboxylate})_2$[4] complexes. To the latter class belong the bis[(π-allyl)nickel haloacetates] which catalyse the stereospecific polymerization of dienes[5]. We considered it worthwhile to synthesize and to investigate the solid state and solution structure of some π-allyl complexes of Pd^{II} with amino acid anions as potentially bidentate chelating agents. To the best of our knowledge the only examples in the literature of transition metal complexes containing both an amino acid anion and coordinated insaturated hydrocarbon are the monochloro(amino acidato)(olefin)platinum(II) compounds previously reported by us[6] and by Nakamoto *et al.*[7].

RESULTS AND DISCUSSION

Complexes of stoichiometry (π-allyl)PdAA (AA = glycinato, (D,L)-β-phenylalaninato anions etc.) were prepared by treating a solution or a suspension of the

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TABLE 1

ANALYTICAL AND INFRARED DATA[a]

Compound		*Analysis found (calcd.) (%)*			*Dec. (°C)*	*IR*		
		C	*H*	*N*		$\nu(COO)_s$	$\nu(COO)_{as}$	$\delta(NH_2)$
(I)	(π-2-Methylallyl)-(glycinato) palladium (II)	30.59 (30.63)	4.76 (4.68)	6.11 (5.95)	140	1380	1595	1613
(II)	(π-2-Methylallyl)-(*N*,*N*-dimethylglycinato)-palladium (II)	36.28 (36.50)	5.63 (5.70)	5.33 (5.32)	135	1382	1628	
(III)	(π-2-Methylallyl)-[(D,L)-β-phenylalaninato]-palladium (II)	47.79 (48.00)	5.38 (5.23)	4.44 (4.31)	140	1388	1607	≈1610
(IV)	(π-1-Phenylallyl)-(glycinato)palladium (II)	44.25 (44.44)	4.52 (4.41)	4.87 (4.71)	145–150	1389	1605	1620

[a] IR spectra were obtained using the KBr disk method.

appropriate $[(\pi\text{-allyl})PdCl]_2$ compound in acetone with the potassium salt of the amino acid dissolved in a minimum quantity of methanol:

$$[(\pi\text{-allyl})PdCl]_2 + 2K^+AA^- \rightarrow 2\,(\pi\text{-allyl})Pd(AA) + 2KCl\downarrow$$

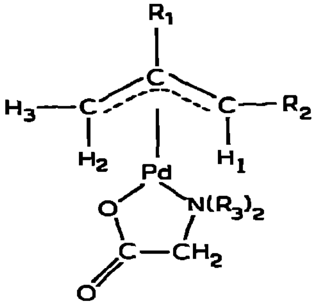
The complexes, prepared as white or pale yellow crystalline solids, are listed in Table 1 together with their elemental analyses, decomposition points and most relevant infrared data. All the complexes are sparingly soluble in ethanol and almost insoluble in common organic solvents excepting complex (II) which is readily soluble in polar organic solvents. It is noteworthy that compounds (I) and (II) are readily water-soluble, and are monomeric in solution as revealed by molecular weight determinations of (I) in water and ethanol.

The amino acid moiety may be easily removed by reaction with acids (*e.g.* HCl) or with excess of anions such as I^-, SCN^-, etc. regenerating the $[(\pi\text{-allyl})PdX]_2$ bridged complexes.

The NMR data reported in Table 2 confirm the presence of one amino acid group for each π-allyl unit. With complexes (I) and (II), both the *syn* and *anti* protons of the π-2-methylallyl group give rise to a single resonance indicating fast exchange in solution on the NMR time scale, between the amine and the carboxylate group at the respective coordination sites. We did not investigate the mechanism of exchange, but on the basis of previous NMR studies on π-allyl systems[8] it is conceivable that a bimolecular mechanism, probably accompanied by ligand transfer, is responsible for the above averaging. The same behaviour was observed for complex (IV); in addition, the phenyl ring was found to be *syn* with respect to the central proton of the allyl moiety as expected on the basis of previous NMR investigations on (π-1-phenylallyl)aminochloropalladium complexes[9].

The infrared spectra show two strong absorptions at 1595–1630 and 1380 cm^{-1} assigned to asymmetric and symmetric stretching vibrations of a coordinated carboxylate group. A comparison of literature data[10] on the transition metal–amino acid complexes, revealed a lowering of 20–40 wavenumbers within our complexes

TABLE 2



NMR DATA FOR (π-ALLYL)(AMINO ACIDATO)PALLADIUM(II) COMPLEXES[a,b]

Compound	*Solvent*	*Chemical shift, τ*						
		H_1	H_2	H_3	CH_2	R_1	R_2	R_3
(I) R_1=CH_3; R_2, R_3=H	D_2O	7.23	7.23	6.54	6.23	7.93	6.54	
(II) R_1, R_3=CH_3; R_2=H	D_2O	7.15	7.15	6.69	6.29	7.88	6.69	7.26
(IV) R_1, R_3=H; R_2=C_6H_5[c]	CD_3OD	5.44	7.02	6.08	[d]	4.03	2.5–2.7	

[a] TMS or DSS was used as internal standard and lock signal. [b](III) is not sufficiently soluble for NMR spectroscopy. [c] $J(H_1, R_1)$ 11.5, $J(H_2, R_1)$ 12.0, $J(H_3, R_1)$ 7.0±0.5 Hz. [d] The resonance is obscured by the solvent methyl resonance.

for the asymmetrical stretch of the CO_2 group.

The crystal structure of the (π-2-methylallyl)(glycinato)palladium(II) complex has been elucidated by X-ray analysis. Crystals of suitable size were obtained from an ethanol solution; they belong to the monoclinic system, space group $P2_1/c$ with $a = 12.03(1)$, $b = 12.85(1)$, $c = 10.86(1)$ Å and $\beta = 103°\ 50'\ (10)$ and $Z = 8$ which imposes that the independent unit contains two formula units $C_6H_{11}NO_2Pd$. The density, calculated on the basis of 8 formula units in the unit cell, ($d_{\text{calcd.}}$ 1.90 g/cm^3) agrees well with the experimental ($d_{\text{exp.}}$ 1.90 g/cm^3). 1900 Independent non-zero reflections were collected with an automated diffractometer using the Cu–K_α radiation. The structure was solved by the Patterson method. The heaviest interatomic vectors were interpreted and, accordingly, the positions of the two independent palladium atoms were derived. The Fourier map, calculated by phasing the reflections with only these two atoms, revealed the remaining atoms present in the structure excepting the hydrogen atoms. Subsequently the refinement was achieved by means of six cycles of 9×9 block diagonal least-squares procedure until the maximum shift in the atomic coordinates and anisotropic thermal factors was less than one-third of the corresponding standard deviation. The weighting scheme adopted throughout the refinement corresponds to that suggested by Cruickshank[11]. The atomic scattering factors for all atomic species were calculated from the analytical constants given by Moore[12]. At the end of the refinement, neglecting hydrogen atoms, the disagreement factor:

$$R = \frac{\Sigma \lVert F_o \rvert - \lvert F_c \rVert}{\Sigma \lvert F_o \rvert}$$

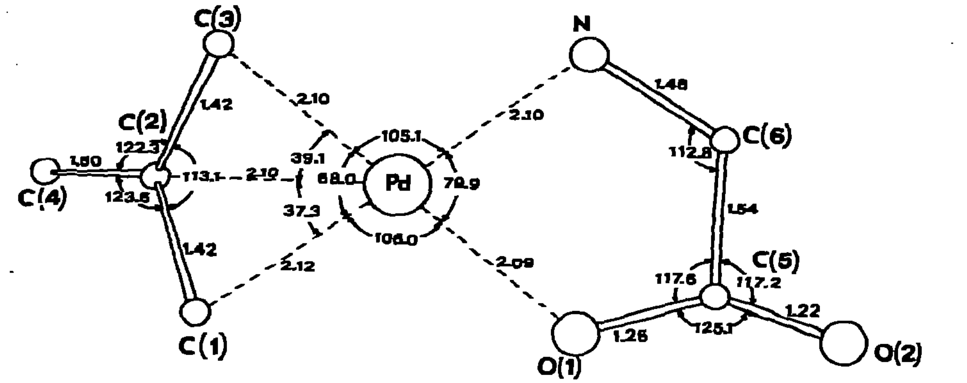


Fig. 1. Molecular geometry averaged over the two crystallographically independent units. The O(1)–Pd–C(3) and C(1)–Pd–N bond angles are 173.2° and 170.5°, respectively.

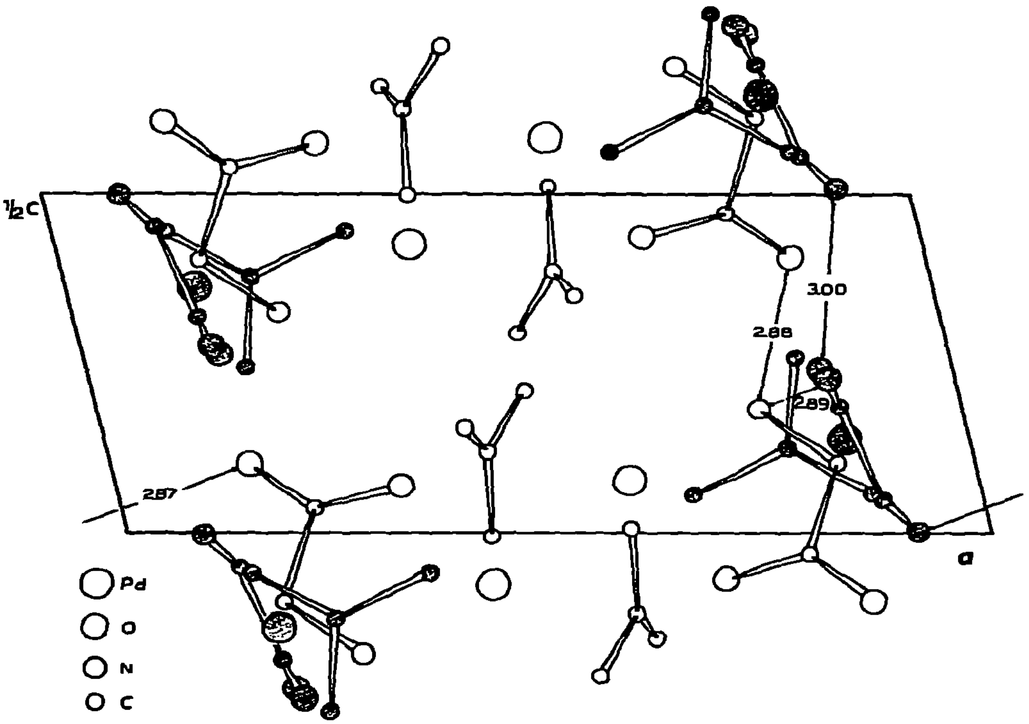


Fig. 2. Molecular packing as viewed along the *b* axis. The four hydrogen bond distances are indicated. The atoms belonging to molecule (b) are shaded.

is 0.059 for the 1900 independent non-zero reflections. Corresponding bond lengths and bond angles of the two molecules in the independent unit cell (Fig. 2) (a and b) are not substantially different; in Fig. 1 the average dimensions of the complex molecule are reported*. Both molecules show a distorted square-planar coordination of the

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* Final atomic coordinates and thermal factors can be obtained upon request from the authors.

ligands around the palladium atoms. Furthermore, the dihedral angle between the plane defined by carbon atoms C(1), C(2) and C(3) and that defined by the palladium, O(1) and the nitrogen atoms is 106° in molecule (a) and 113° in molecule (b) in agreement with corresponding values found and theoretically predicted for other (π-allyl)palladium compounds[14]. The methallyl ligand itself is significantly non-planar, the methyl group being displaced 0.3 and 0.2 Å out of the C(1)–C(2)–C(3) plane towards the palladium atom for molecules (a) and (b) respectively. The two independent amino acid moieties differ slightly from each other: in molecule (a) the chelating amino acid is almost exactly planar [for the five atoms the mean square distance from the best plane is 0.008 Å, with an internal rotation angle* O(1)–C(5)–C(6)–N of −1°], while in molecule (b) the five atoms of the amino acid are not coplanar [the mean square distance is 0.08 Å with an internal rotation angle O(1)–C(5)–C(6)–N of +13°]. In fact, in the α-amino acid complexes, the values of the internal rotation angle around the C(5)–C(6) bond in more than twenty known rings lie between 0° and 30°[15].

The results of the structure are therefore in agreement with the literature data showing in addition that, since in our system the same glycinato group exhibits different conformations, the chelate ring has to be rather flexible and the various conformations observed are probably the result of a balance of interactions between atoms in the same ring and crystal packing forces. As one would expect the bonding of a metal atom to O(1) would increase the length C(5)–O(1) and decrease the length of C(5)–O(2) in keeping with a decrease in the bond order of the first and an increase in that of the second. This trend is indeed verified as shown in the dimensions of the average molecule. (*cf.* Fig. 1).

One additional factor must be taken into account in analyzing the conformation of the chelate ring, that is the hydrogen bond system in the crystal. Each nitrogen atom in the two independent molecules is associated with two hydrogen bonds, as shown in Fig. 2.

In particular the nitrogen atom of molecule (a) forms one hydrogen bond with O(2) of the same molecule reported at $(x, \frac{1}{2}-y, \frac{1}{2}+z-1)$ (2.88 Å) and a second hydrogen bond with O(2) of molecule (b) reported at $\bar{x}+1, \bar{y}, \bar{z}+1$ (2.89 Å). The nitrogen atom of molecule (b) forms a strong hydrogen bond with O(2) of molecule (a) reported at $x+1, y, z$ (2.87 Å) and a weaker bond with O(1) of the same molecule reported at $x, \frac{1}{2}-y, \frac{1}{2}+z-1$ (3.00 Å). Only one of the oxygen atoms. O(1) of molecule (b), is not involved in hydrogen bonding. The shortest intermolecular contacts, neglecting hydrogen bond distances, are the following: C·C, 3.71; C·N, 3.69; C·O, 3.34 and N·O, 3.69 Å.

EXPERIMENTAL

IR spectra were obtained using a Beckman IR-9 spectrophotometer. NMR spectra were run on a Varian Associates HA-100 spectrometer. Elemental analyses were performed by A. Bernhardt Mikroanalytisches Laboratorium, Elbach, W. Germany. An Hitachi–Perkin–Elmer 115 instrument was employed in molecular weight determinations. (π-2-Methylallyl)- and (π-1-phenylallyl)palladium(II) chloride complexes were prepared according to the method of Dent *et al.*[16].

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* *trans* Conformation = 180°.

Preparation of (π-methylallyl) (glycinato)palladium(II)

To a stirred solution of 1.97 g (10 mmol) of $(C_4H_7PdCl)_2$ in 100 ml of acetone was added dropwise at room temperature a solution of potassium glycinate 1.13 g. (10 mmol) in 15 ml of methanol.

During the addition the yellow solution became colourless. After 1 h of additional stirring the white precipitate of KCl was filtered off and solvent was removed *in vacuo*. The residue was washed with CH_2Cl_2 to remove traces of unreacted $(C_4H_7$-$PdCl)_2$ and then recrystallized from ethanol to give colourless plates (yield 87%). Mol. wt.: 233 (water), 236 (ethanol); calcd.: 235. Similarly were prepared the complexes *(π-2-methylallyl)[(D,L)-β-phenylalaninato]palladium(II)* (85%), white powder from ethanol; *(π-1-phenylallyl)(glycinato)palladium(II)* (78%), pale yellow powder from ethanol/diethyl ether; *(π-2-methylallyl)(N,N-dimethylglycinato)palladium(II)*, very pale yellow needles from acetone/hexane (68%). All complexes decompose in air in the range of 135–150°.

Reactions of (π-2-methylallyl)(glycinato) palladium(II) with KI, HCl, KSCN

To a suspension of (π-2-methylallyl)(glycinato)palladium(II) in chloroform was added a saturated aqueous solution of the appropriate inorganic reactant, with stirring. The bridged $[(\pi\text{-2-methylallyl})\text{-}Pd^{II}X]_2$ complexes were obtained from the chloroform phase by evaporating solvent and recrystallizing the residue from a toluene/diethyl ether mixture.

(Found: C, 16.72; H, 2.41. $C_8H_{14}Pd_2I_2$ calcd.: C, 16.67; H, 2.42%.)

(Found: C, 24.23; H, 3.41. $C_8H_{14}Pd_2Cl_2$ calcd.: C, 24.49; H, 3.57%.)

(Found: C, 27.47; H, 3.30; N, 6.4. $C_{10}H_{14}Pd_2S_2N_2$ calcd.: C, 27.40; H, 3.19; N, 6.30%.)

X-RAY DATA AND INTENSITY COLLECTION

Approximate unit-cell parameters and systematic extinctions were obtained from zero and upper level Weissenberg's photographs. Precise lattice constants and their estimated standard deviations were determined from a least-squares refinement[17] of the setting angles of twelve high angle reflections on a Siemens AED automatic diffractometer with Cu–K_α radiation ($\lambda = 1.5418$ Å) at 25±3°. For the intensity measurements Ni-filtered Cu–K_α radiation was used. A crystal was mounted on a Siemens AED automatic single crystal diffractometer equipped with a PDP-8 digital computer, a scintillation counter and pulse-height analyser. The $\theta - 2\theta$ scan mode was employed with the five value measurements technique[18]. A fixed symmetrical scan range of 0.65° from the computed Cu–K_α peak was used. Intensity data were collected for the independent reflections up to $\theta = 60°$. A standard reflection was measured at regular intervals to monitor crystal stability and crystal orientation. Its intensity remained essentially constant throughout the run. A total of 1900 non-zero independent reflections [their values being greater than $2\sigma(I)$] was collected and their intensities were corrected for Lorentz and polarization effects in the usual way; no absorption correction was applied.

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