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MIXED COMPLEX COMBINATIONS OF Pd(II) WITH α-AMINO ACIDS

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The present work deals with the synthesis of eight mixed complex combinations of Pd(II) with different α-amino acids. In order to prove the coordination of the ligands to the Pd(II) ion and to establish the structure of the prepared compounds, chemical analyses and physicochemical studies (IR spectra and thermogravimetric analysis) were performed.

The possibility of obtaining mixed chelate compounds of Pt(II) with α-amino acids is indicated in the literature [1, 2]. The analogy between Pd(II) and Pt(II) in their behaviour toward amino acids prompted us to attempt the synthesis and physicochemical characterization of mixed chelate compounds of Pd(II) with these ligands and some related derivatives. Compounds of the general formula $K[PdLCl_2]$ were used as starting materials for these synthesis. These compounds were treated with another amino acid. The reaction can be written

$$K[PdLCl_2] + L'H \rightarrow [PdLL'] + KCl + HCl \qquad (1)$$

where L = alanine (Ala), proline (Pro), L' = valine (Val), glycine (Gly), proline (Pro).

The *trans* isomers of the chelates were obtained from these interactions. This led us to assume that the amino group of the L'H molecule preferentially replaces the Cl^- ion *trans* to the NH_2 group of the LH ligand in the parent compound.

This is due to the greater *trans* effect of the amino group than that of the carboxyl group.

Experimental

The $K[PdAlaCl_2]$ and $K[PdProCl_2]$ complexes obtained previously [3, 4] were used in our syntheses. The molar ratio used was $K[PdLCl_2]$: amino acids = 1:4, with Val, Gly and Pro as L'H ligands. The mixture of two compounds was heated for 4 h in a water-bath, at constant volume. Crystals crystallized out quantitatively from hot solution.

The chemical analyses, reported in Table 1, confirm that mixed chelates of the general form [PdLL'] were obtained.

Table 1 Chemical analysis of the mixed chelate compounds of the Pd(II) with α-amino acids

Compound	Pd, %		N, %	
	Calculated	Found	Calculated	Found
[PdAlaGly]	39.94	39.87	10.42	10.69
[PdAlaVal]	34.32	34.02	9.01	9.00
[PdProVal]	31.6	31.2	8.20	8.60
[PdAlaPro]	34.3	33.9	9.03	8.90

A series of chelate derivatives was prepared by treating the mixed chelates with concentrated HCl (2 ml conc. HCl for 0.4 g substance). Under these conditions, dichlorides of the form $[Pd(LH)(L'H)Cl_2]$ resulted. The dichlorides were treated with aqueous ammonia (2:8), when complex cations of the general form $[Pd(LH)(L'H)(NH_3)_2]^{2+}$ were obtained and separated as violet precipitates (Vauquelin salts) when treated with $K_2[PdCl_4]$.

Four new complex combinations were synthesized in this way:

$$K[PdLCl_2] + L'H \rightarrow [PdLL'] + KCl + HCl$$

$$[PdLL'] + 2\ HCl \rightarrow [Pd(LH)(L'H)Cl_2]$$

$$[Pd(LH)(L'H)Cl_2] + 2\ NH_3 \rightarrow [Pd(LH)(L'H)(NH_3)_2]Cl_2$$

$$[Pd(LH)(L'H)(NH_3)_2]Cl_2 + K_2[PdCl_4] \rightarrow [Pd(LH)(L'H)(NH_3)_2][PdCl_4] + 2\ KCl$$

The chemical analyses performed on the four new complexes (Table 2) confirm these formulae of the compounds.

Table 2 Chemical analysis of the mixed compounds of the α-amino acids

Compound	Pd, %		N, %	
	Calculated	Found	Calculated	Found
$[PdAlaHGlyH(NH_3)_2][PdCl_4]$	38.46	39.09	10.12	10.20
$[PdAlaHValH(NH_3)_2][PdCl_4]$	37.42	37.92	9.41	9.43
$[PdAlaHProH(NH_3)_2][PdCl_4]$	35.9	36.20	9.44	9.32
$[PdProHValH(NH_3)_2][PdCl_4]$	33.9	33.95	8.90	8.82

Results and discussion

In order to elucidate the structures of the mixed chelates and their derivatives, the IR spectra of these compounds and of the free amino acids were recorded and their thermal behaviour too was investigated.

Spectral studies on the complex combinations of the α-amino acids with various metals have led to the conclusion that complexing causes come of the bands in the IR spectra of the free amino acids to disappear, while others undergo considerable shifts. This is the case for the valence vibrations of the COO^- and NH_2 groups. The literature data [5–9] allow conclusions as to the coordination of the ligands to the central metal ion from the modifications in the IR spectra.

The vibration frequencies of the carboxyl group, ν_{COO^-}, and their separations as compared with those found for crystalline CH_3COONa and free amino acids, offer an interesting field for investigation. Nakamoto et al. [8] observed that, as a result of complexing, the ν_{COO^-} *antisymmetric peaks shift toward greater frequencies, whereas* the symmetric ones shift towards lower frequencies as the covalent character of the bond increases. This seems plausible, as an increase of the covalent character leads to more asymmetric structure of the carboxyl group, as revealed by an increase in the separation between these two carboxyl bands. Appreciable shifts of the ν_{COO^-} antisymmetric and ν_{COO^-} symmetric frequencies and large $\Delta\nu_{COO^-}$ differences as compared with those for the free ligands were found for the chelate compounds we prepared.

This led us to assume that in our chelates M–O bonds are formed, showing a strong covalent character in accordance with the position of Pd(II) in the Irving–Williams series.

The coordination of the amino acids to the central metal ion was also checked by observing the shift in the valence vibration of the amino group.

Quagliano [10] and others [11, 12] ascribe the band in the 3000 cm^{-1} region to the stretching vibration ν_{NH_2}. The shifts of these bands to lower frequencies in the chelates we prepared as compared with the sodium salt show the presence of the M–N bond. On the other hand, Condrate and Nakamoto [13] ascribe the bands in the 3360 cm^{-1} region to the ν_{NH_2} antisymmetric vibration and those in the 3260 cm^{-1} region to the ν_{NH_2} symmetric one.

*The modifications observed in the IR spectra of the complex compounds as com*pared with those of the free ligands (Table 3) indicate that the Pd(II) is bonded to the α-amino acids via COO^- and NH_2 groups.

Table 3 IR spectra of mixed chelates of Pd(II) with α-amino acids

GlyH	AlaH	ValH	ProH	[PdAlaGly]	[PdAlaVal]	[PdAlaPro]	[PdProVal]	Bands attribution
3360	3410	3430	3400	3420	3418	3415	3420	ν_{HN_2} antisymmetric
3260	3090	3100	3020	3220	3240	3100	3240	ν_{NH_2} symmetric
				3120	3100		3130	
1595	1597	1595	1560	1618	1625	1630	1650	ν_{COO^-} antisymmetric
1411	1418	1415	1450	1360	1360	1370	1360	ν_{COO^-} symmetric
184	179	180	110	258	255	270	290	$\Delta\nu_{COO^-}$

A thermogravimetric analysis of the complex compounds was performed to obtain information about the composition proposed from the analytical data, and also data relating to the structure – thermal stability dependence.

The thermogravimetric analysis was performed under dynamic temperature conditions with a MOM derivatograph.

The recordings were made in air at a heating rate of 12 degree min^{-1}, with aluminium oxide ignited at 1000° as reference.

The recorded curves suggest a one-stage or multistage degradation, depending on the complex combination used.

The DTG curves in Fig. 1 indicate two degradation stages for the complex [PdLL′] where LL′ = Ala + Gly, and three degradation stages for LL′ = Ala + Pro. The presence of Val leads to a one-stage degradation.

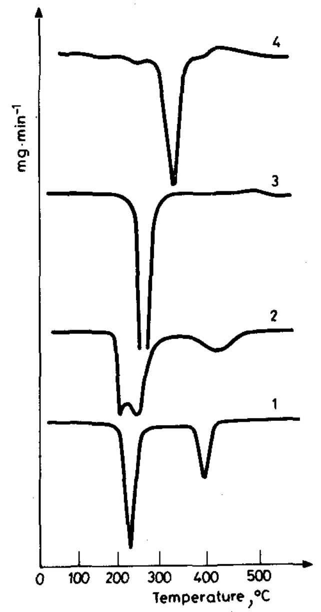

Fig. 1 DTG curves for some Pd(II) – α-amino acid mixed complexes inregistrated with a heating rate of 12 degree/min.
1 – [PdAlaGly], 2 – [PdAlaPro], 3 – [PdAlaVal], 4 – [PdAlaHValH$(NH_3)_2$][$PdCl_4$]

The complexes [Pd(LH)(L′H)$(NH_3)_2$][$PdCl_4$] degrade predominantly in one stage too.

The thermogravimetric characteristics (Table 4) confirm the chemical structure proposed from the analytical data and the IR spectra.

Analysis of the initiation temperatures for the degradation process suggests the influence of the structure complexity and the nature of the ligands on the thermal stability.

Table 4 Thermogravimetric characteristics of mixed complex combinations of Pd(II) with α-amino acids

Complex combination	Temperature range, °C	Residue, %		
		Compound	Calculated	Found
[Pd(AlaGly)]	160–450	Pd	39.68	38.02
[PdAlaVal]	200–340	Pd	34.31	32.91
[PdAlaPro]	200–480	Pd	34.31	32.80
[PdProVal]	190–320	Pd	31.50	30.25
$[PdAlaHGlyH(NH_3)_2][PdCl_4]$	100–370	$PdO + PdCl_2$	55.29	53.52
$[PdAlaHValH(NH_3)_2][PdCl_4]$	150–400	$PdO + PdCl_2$	51.85	50.61
$[PdAlaHProH(NH_3)_2][PdCl_4]$	180–430	$PdO + PdCl_2$	51.28	49.74
$[PdProHValH(NH_3)_2][PdCl_4]$	180–400	$PdO + PdCl_2$	49.19	50.26

The kinetic criterion [14] was selected for a more rigorous characterization of the thermal endurance. For this purpose the data were processed by the Freeman–Carroll method [15], which resulted in the kinetic parameters in Table 5.

The kinetic criterion also confirms the existence of a dependence between the thermal stability and the nature of the ligands.

The following stability series can be established: [PdAlaPro] > [PdAlaVal] > > [PdProVal] > [PdAlaGly]. A similar series concerning the L—L′ pair can also be established for the complexes containing ammonia, but the thermal stabilities of the latter are lower than those of the more simple chelate compounds.

The analytical and kinetic processing of the thermogravimetric data confirmed the structures of the mixed complexes of Pd(II) and the structure – thermal stability dependence.

Table 5 Kinetic characteristics of mixed complex combination of Pd(II) with α-amino acids

Complex combination	Reaction order	E_a, kJ/mol
[PdAlaPro]	0	452
[PdAlaVal]	0	312
[PdProVal]	0.5	240
[PdAlaGly]	1.5	220
$[PdAlaHProH(NH_3)_2][PdCl_4]$	1.0	208
$[PdAlaHValH(NH_3)_2][PdCl_4]$	0.6	184
$[PdProHValH(NH_3)_2][PdCl_4]$	0.6	184
$[PdAlaHGlyH(NH_3)_2][PdCl_4]$	0.6	128

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Zusammenfassung — Die vorliegende Arbeit handelt über die Synthese von 8 Komplexkombinationen von Pd(II) mit verschiedenen α-Aminosäuren. Chemische Analysen und physikalisch-chemische Untersuchungen (IR-Spektroskopie und Thermogravimetrie) wurden ausgeführt, um die Koordination der Liganden am Pd(II)-ion und die Struktur der synthetisierten Verbindungen zu ermitteln.

Резюме — Приведен синтез восьми смешанных комплексов двухвалентного палладия с различными α-аминокислотами. Для доказательства типа координации лигандов и установления структуры полученных комплексов, проведен химический анализ, термогравиметрическое и ИК спектроскопическое исследование.