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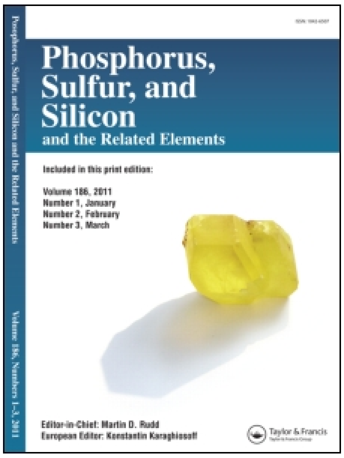

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COMPLEXES OF AMINOALKYLPHOSPHONIC ACIDS AND PHOSPHONODIPEPTIDES WITH Pt(II) AND Pd(II)

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Abstract Complexing properties of aminomethylenephosphonic acid and dipeptides glycyl-aminomethylenephosphonic acid and both diastereoisomers of (*S*)-methionyl-1-aminoethylphosphonic acid with Pt(II) and Pd(II) were investigated pH-metrically at 25 °C and at ionic strength of 0.1 mol dm^{-3} (KNO_3). The stability constants calculated indicate formation of the complexes with a metal : ligand molar ratio of 1 : 1 and 1 : 2. The differences found for diastereoisomers are much higher than for systems with common dipeptides. Distribution of all species found by potentiometry were confirmed by ^{31}P and ^{1}H NMR titrations.

INTRODUCTION

Aminoalkylphosphonic acids and their dipeptides with terminal aminoalkylphosphonic acid have obtained much interest due to biological activity and coordination ability. The coordination ability of the acid was intensively investigated and even a few papers were focused on the phosphonodipeptides [1]. Except NMR study of coordination ability of the aminoalkylphosphonic acid with Pt(II) and Pd(II) [2], all papers have been focused on the hard transition metals.

The aim of the present paper was to determine the stability formation constants of aminomethylenephosphonic acid (Amp), glycyl-aminomethylenephosphonic acid (GlyAmp) and *S,S* and *S,R* diastereoisomers of (*S*)-methionyl-1-aminoethylphosphonic acid (MetAmp).

RESULT AND DISCUSSION

The stability formation constants determined in the systems $[PdCl_4]^{2-}$ or $[PtCl_4]^{2-}$ - Amp or phosphonodipeptide are listed in Table I. The stability formation constants of Pt(II) and Pd(II) chlorocomplexes were taken from ref. [3].

Distribution diagrams of Amp with Pt(II) and Pd(II) are shown in Fig. 1. From the distribution diagrams and from Table I, it is evident, that both the metals form complexes with metal : Amp molar ratio = 1:1 and 1:2. Pd(II) starts to form the protonated 1:1 complexes below pH = 2 and consequently, after deprotonation of phosphonic group the non-protonated species. The 1:2 complexes were determined as the major species in this system. I addition to the hydroxo complexes found in alkali region, a dimeric hydroxo-complexes were determined at about pH 4.

TABLE I. Stability formation constants (log β_{pqrss})

$H^+L^{2-}Cl^-Pd^{2+}$	Amp	GlyAmp	SS-MetAep	SR-MetAep
1 1 2 1	24.66(1)	24.48(9)	-	-
0 1 1 1	21.52(1)	-	-	-
0 1 1 1	-	21.35(6)	-	-
-1 1 1 1	-	17.35(7)	-	-
-2 1 0 1	4.93(3)	9.70(7)	-	-
-3 1 0 1	-	0.48(7)	-	-
-2 2 0 2	30.51(5)	-	-	-
2 2 0 1	-	-	35.35(2)	35.01(2)
1 2 0 1	-	-	29.14(3)	28.71(3)
0 2 0 1	27.70(2)	27.50(6)	21.99(3)	21.54(3)
-1 2 0 1	-	-	12.88(5)	12.85(4)
-2 2 0 1	6.89(6)	12.11(7)	2.85(5)	2.67(4)
-4 2 0 1	-	-8.2(1)	-	-

$H^+L^{2-}Cl^-Pt^{2+}$	Amp	GlyAmp	SS-MetAep	SR-MetAep
1 1 2 1	22.67(9)	23.14(3)	-	-
0 1 2 1	19.55(1)	-	-	-
0 1 1 1	-	17.72(2)	-	-
-1 1 1 1	-	11.93(2)	-	-
-2 1 0 1	0.70(5)	2.00(4)	-	-
-3 1 0 1	-9.9(1)	-7.90(6)	-	-
-2 0 2 2	-	-	-	-
2 2 0 1	-	-	37.27(3)	36.56(2)
1 2 0 1	-	-	30.99(4)	30.16(3)
0 2 0 1	22.28(2)	-	23.70(4)	22.92(3)
-1 2 0 1	-	-	15.21(5)	14.23(4)
-2 2 0 1	3.40(5)	3.9(1)	5.74(5)	4.65(4)
-4 2 0 1	-	-15.8(1)	-	-

Chloro-complexes of Pt(II) are more stable than the Pd(II) analogous species and therefore, a formation of Pt(II) complexes with Amp starts at higher pH range. Two dominant species 0121 and 0201 were found in this system. As well as in the Pd(II) system, in the Pt(II) system the hydroxo-complexes were also determined. Comparison of Amp-Pd(II) system with the system Amp-Pt(II) we can see that Pd(II) prefers 1:2 complexes and Pt(II) 1:1 complexes, probably due to higher stability of the chloro-complexes.

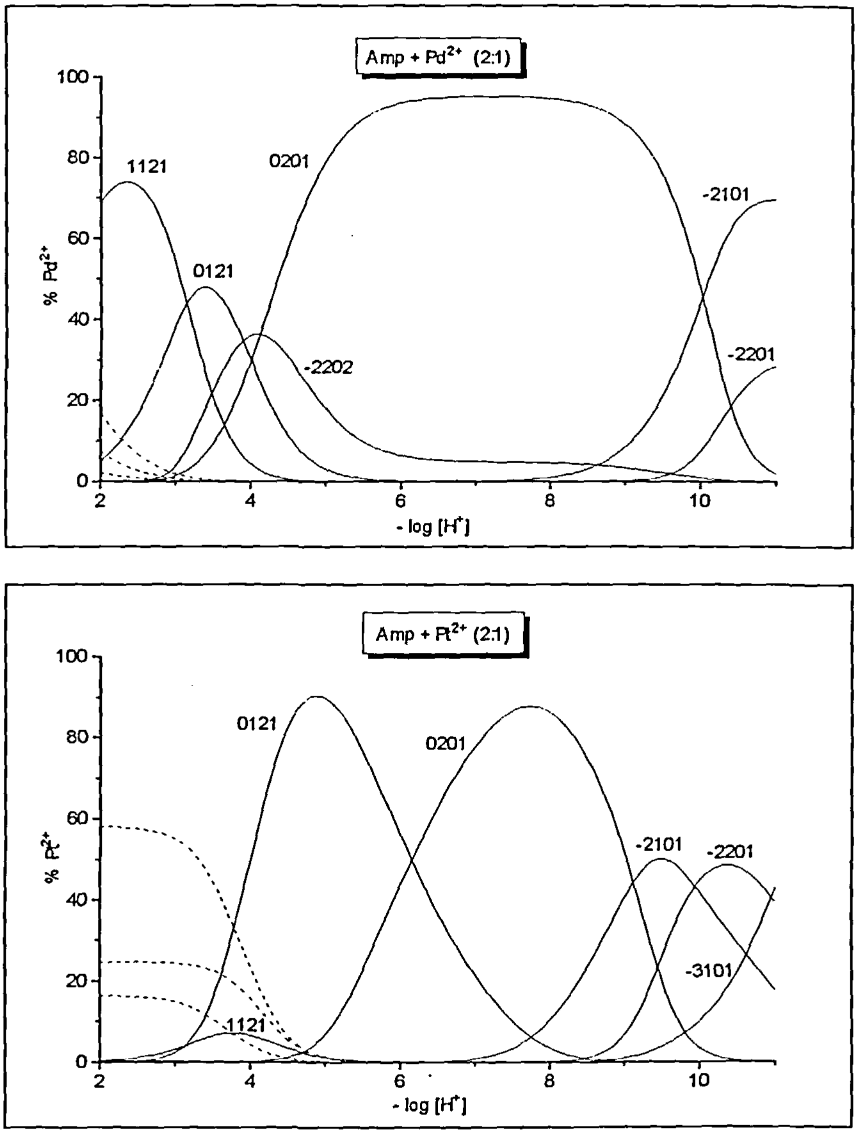

FIGURE 1 Distribution diagrams of Pd(II) and Pt(II) with Amp.
(- - - represents $[MCl_{4-n}(H_2O)_n]^{n+2-}$ species)

GlyAmp $H_2NCH_2C(O)NHCH_2PO_3H_2$ is a tridentate ligand. The ligand can be coordinated to a metal through amine, peptide-amide and phosphonic groups. This way of coordination was found in both Pd(II) and Pt(II) systems. The same tendency at formation of 1:1 and 1:2 complexes as in Amp series was observed in the GlyAmp systems. In the alkali-region, several types of hydroxocomplexes were determined. Both diastereoisomers of MetAep $CH_3SCH_2CH_2CH(NH_2)C(O)NHCH(CH_3)PO_3H_2$ form only 1:2 complexes and are coordinated to the both metals through sulfur and amino groups in acid and neutral region of pH. In alkali region the coordination through amine and peptide-amide groups were confirmed.

Complexes of Pd(II) and Pt(II) are kinetically stable and, thus, a presence of these species determined potentiometrically could be confirmed by ^{31}P and ^{1}H NMR titrations. The NMR titrations were done at concentration 0.15 mol.dm^{-3}, *e.g.* the concentration was 15 times higher than for the potentiometry titrations. In spite of that, the NMR titrations confirmed the potentiometrically found species and their distribution in acidic and neutral region of pH. At higher pH than 9, the same species were observed, however, their distribution was different. If the potentiometric titration was done at the same concentration as the NMR titrations, we found very good agreement of both used method.

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