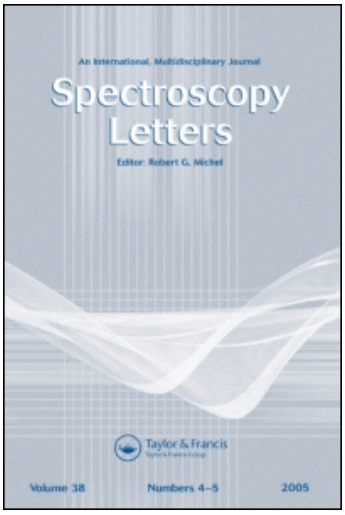

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Spectra Studies of Complexes Between Palladium (II), Nickel (II) and Amino Acids

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SPECTRA STUDIES OF COMPLEXES BETWEEN PALLADIUM(II), NICKEL(II) AND AMINO ACIDS

Key words: PA spectrum, electronic spectrum, complexes

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ABSTRACT

The complexes of $Ni(His)_2 \cdot H_2O$, $Ni(Gly)_2 \cdot 2H_2O$, $Pd(His)Cl_2 \cdot H_2O$ and $Pd(Gly)_2 \cdot 2H_2O$ were synthesized. And the IR, electronic absorption and photoacoustic spectra of these complexes were measured in solid state. The nature of the metal-carboxylate coordinate bond were deduced from the variation in the carboxyl stretching frequencies. And the d-d transition absorptions of these complexes were interpreted quantitatively with the 3d scaling radial theory. Therefore, the structural characterizations were also discussed with their spectral behaviors.

INTRODUCTION

The interactions between nucleic acids and proteins usually lead to the formation of stable complexes. Their stability is due to various forces exercised between the side-chain of the amino acids and the peptide bonds of the proteins on the one band and the aromatic rings or the phosphate groups of the polynucleic acid chain on the other. There are electrostatic forces, hydrophobic interaction etc. It is also known that such nucleic acid-protein interaction may be created in biological systems with the interaction of metal ions to form binary or ternary complexes[1,2] . The complexes system of the type metal-amino acids, peptide or nucleoside, therefore, constitute the simplest models for the study of the more complex DNA-protein interactions. For the essential significance in biological systems, the transition metal-amino acids complexes have been widely studied by chemists and biochemists. In a lot of metalloenzymes, the activity centre are always a complex of transition metal ion and amino acid. Therefore, the research of the complex like the title compounds as a model complex is very interested and important.[2,3]

Interest in the study of the palladium(II) ion with amino acids and some other ligands of biological importance began with the discovery of Rosenberg et al, the certain platinum complexes exhibit carcinostatic activity[4], and the chemistry of palladium(II) with biologically important molecules also became of capital importance together with the analogous chemistry of platinum(II) after the discovery of the antitumor properties of latter[5,6] . The interest arises from the similarity in the properties of Pd(II) and Pt(II) and the advantage in many case of the much faster (10^5 times) ligand substitution reactions that the former presents, making its study more feasible[6,7,8] .

As the interested in palladium-amino acid complexes, their structures have been widely studied[9] , and some

investigators had also studied their synthesis[10], NMR spectroscopes[11], absorption and CD spectroscopes[12] and some other properties[13]. But, the photoacoustic spectroscope of these complexes has not been found. However, the PA spectra of other complexes system are also very limited[14,15].

In this work, the title Pd(II),Ni(II)-amino acids complexes were synthesized. And their IR, electronic absorption and photoacoustic spectra are determined and explained systematically. Their structural characterizations are also discussed.

EXPERIMENT

(I) Synthesizes

[Ni(His)2]·H2O and [Ni(Gly)2(H2O)2]:

The same as the literature, the crystal of Ni(His)2·H2O[16] and Ni(Gly)2·2H2O[17] were obtained from water solutions respectively. And the results of elemental analysis of these two complexes were all corresponded with their formula. That of Ni(His)2·H2O: C 37.65 H 4.72 N 21.59%, calc. C 37.43 H 4.68 N 21.84%; and of Ni(Gly)2·2H2O: C 19.83 H 4.96 N 11.35%, calc. C 19.78 H 4.98 N 11.54%.

[Pd(Gly)2]·2H2O:

Pd(glycine)·2H2O was prepared by dissolving 1mmol $PdCl_2$ in hot HCl solution with constant stirring, and 2mmol glycine dissolved in a little distilled water was added to the former solution, raising the PH values of the mixture to 7 with NaOH solution. The mixture solution was slowly evaporated at room temperature and the fibriform orange crystals were obtained after several days. The results of elemental analysis of Pd(Gly)2·2H2O crystal were: C 16.70 H 4.89 N 9.60%, calc. C 16.42 H 4.82 N 9.57%.

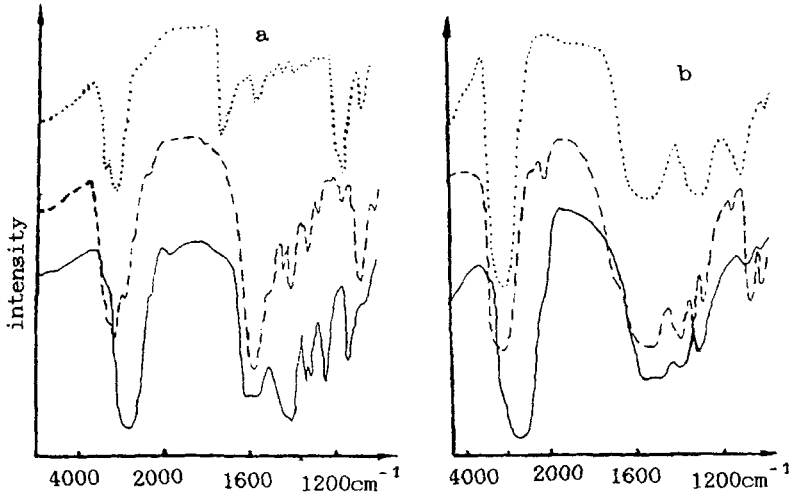


Figure 1. The IR spectra of the title compounds.
a: ——— histidine; - - - $Ni(His)_2 \cdot H_2O$; ····· $Pd(His)CL_2 \cdot H_2O$
b: ——— glycine; - - - $Ni(Gly)_2 \cdot 2H_2O$; ····· $Pd(Gly)_2 \cdot 2H_2O$

[Pd(His)Cl2]·H2O:

The preparation of this complex crystal were nearly the same program as that of [Pd(Gly)2]·2H2O crystal. Considerably, the PH value of the solution in this complex system must be controlled PH<3. Then, the orange-red column crystals were obtained. The results of elemental analysis of this crystal were: C 20.74 H 2.86 N 11.91%, calc. C 20.62 H 2.86 N 12.01%.

(II). IR and electronic absorption spectra

The IR spectrum measurements were made as reflectance spectra, using KBr as diluent on IR instrument under standard operating conditions,see Figure 1.

The electronic absorption spectra of the title compounds were recorded at room temperature in the region of 6000--30000cm^{-1} using the absorption spectrograph for small crystal produced by the Geochemistry Institute of Chinese Academy

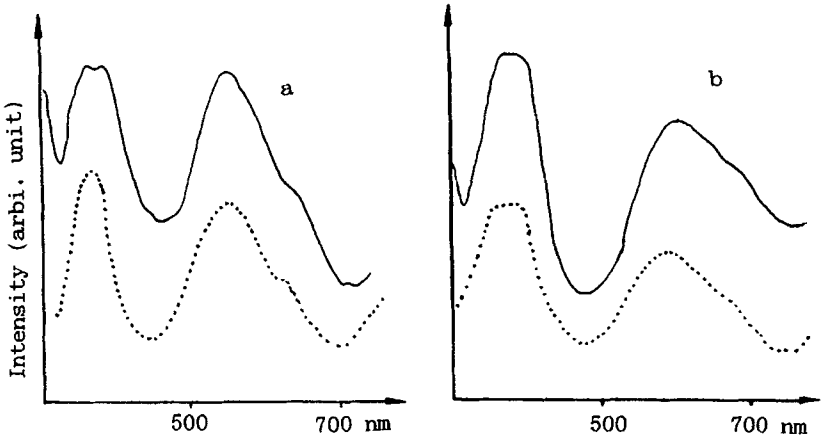


Figure 2. EA and PA spectra of Ni(II) complexes.
a: ····· EAS of $Ni(His)_2 \cdot H_2O$; ——— PAS of $Ni(His)_2 \cdot 2H_2O$
b: ····· EAS of $Ni(Gly)_2 \cdot 2H_2O$; ——— PAS of $Ni(Gly)_2 \cdot 2H_2O$

of Science, see Figure 2 and 3. Because of the opacity of the fibriform $[Pd(Gly)_2] \cdot 2H_2O$ crystal, its electronic absorption spectrum was absented.

(III). Photoacoustic spectra

The excitation source was a 500W Xenon lamp. The optical system was a CT-30F monochromater and a variable speed mechanical chopper at frequency of 12HZ which used to modulate the light source intensity. The acoustic signal was monitored with the sample placed in an indigenous photoacoustic cell fitted with an electret microphone. The output signal from the microphone was amplified by a preamplifier and then fed to a lock-in-amplifier with a reference signal imputed from the chopper. The final signal was normalized for the changes in lamp intensity using a reference by carbon-black. The PA spectra of all the title complexes were recorded at room temperature in the region of 300-800nm, see Figure 2 and 3.

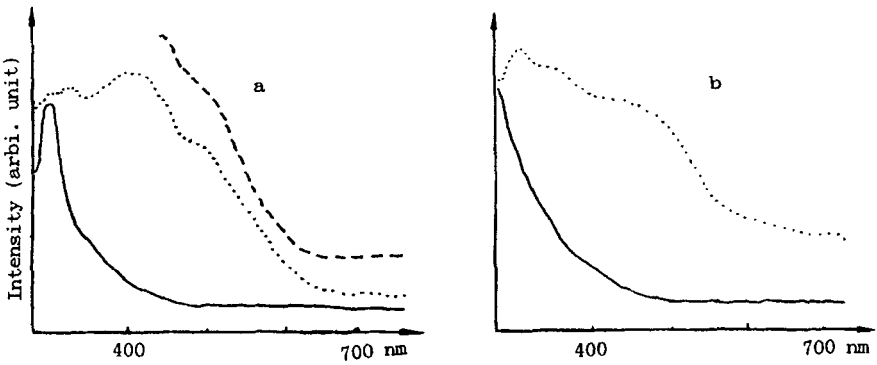


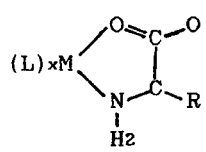
Figure 3. EA and PA spectra of Pd(II) complexes and amino acids.
a: ——— PAS of histidine; ····· PAS of Pd(His)Cl2·H2O;
- - - EAS of Pd(His)Cl2·H2O
b: ——— PAS of glycine; ····· PAS of Pd(Gly)2·2H2O

RESULTS AND DISCUSSION

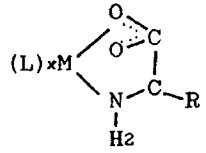
(I).IR spectra

The IR spectra of the title complexes and amino acids are shown in Figure 1. However, the IR spectra of these complexes are corresponded with their structure formula. Of the various vibratory models of the amino acids, the carboxyl stretching frequencies which are usually identified with certainty and the most sensitive to a change in the strength of the metal-oxygen interaction have been widely discussed.

In purity amino acids compounds, the carboxylic acid exists in amphoteric ion $-C(NH_3^+)-COO^-$, and their carboxyl stretching frequencies are decreased at 1600-1590 and 1400 cm^{-1}, see Figure 1. In the complexes system, usually the covalent character of the metal-oxygen bond has two type indicated by formula I and II[18]. However, in one compound, two metal-oxygen bond type may be coexistence but only one is dominant.



(I)



(II)

The IR spectra of $Pd(Gly)_2 \cdot 2H_2O$ and $Ni(His)_2 \cdot H_2O$ show that the carboxyl stretching frequencies are observed at 1600 and $1400cm^{-1}$. Comparing to the amino acids, the antisymmetric carboxyl stretching of $Pd(Gly)_2 \cdot 2H_2O$ complex has a something large violet shift, $\Delta\nu=60cm^{-1}$ and that of $Ni(His)_2 \cdot H_2O$ has a few red shift $\Delta\nu=40cm^{-1}$. On the other hand, the symmetric carboxyl stretching of Pd-Gly complex has a red shift $\Delta\nu=60cm^{-1}$ and that of $Ni(His)_2 \cdot H_2O$ complex with few violet shift. For this reason, it is seen to be that the metal-oxygen bond of $Pd(Gly)_2 \cdot 2H_2O$ and $Ni(His)_2 \cdot H_2O$ complexes are dominated by formula (II), and the interaction between metal ion and ligands in $Pd(Gly)_2 \cdot 2H_2O$ complex is stronger than that of $Ni(His)_2 \cdot H_2O$ complex..

The IR spectra of $Pd(His)Cl_2 \cdot H_2O$ and $Ni(Gly)_2 \cdot 2H_2O$ show that the carboxyl stretching frequency are lying at $1710cm^{-1}$. It is seen to be that the type of metal-oxygen bond of these two complexes is in formula (I). On the other hand, in IR spectra, the strength of C-O bond stretching absorption of formula (I) complexes is more large than that of formula (II) complexes and amino acids, see Figure 1. However, that is another evidence of this conclusion. Therefore the C-O bond stretching frequencies of $Pd(His)Cl_2 \cdot H_2O$ and $Ni(Gly)_2 \cdot 2H_2O$ complexes are also show the same behaves as that of carboxyl stretching frequencies in complexes with formula (II), see Figure 1. The C-O bond stretching frequency decreased in $Ni(Gly)_2 \cdot 2H_2O$ and increased in $Pd(His)Cl_2 \cdot H_2O$ complex. It is also shown that the type of metal-oxygen bond of this two compound is in formula (I).

(II) Electronic Absorption Spectra And Photoacoustic Spectra

Ni(II)-amino acid complexes:

Between electronic absorption spectrum and photoacoustic spectrum of $Ni(His)_2 \cdot H_2O$ complex, there are the same absorption

bands observed in the region of 300-800nm. There are three strong absorption peaks lying at 28800, 18300 and 10600 cm^{-1} which may be due to the d-d transition absorption of Ni(II) ion. They are assigned as the transition $^3T_{2g}(^3F)$--$^3A_{2g}(^3F)$(band of 10650cm^{-1}), $^3T_{1g}(^3F)$--$^3A_{2g}(^3F)$(band of 18000cm^{-1}) and $^3T_{1g}(^3F)$--$^3A_{2g}(^3F)$(band of 28850cm^{-1})[19]. According to the Figure 2(a). we could see that the PA spectrum may be with a high sensitivity than that of electronic absorption spectrum. In PA spectrum, there exists three separated absorption peaks observed at 29356, 27807 and 26414 cm^{-1} which may be assigned as the transitions of $^3T_{1gx}$, $^3T_{1gz}$ and $^3T_{1gy}(^3P)$ --$^3A_{2g}(^3F)$, and there also exist several low intensity absorption bands which are due to the spin forbidden transitions, see Table 1.

In $Ni(Gly)_2\cdot 2H_2O$ complex, there are also the same absorption bands between electronic absorption spectrum and PA spectrum. And the d-d transition absorptions are also similar with that of $Ni(His)_2\cdot H_2O$ complex[20], see Table 1. But, from the spectra of this complex in Figure 2(b). we could see that there have several more broad absorption bands than that of $Ni(His)_2\cdot H_2O$. It is seen to be that $Ni(Gly)_2\cdot 2H_2O$ complex forms a more strong ligand field that may be verified by their crystal structures[16,17]. However, bond length of Ni--O,N of $Ni(His)_2\cdot H_2O$ is 2.097A and it is large than that of $Ni(Gly)_2\cdot 2H_2O$ complex 2.0807A. But, for the $Ni(His)_2\cdot H_2O$ complex is in approximately C_2 symmetry, there has a additional low field split. For this reason the calculated Dq values of these two complexes are similar: 1382cm^{-1} for $Ni(His)_2\cdot 2H_2O$ and 1239cm^{-1} for $Ni(Gly)_2\cdot 2H_2O$ complex.

The electronic absorption spectra of transition metal-amino acids and their additives had been studies and their absorption bands were assigned experimentally and arbitrarily by some investigators[11,12]. The theoretical quantitative interpretations of the d-d transition spectra of these complexes have not be seen by now. In ligand field theory, we have suggested the scaling radial theory of non-free ions and proposed the double-ζ radial wave functions of non-free transition metal

TABLE 1

The d-d transition energies of Ni(II) complexes.(cm^{-1})

complexes	energy levels	calc.	obvs. EAS	obvs. PAS
Ni(His)2·H2O	$^3A_{2g}$ (^3F)	0.	0.	0.
	$^3T_{2gb}$(^3F)	10466.		
	$^3T_{2gc}$(^3F)	10547.	10650.	
	$^3T_{2ga}$(^3F)	10967.		
	^1E_g (^1D)	13119.		14000.
	$^3T_{1gx}$(^3F)	16768.		16000.
	$^3T_{1gz}$(^3F)	17338.		
	$^3T_{1gy}$(^3F)	17522.	18000.	18100.
	$^1T_{1g}$ (^1G)	23463.		22680.
	$^3T_{1gy}$(^3P)	27346.		26414.
	$^3T_{1gz}$(^3P)	28372.	28850.	27807.
	$^3T_{1gx}$(^3P)	29180.		29356.
Ni(Gly)2·2H2O	$^1A_{2g}$ (^3F)	0.	0.	0.
	$^3T_{2gb}$(^3F)	8998.	9000.	
	$^3T_{2gc}$(^3F)	9650.	10100.	
	$^3T_{2ga}$(^3F)	10200.	11000.	
	$^3T_{1gx}$(^3F)	14787.	15000.	
	$^3T_{1gz}$(^3F)	15699.	16400.	16700.
	$^3T_{1gy}$(^3F)	16997.	17500.	
	$^3T_{1gy}$(^3F)	24018.	24500.	25000.
	$^3T_{1gz}$(^3F)	26948.	27000.	27000.
	$^3T_{1gx}$(^3F)	29841.	29500.	29120.

ions[21,22] . Therefore, a program package was developed to be used for the calculation of the ligand field theory by which the calculated results are always corresponded perfectly with the observed ones[23,24] . However, the d-d transition energy levels of this two Ni(II) complexes are also calculated in this way and the results are presented in Table 1. It is clearly that the calculated results are in good agreement with the EA and PA spectra of these complexes, see Table 1.

In addition, the stability, strength and density of $Ni(Gly)_2 \cdot 2H_2O$ complex crystal we obtained are something more large than that of similar complexes, such as $Ni(His)_2 \cdot H_2O$, $Ni(DL\text{-}Ala)_2 \cdot H_2O$[3] etc. This special property may be due to such two reasons. First, there exists a widely and strong hydrogen bonds in the $Ni(Gly)_2 \cdot 2H_2O$ complex molecule. And then the coordination bonds of this complex are more stability and forms a strong ligand field.

Palladium(II)-Amino Acid Complexes

The PA spectra of $Pd(His)Cl_2 \cdot H_2O$ and $Pd(Gly)_2 \cdot 2H_2O$ complexes and amino acids are recorded and presented in Figure 3. For the reason of crystal, we can only obtained the electronic absorption spectrum of $Pd(His)Cl_2 \cdot H_2O$ complex and for the strong violet absorption we could not get its clear and completed absorption bands , see Figure 3.

The PA spectrum of Histidine shows a strong absorption band at 300nm region which may be assigned as $L\text{-}L^*$ transition and it is also shown in the PA spectrum of $Pd(His)Cl_2 \cdot H_2O$ complex[25,26]. However, it is the imidazole ring of histidine molecule that the $\pi\text{-}\pi^*$ ligand transfers form this strong violet absorption band. And without any conjugate system in glycine molecule, the PA spectrum of glycine is also not shown any absorption bands in the region of 300-800nm.

In the PA spectrum of $Pd(His)Cl_2 \cdot H_2O$ complex, there exists several strong absorption peaks at 300, 330 and 405nm and a shoulder peak at 495nm. It is clear that the 300nm band is due to

TABLE 2

EA and PA spectra data of Pd(II) complexes.

complexes	absorption bands (nm)	assignment
Pd(His)Cl2·H2O	300.	d--π^*
	330.	$^1A_1$--^1E
	405.	$^1A_1$--$^1B_2$
	495.	$^1A_1$--$^1B_1$
Pd(Gly)2·2H2O	310.	$^1A_1$--^1E
	360.	$^1A_1$--$^1B_2$
	450.	$^1A_1$--$^1B_1$

the charge transfer from metal ion to ligand (d-π^*)[15]. And the other absorption bands lying at 330, 405 and 495nm may be assigned as the d-d transitions of $^1A_1$--^1E, $^1A_1$--$^1B_2$ and $^1A_1$--$^1B_1$ respectively[7,26], see Table 2. However, the electronic absorption spectrum of this complex shows the same absorption bands in the same region as that of PA spectrum.

In the Pd(Gly)2·2H2O complex, the bands observed at 310nm is assigned as $^1A_1$--^1E transition and the band lying at 360 and 450nm may be due to the transitions of $^1A_1$--$^1B_2$ and $^1A_1$--$^1B_1$ respectively[8].

According to the PA spectra in Figure 3, the wavelengths of d-d transition absorption bands of Pd(Gly)2·2H2O are all less than that of Pd(His)Cl2·H2O complex, and the $\Delta\nu$ is nearly 33nm. It is said that the d-d transition absorptions of Pd(Gly)2·2H2O complex has a violet shift comparing to that of Pd(His)Cl2·H2O complex. The same as the Ni(II)-amino acid complexes, the Pd(Gly)2·2H2O complex forms a more strong ligand field than that of Pd(His)Cl2·H2O and has a large strength of the spectral terms split. So the Pd-Glycine complex has a large d-d transition energies.

In $4d^8$ configuration, because of the shielded effect of the full 3d orbits, the interaction between 4d electron and the nuclear is strongly decreased. And it makes the valence electron of 4d orbits be more sensitive to the surrounding. So the interaction between valence orbits and ligand in 4d transition metal complexes is more large than that of 3d transition metal complexes. It is said that the strength of ligand field in palladium(II) complexes is more large than that of nickel(II) complexes and it makes the energy levels of Pd(II) complex have a more large split strength, and this is also apparently shown in their spectrum, see Tables 1 and 2.

In addition, the photoacoustic spectra and their electronic absorption spectra of these Pd(II) and Ni(II) complexes show almost the same absorption positions and intensities in visible wavelengths region, it is seen to be that all these Pd(II) and Ni(II)-amino acid complexes are without fluorescence in this region[15].

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