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Amino acid complexes of ruthenium: synthesis, characterization and cyclic voltammetric studies

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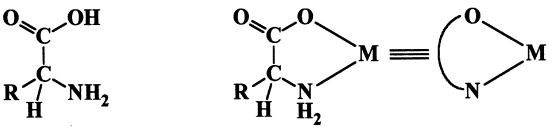
Abstract

Reaction of α-amino acids (HL) with $[Ru(PPh_3)_3Cl_2]$ in the presence of a base afforded a family of complexes of type $[Ru(PPh_3)_2(L)_2]$. These complexes are diamagnetic (low-spin d^6, $S=0$) and show ligand-field transitions in the visible region. ^1H and ^{31}P NMR spectra of the complexes indicate the presence of C_2 symmetry. Cyclic voltammetry on the $[Ru(PPh_3)_2(L)_2]$ complexes show a reversible ruthenium(II)–ruthenium(III) oxidation in the range 0.30–0.42 V vs. SCE. An irreversible ruthenium(III)–ruthenium(IV) oxidation is also displayed by two complexes near 1.5 V vs. SCE.

Keywords: Ruthenium; α-Amino acids; Synthesis; Characterization; Electrochemistry

1. Introduction

Amino acids, being the building blocks of protein, are an essential component of all living matter. Therefore, to investigate the interaction between metals and proteins, the necessary prerequisite is to study the interaction between amino acids and different metals. The chemistry of transition metal complexes of amino acids has been of significant interest in this respect [1–5]. Synthesis of different types of complexes using various amino acids is becoming increasingly important primarily because of the various applications of such complexes in biological fields [6–8]. With this background we set out to explore the chemistry of amino acid complexes of ruthenium. Among many transition metals ruthenium has been chosen because of its efficiency in electron-transfer reactions and particularly because of its remarkable role in DNA intercalation reactions [9,10]. It may be mentioned here that ruthenium chemistry of amino acids appears to have received very little attention [11–15]. For the present study we have chosen α-amino acids (**1**), abbreviated in general as HL where H stands for the dissociable carboxylic proton, as the principal ligand. The α-amino acids are known to bind to metal ions, via dissociation of the acidic proton, as bidentate N,O-donor forming five-membered chelate rings (**2**) [4,16]. A family of bis α-amino acid complexes of ruthenium(II) has been synthesized, where triphenylphosphine has served as the coligand. The synthesis, characterization and electrochemical properties of complexes of type $[Ru(PPh_3)_2(L)_2]$ are described in this paper.



1 **2**

2. Experimental

2.1. Materials

Commercial ruthenium trichloride (Arora Matthey, Calcutta, India) was converted to $RuCl_3 \cdot 3H_2O$ by repeated evaporation with concentrated hydrochloric acid. Triphenylphosphine (PPh_3) was purchased from SD Fine Chemicals, Mumbai, India. $[Ru(PPh_3)_3Cl_2]$ was synthesized, starting from $RuCl_3 \cdot 3H_2O$, by following a reported procedure [17]. The α-amino acids were purchased from Loba Chemie, India. HPLC-grade dimethylsulfoxide for electrochemical work was purchased from Spectrochem,

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Mumbai, India. Purification of dichloromethane and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work and was performed as reported in the literature [18,19]. All other chemicals and solvents were commercial reagent-grade and were used as received.

2.2. Preparations

2.2.1. $[Ru(PPh_3)_2(L^1)_2]$

To a solution of glycine (HL^1) (17 mg, 0.22 mmol) in warm ethanol (30 cm^3) were added $[Ru(PPh_3)_3Cl_2]$ (100 mg, 0.10 mmol) and triethylamine (0.03 cm^3, 0.22 mmol) with constant stirring. Stirring was continued for 1.5 h keeping the solution warm (~40°C). Within 30 min, a yellow microcrystalline compound began to separate out. The reaction mixture was then allowed to settle at room temperature (~25°C). The precipitated solid was collected by filtration, washed thoroughly with water followed by hexane and acetonitrile and dried in vacuo over P_4O_{10}. The yield was 66% (53 mg).

2.2.2. $[Ru(PPh_3)_2(L^2)_2]$

This complex was synthesized following the above procedure using alanine (HL^2) instead of glycine (HL^1), methanol instead of ethanol and sodium hydroxide instead of triethylamine. The yield was 62% (52 mg).

2.2.3. $[Ru(PPh_3)_2(L^3)_2]$

This complex was synthesized following the same procedure for $[Ru(PPh_3)_2(L^1)_2]$ using phenylalanine (HL^3) instead of glycine (HL^1). The yield was 64% (64 mg).

2.2.4. $[Ru(PPh_3)_2(L^4)_2]$

To a solution of tyrosine (HL^4) (40 mg, 0.22 mmol) in warm ethanol (30 cm^3) were added $[Ru(PPh_3)_3Cl_2]$ (100 mg, 0.10 mmol) and triethylamine (0.03 cm^3, 0.22 mmol) with constant stirring. Stirring was continued for 1.5 h keeping the solution warm (~40°C). A greenish-yellow solution was obtained, which upon evaporation afforded a solid. This was washed with water followed by hexane and dried in vacuo over P_4O_{10}. Purification was achieved by chromatography through a silica gel (60–120 mesh) column. Using 1:1 benzene–acetonitrile as the eluent, a deep yellow band came out which was collected and evaporation of the eluate gave $[Ru(PPh_3)_2(L^4)_2]$ as a yellow solid. The yield was 60% (62 mg).

2.2.5. $[Ru(PPh_3)_2(L^5)_2]$

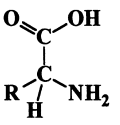
This complex was synthesized following the same procedure for $[Ru(PPh_3)_2(L^4)_2]$ using leucine (HL^5) instead of tyrosine (HL^4). The yield was 61% (56 mg).

2.3. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. NMR spectra were recorded on a Brucker DRX-500 NMR spectrometer. Electronic spectra were recorded on a Shimadzu UV 240 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker scientific L75FBAL magnet. Electrochemical measurements were made using a PAR model 273 potentiostat. A platinum-disc (area 0.04 cm^2) working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A RE 0089 X–Y recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

3. Results and discussion

Five different amino acids have been used in the present work. The ligands and their respective abbreviations are shown in **3**. Reaction of these ligands with $[Ru(PPh_3)_3Cl_2]$ in the presence of a base afforded the desired complexes in decent yields. $[Ru(PPh_3)_3Cl_2]$, our starting material, has served as a useful source of ruthenium(II) because of the considerable substitutional lability of the chlorides and one PPh_3 ligand. The composition of these complexes have been verified by their elemental (C, H, N) analytical data (Table 1). All the $[Ru(PPh_3)_2(L)_2]$ complexes are diamagnetic which corresponds to the bivalent state of ruthenium (low-spin d^6, $S=0$) in these complexes.



R	Abbreviation
H	HL^1 (glycine)
CH_3	HL^2 (alanine)
CH_2–C$_6$H$_5$	HL^3 (phenyl alanine)
CH_2–C$_6$H$_4$–OH	HL^4 (tyrosine)
$CH_2CH(CH_3)_2$	HL^5 (leucine)

3

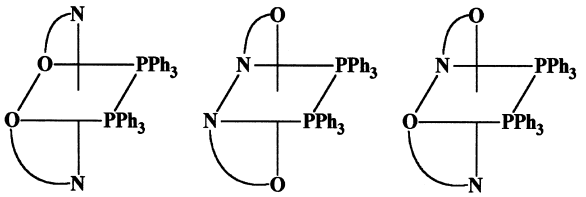
As α-amino acids are unsymmetrical bidentate ligands, the $[Ru(PPh_3)_2(L)_2]$ complexes may exist in five different geometric isomeric forms (**4**–**8**). Complexes of ruthenium having the $Ru(PPh_3)_2$ moiety are known to prefer the two PPh_3 ligands in the *cis* position for better dπ–dπ interaction [20,21]. Assuming a similar *cis* disposition of the triphenylphosphines in these $[Ru(PPh_3)_2(L)_2]$ complexes, the number of possible stereoisomers reduces to three (**4**–**6**). Out of these three isomers, two (**4** and **5**) have a C_2

Table 1
Characterization data of the $[Ru(PPh_3)_2(L)_2]$ complexes

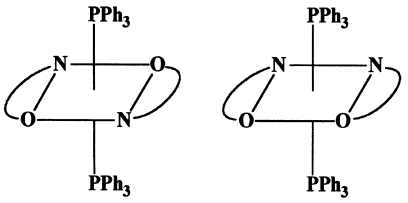
Compound	Microanalytical data[a]			Electronic spectral data[b]	Cyclic voltammetric data[c]
	%C	%H	%N	λ_{max} (nm) [ε (M^{-1} cm^{-1})]	$E_{1/2}$ (V) (ΔE_p (mV)]
$[Ru(PPh_3)_2(L^1)_2]$	62.06 (62.09)	4.94 (4.91)	3.63 (3.62)	524 (359), 424 (671), 340[d] (1661), 292[d] (3767), 268 (5712)	0.33 (60)
$[Ru(PPh_3)_2(L^2)_2]$	62.98 (62.92)	5.20 (5.24)	3.50 (3.49)	524 (257), 420 (485), 344[d] (1149), 296[d] (2234), 260 (3828)	0.30 (60)
$[Ru(PPh_3)_2(L^3)_2]$	67.86 (67.90)	5.27 (5.24)	2.88 (2.93)	420 (286), 344[d] (1072), 300[d] (2287), 270 (5289)	0.37 (60)
$[Ru(PPh_3)_2(L^4)_2]$	65.83 (65.78)	5.10 (5.07)	2.86 (2.84)	420 (563), 344[d] (1408), 302[d] (5582), 272 (8989)	0.42 (60)[e], 1.56[e,f]
$[Ru(PPh_3)_2(L^5)_2]$	65.11 (65.08)	6.10 (6.10)	3.17 (3.16)	420 (411), 344[d] (1643), 304[d] (3481), 276 (7744)	0.39 (60)[e], 1.48[e,f]

[a] Calculated values are within parentheses.
[b] In dimethylsulfoxide solution.
[c] Solvent, dimethylsulfoxide; supporting electrolyte, TBAP; reference electrode, SCE; $E_{1/2}=0.5(E_{pa}+E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p=E_{pa}-E_{pc}$; scan rate 50 mV s^{-1}.
[d] Shoulder.
[e] In dichloromethane solution.
[f] E_{pa} value.

axis while the other (**6**) does not have C_2 symmetry. ^1H NMR spectra of the $[Ru(PPh_3)_2(L)_2]$ complexes are a little complicated. However, ^{31}P NMR spectra of these complexes show only one sharp resonance near 47 ppm which clearly indicates the presence of a C_2 axis. Therefore, the $[Ru(PPh_3)_2(L)_2]$ complexes have structure **4** or **5**.



4 **5** **6**



7 **8**

Further distinguishing between these two structures could not be done from the NMR spectral results. However, all the complexes are assumed to have structure **4**, where the nitrogens of the amino acid ligands are *trans* and the less crowded carboxylate oxygens are *cis* and hence this geometry is expected to be sterically more favorable.

IR spectra of all the $[Ru(PPh_3)_2(L)_2]$ complexes are qualitatively similar, each complex showing several vibrations of different intensities below 1700 cm^{-1}. All the $[Ru(PPh_3)_2(L)_2]$ complexes show strong vibrations near 530, 700 and 750 cm^{-1} which are also displayed by $[Ru(PPh_3)_3Cl_2]$. Hence these vibrations are attributed to the $Ru(PPh_3)_2$ moiety of $[Ru(PPh_3)_2(L)_2]$. In the spectra of all the $[Ru(PPh_3)_2(L)_2]$ complexes a broad and very strong vibration is observed near 1610 cm^{-1} and a sharp and strong vibration near 1380 cm^{-1}, which are absent in the spectrum of $[Ru(PPh_3)_3Cl_2]$ and these are assigned [22] to the $\nu_{as(CO)}$ stretching and $\nu_{s(CO)}$ stretching of the coordinated carboxylate groups. The distinct peaks near 3300 cm^{-1} are attributed to the N–H stretching vibrations. The infrared spectral data are therefore in accordance with the composition of the complexes.

The $[Ru(PPh_3)_2(L^1)_2]$, $[Ru(PPh_3)_2(L^2)_2]$ and $[Ru(PPh_3)_2(L^3)_2]$ complexes are soluble only in dimethylsulfoxide and dimethylformamide, while the other two complexes, viz. $[Ru(PPh_3)_2(L^4)_2]$ and $[Ru(PPh_3)_2(L^5)_2]$, are soluble in dichloromethane, acetonitrile and chloroform as well as in dimethylsulfoxide and dimethylformamide. All the solutions are yellow in colour. Electronic spectra of these complexes have been recorded in dimethylsulfoxide solution. Spectral data are presented in Table 1 and selected spectra are shown in Fig. 1. Each complex shows absorptions in the visible and ultraviolet region. The intense absorptions in the ultraviolet region are assignable to transitions within the ligand orbitals. The absorptions in the visible region are rather weak and are probably due to ligand-field transitions [23,24].

Electron transfer properties of the $[Ru(PPh_3)_2(L)_2]$ complexes have been studied by cyclic voltammetry in dimethylsulfoxide (for $L=L^1$, L^2 and L^3) and dichlorome-

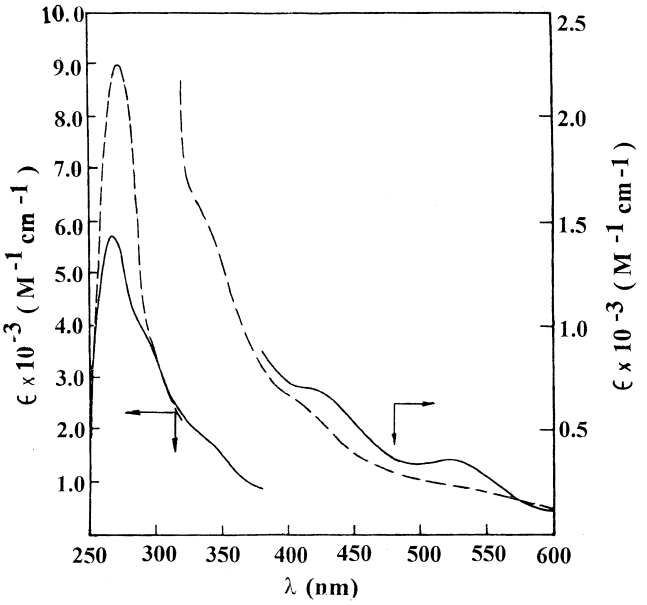


Fig. 1. Electronic spectra of $[Ru(PPh_3)_2(L^1)_2]$ (——) and $[Ru(PPh_3)_2(L^4)_2]$ (- - - - -) in dimethylsulfoxide solution.

thane (for $L = L^4$ and L^5) solutions. Voltammetric data are given in Table 1 and a selected voltammogram is shown in Fig. 2. Each complex shows an oxidative response on the positive side of SCE in the range 0.30–0.42 V vs. SCE.

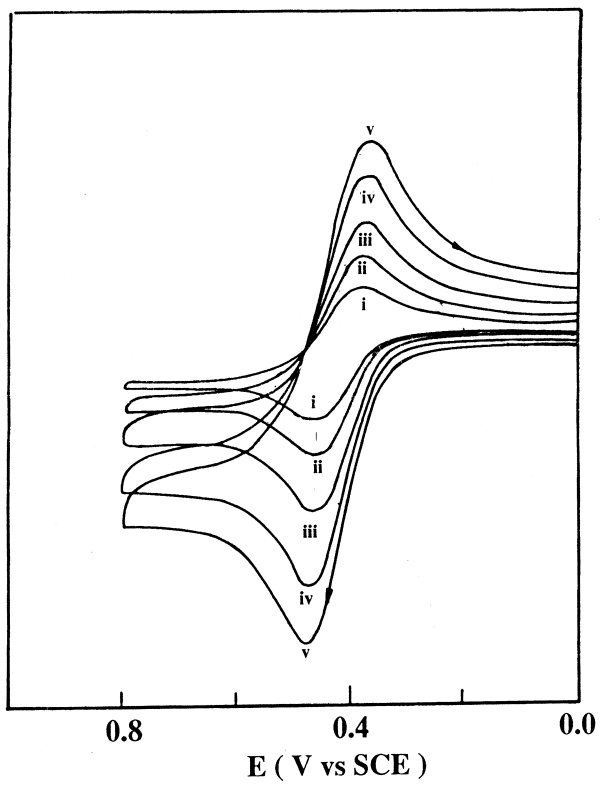


Fig. 2. Cyclic voltammograms of $[Ru(PPh_3)_2(L^4)_2]$ in dichloromethane solution (0.1 M TBAP) at scan rates of 50, 100, 200, 400 and 500 mV s^{-1}.

This oxidative response is assigned to the ruthenium(II)–ruthenium(III) oxidation. The oxidation is reversible with a peak-to-peak separation (ΔE_p) of ~60 mV which does not vary with variation in scan rates and the anodic peak current (i_{pa}) is almost equal to the cathodic peak current (i_{pc}). The one-electron nature of this oxidation was established by comparing its current height with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. The magnitudes of the oxidation potential indicate that the bivalent state of the ruthenium is comfortable in this $N_2O_2P_2$ coordination sphere. A second irreversible oxidation is observed in $[Ru(PPh_3)_2(L^4)_2]$ and $[Ru(PPh_3)_2(L^5)_2]$ near 1.5 V which is tentatively assigned to the ruthenium(III)–ruthenium(IV) oxidation. The one-electron nature of this oxidation is confirmed by comparing its current height (i_{pa}) with that of the respective ruthenium(II)–ruthenium(III) oxidation. This oxidation has not been observed in the first three $[Ru(PPh_3)_2(L)_2]$ ($L = L^1$, L^2 and L^3) complexes because of the smaller voltage window offered by dimethylsulfoxide.

4. Conclusions

The present study shows that α-amino acids can form stable complexes with ruthenium, and in the presence of π-acid ligands such as PPh_3 the +2 state of the metal becomes stabilized. Replacement of the PPh_3 ligands by hard donors is expected to favour the higher oxidation states of the metal and this work is currently in progress.

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