

Stabilities and Coordination Modes of α -Alaninephosphonic Acid in Copper(II) Heteroligand Complexes with Ethylenediamine, Diethylenetriamine or N,N,N',N',N'' -Pentamethyldiethylene Triamine in Aqueous Solution

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Received: 20 July 2010 / Accepted: 17 November 2010 / Published online: 24 May 2011
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Abstract Solution equilibrium studies on Cu^{2+} - L_1 - L_2 ternary systems have been performed by pH-potentiometry, UV-Vis spectrophotometry and EPR methods (L_1 corresponds to polyamines such as ethylenediamine (en), diethylenetriamine (dien), or N,N,N',N',N'' -pentamethyldiethylenetriamine (Me_5dien) and L_2 represents 1-aminoethylphosphonic acid (α -alaninephosphonic acid)). The obtained results suggest the formation of heteroligand complexes with $[\text{Cu}(\text{L}_1)(\alpha\text{-Ala}(\text{P}))]$ stoichiometry in all studied systems. Additionally, in the system with en the $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))\text{H}_{-1}]^-$ species is formed in basic solution. Our spectroscopic results indicate tetragonal geometry for the $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))]$ species, geometry slightly deviated from square pyramidal for the $[\text{Cu}(\text{dien})(\alpha\text{-Ala}(\text{P}))]$ complex and strongly deviated from square pyramidal towards trigonal bipyramidal for the $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala}(\text{P}))]$ species. The coordination modes in these heteroligand complexes are discussed.

Keywords Copper(II) complexes · Heteroligand complexes · Aminophosphonic acids · EPR · Vis spectroscopy · Potentiometry · Equilibria · Stability constants · Polyamines · Five-coordinate complexes

1 Introduction

This article is a continuation of our study on the ternary systems with some polyamines and aminophosphonic acids. According to our knowledge new data on the ternary systems with α -aminophosphonic acids do not exist. Our earlier results on the ternary systems with en,

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dien or Me₅dien and Gly(P) [1] support the formation of the heteroligand complexes in all of these systems in basic solutions. In the case of the [Cu(en)(Gly(P))] species the formation of (NH₂, NH₂) and (NH₂, PO₃²⁻) chelates in the equatorial plane of the copper(II) ion is supported. For the [Cu(dien)(Gly(P))] species the binding of Cu²⁺ in the equatorial plane is realized by three amine nitrogens of dien and the amine nitrogen of Gly(P), and the phosphonic oxygen completes the coordination number to five by binding Cu²⁺ in an axial position and the geometry is slightly deviated from square pyramidal. The co-ordination mode in the [Cu(Me₅dien)(Gly(P))] species is the same as in the case of [Cu(dien)(Gly(P))], but the geometry of this species is strongly deviated from square pyramidal towards trigonal bipyramidal due to the dominant bulky effect of two methyl substituents at each nitrogen atoms.

The present paper concerns the studies on the system: Cu²⁺-L₁L₂ (when L₁ = ethylenediamine (en), diethylenetriamine (dien) or *N,N,N',N',N''*-pentamethyldiethylene triamine (Me₅dien) and L₂ = R(-)-1-aminoethylphosphonic acid (α -alaninephosphonic acid) (Ala(P)) using pH-metric, spectrophotometric, and EPR methods.

Systematic comparison between Cu²⁺-L₁L₂ ternary systems with L₂ = Ala or Ala(P) is performed. Though both systems exhibit many similarities, some important differences were found also. The differences between the complex-forming properties of aminophosphonates and aminocarboxylates in ternary systems have been explained by the differences in basicity, charge and size of the -PO₃²⁻ and -COO⁻ groups.

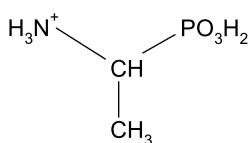
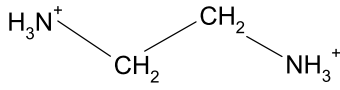
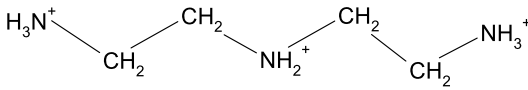
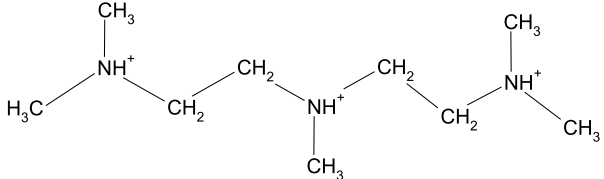
2 Experimental

2.1 Materials

All chemicals and solvents were used without further purification. Ethylenediamine dihydrochloride (en·2HCl), diethylenetriamine (dien, purity greater than 99%) and *N,N,N',N',N''*-pentamethyldiethylene triamine (Me₅dien, purity 99%) were purchased from Sigma-Aldrich Chemical Co, and R(-)-1-aminoethylphosphonic acid (α -alaninephosphonic acid, purity \geq 99%) was obtained from Fluka Chemie GmbH (Switzerland). The exact concentrations of the ligand stock solutions used for potentiometric measurements were determined by Gran's method [2]. The Cu²⁺ stock solutions were prepared from CuCl₂ Titrisol concentrate which was purchased from Merck. The exact copper ion concentration was checked by complexometric ethylenediaminetetraacetate (EDTA) titration. Carbonate-free potassium hydroxide solution (the titrant) was prepared from cc. KOH and standardized against a standard potassium hydrogen phthalate solution. The HCl stock solution was purchased from Merck as a Titrisol concentrate for the preparation of standard solutions. The concentration was determined by pH-potentiometric titrations using Gran's method [2]. All solutions were prepared with bi-distilled water. The formulae of the fully protonated form of the ligands used in this study are shown in Scheme 1.

2.2 Potentiometric Measurements

The pH-potentiometric measurements were carried out at an ionic strength of 0.2 mol·dm⁻³ (KCl) and temperature 25.00 \pm 0.1 °C. Carbonate-free KOH solution of known concentration (ca. 0.15 or 0.3 mol·dm⁻³) was used as titrant. A MOLSPIN automatic titrator system equipped with a combination pH electrode (SINGLE PORE PLAST or SINGLE PORE GLASS, Hamilton) was used for pH-potentiometric measurements. The electrode system was calibrated by periodic titrations of HCl solution (0.008 mol·dm⁻³ in KCl) against standard KOH solution. The resulting titration data were used to calculate the standard electrode potentials, E° , and the dissociation constant for water ($pK_w = 13.74 \pm 0.02$). These

Ligands	Abreviation
 <p data-bbox="299 388 599 423">α-alaninephosphonic acid</p>	[H₃L]⁺
 <p data-bbox="346 555 546 590">Ethylenediamine</p>	[H₂-en]²⁺
 <p data-bbox="346 723 558 758">Diethylenetriamine</p>	[H₃-dien]³⁺
 <p data-bbox="182 970 717 1005">N,N,N',N',N''-pentamethyldiethylenetriamine</p>	[H₃-Me₅dien]³⁺

Scheme 1 The formulae of the fully protonated form of the ligands

values were then used to calculate the hydrogen ion concentration $[H^+]$ from the emf readings [3]. All the pH-potentiometric titrations were performed under argon atmosphere over the pH range of 2–11 or until precipitation occurred. Initial volumes of the samples were 5.00–6.00 cm³. For the binary systems the ligand concentration was $2.5\text{--}3 \times 10^{-3}$ mol·dm⁻³ and the copper ion concentrations were varied in the range of $0.6\text{--}3 \times 10^{-3}$ mol·dm⁻³ according to the metal ion to ligand ratios: 1:1, 1:2 and 1:4. For the ternary systems the ratios of copper(II):en/dien/Me₅dien: α -Ala(P) were 1:1:1, 1:1:2, 1:2:1, 1:2:2 and 0.5:1:1. Titrations were usually made on samples containing copper(II) ion concentrations of $2.5\text{--}3 \times 10^{-3}$ mol·dm⁻³ or 1.25×10^{-3} mol·dm⁻³ (in the case of 0.5:1:1 molar ratio).

The pH-metric results were used to establish the stoichiometry of the species and to calculate the stability constants of the species formed in the ternary systems. The equilibrium calculations were performed using the HYPERQUAD 2006 computer program [4]. The reported standard deviations were calculated by assuming random errors. The values of stability constants of the complexes formed in the binary systems were kept constant during calculating the potentiometric data of the ternary systems. The equilibrium models for the

Table 1 Cumulative formation constants ($\log_{10} \beta$), derived equilibrium constants ($\log_{10} K$) and characteristic parameters for the stability of complexes formed in the ternary systems Cu^{2+} –amine (en, dien or Me_5dien)– α -alaninephosphonic acid (α -Ala(P)) at 25.00 °C and $I = 0.2 \text{ mol}\cdot\text{dm}^{-3}$ (KCl)

Nr.	Assignments	System Cu^{2+} – L_1 – α -Ala(P); ($\text{L}_1 = \text{en, dien or Me}_5\text{dien}$)		
		Cu^{2+} –en– α -Ala(P)	Cu^{2+} –dien– α -Ala(P)	Cu^{2+} – Me_5dien – α -Ala(P)
1.	$\log_{10} \beta_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P)})]}$	17.929 (7)	20.47 (1)	16.57 (1)
2.	$\log_{10} \beta_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P))H}_{-1}]^-}$	6.22 (1)	–	–
3.	${}^a\log_{10} K_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P)})]}$	7.349	4.46	4.10
4.	χ^2	11.03	10.10	8.83
5.	σ	3.89	5.54	7.26
6.	$\Delta \log_{10} K$	–0.945	–3.834	–4.194
7.	${}^b\log_{10} X$	1.178	5.23	–

${}^a\log_{10} K_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P)})]} = \log_{10} \beta_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P)})]} - \log_{10} \beta_{[\text{Cu}(\text{L}_1)]}$; $\log_{10} \beta_{[\text{Cu}(\text{en})]} = 10.58$,
 $\log_{10} \beta_{[\text{Cu}(\text{en})_2]} = 19.73$ [14], $\log_{10} \beta_{[\text{Cu}(\text{dien})]} = 16.01$, $\log_{10} \beta_{[\text{Cu}(\text{dien})_2]} = 20.76$ [7],
 $\log_{10} \beta_{[\text{Cu}(\text{Me}_5\text{dien})]} = 12.47$ [20], $\log_{10} \beta_{[\text{Cu}(\alpha\text{-Ala(P)})]} = 8.294$, $\log_{10} \beta_{[\text{Cu}(\alpha\text{-Ala(P))}_2]} = 14.95$,
 $pK_{\text{PO}_3\text{H}^-} = 5.5295$ and $pK_{\text{NH}_3^+} = 10.058$ of α -Ala(P) in presence of $0.2 \text{ mol}\cdot\text{dm}^{-3}$ KCl

b For the $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala(P)})]$ heteroligand species the $\log_{10} X_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P)})]}$ value cannot be calculated, since the complex with 1 : 2 metal to ligand ratio is not formed in the Cu^{2+} – Me_5dien binary system [20]

ternary systems and corresponding stability constants giving the best fits of the pH-metric titration curves are presented in Table 1.

2.3 UV/Vis Spectroscopy

A BECKMAN DU68 spectrophotometer was used to record the electronic absorption spectra in the visible range for the copper(II) complexes. The spectra were recorded digitally (0.5 nm steps) in the range of 300–900 nm, using 1 or 2 cm path length quartz cuvettes, at room temperature. The measurements were carried out in water, at different pH values (0.3 pH unit step) between 2.5 and 11, at all metal to ligand ratios studied, and with $4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ copper(II) ion. All the solutions were freshly prepared using deionized water. The metal ion to ligand ratios for the copper(II): α -Ala(P) binary system were 1:1 and 1:2. For the ternary systems copper(II):en: α -Ala(P), copper(II):dien: α -Ala(P) and copper(II): Me_5dien : α -Ala(P) the concentration ratios were 1:1:1 and 1:1:2. The concentration ratios of the reagents were chosen in order to achieve as high as possible concentration of the heteroligand species and to get the lowest concentration of the co-existing species in the solution. The net ligand-field absorption band of each heteroligand species was extracted from the absorption spectra applying the procedure described in Ref. [5].

2.4 EPR Spectroscopy

Electron paramagnetic resonance (EPR) spectra were performed on a Bruker 300E X-band spectrophotometer equipped with a Bruker NMR gaussmeter ER 035M and a Hewlett-Packard frequency counter HP 5350B at -196.15°C and at room temperature. Due to the strong absorption of microwave energy by water, very narrow sample tubes were used for liquid solution measurements. Samples for EPR studies were prepared in water/ethylene glycol (4:1 v/v) solution to ensure good glass formation with a copper(II) concentration of

$4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$. The copper ion to ligand molar ratios were the same as those used in the electronic absorption spectra. The binary and ternary systems solutions were usually measured at the same pH range as in the potentiometric studies. The pH of solutions was measured using a Mettler-Toledo, MP 2300 pH-meter with a combined pH electrode (SINGLE PORE GLASS, Hamilton). The EPR parameters were calculated by computer simulation of the experimental spectra using Bruker's WIN-EPR SimFonia Software Version 1.25.

3 Results and Discussion

The values of the protonation constants for the studied ligands and the stability constants of the complexes formed in the binary systems were re-determined under the same experimental conditions as those applied for the ternary systems (the same ionic strength $0.2 \text{ mol}\cdot\text{dm}^{-3}$, which was fixed with KCl solution). The detailed discussions about the acid-base properties of these ligands can be found in earlier papers [6–13]. The results for the binary systems $\text{Cu}^{2+}\text{-en}$ [14–18], $\text{Cu}^{2+}\text{-dien}$ [5, 6, 17–19], $\text{Cu}^{2+}\text{-Me}_5\text{dien}$ [15, 20, 21] and $\text{Cu}^{2+}\text{-}\alpha\text{-Ala(P)}$ [22, 23] are in good agreement with the literature data.

The equilibrium models for ternary systems and corresponding stability constants giving the best fits of the pH-metric titration curves are collected in Table 1 and the respective species distribution curves for $\text{Cu}^{2+}\text{-en-}\alpha\text{-Ala(P)}$, $\text{Cu}^{2+}\text{-dien-}\alpha\text{-Ala(P)}$ and $\text{Cu}^{2+}\text{-Me}_5\text{dien-}\alpha\text{-Ala(P)}$ ternary systems are presented in Fig. 1. According to these data, the heteroligand complexes with $[\text{Cu(L}_1)(\alpha\text{-Ala(P))}]$ stoichiometry are formed in all of the studied ternary systems. In the $\text{Cu}^{2+}\text{-en-}\alpha\text{-Ala(P)}$ ternary system the hydroxo heteroligand $[\text{Cu(en)(}\alpha\text{-Ala(P))OH}]^-$ species also exist in basic solution.

Similarly, as it was found in ternary systems of the same polyamines and glycinephosphonic acid [1] or different amino acids in copper(II) solution [13, 14], the equilibrium constant, $K_{[\text{Cu(L}_1)(\alpha\text{-Ala(P))}]}$ (Table 1, row 3), is much lower for the heteroligand species involving tridentate dien and Me_5dien than for the species containing bidentate en.

It is very interesting to compare the stability of the binary complexes with that of the ternary one. The difference in stability between the binary and ternary complexes, $\Delta \log_{10} K$ (the constant due to the equilibrium $[\text{Cu(L}_1)] + [\text{Cu}(\alpha\text{-Ala(P))}] \rightleftharpoons [\text{Cu(L}_1)(\alpha\text{-Ala(P))}] + \text{Cu}$), is a way to characterize the tendency toward formation of heteroligand complexes [24]. The constant for this equilibrium can be calculated from experimentally measured stability constants according to the equation:

$$\Delta \log_{10} K = \log_{10} \beta_{[\text{Cu(L}_1)(\alpha\text{-Ala(P))}]} - (\log_{10} \beta_{[\text{Cu(L}_1)]} + \log_{10} \beta_{[\text{Cu}(\alpha\text{-Ala(P))}]}).$$

The obtained value of $\Delta \log_{10} K$ for the $[\text{Cu(en)(}\alpha\text{-Ala(P))}]$ species (equal to -0.945), which express its relative stability, is typical for a complex with distorted octahedral geometry and two different bidentate ligands in the coordination sphere of the Cu^{2+} ion [25, 26]. The values of $\Delta \log_{10} K$, close to -1 , were obtained earlier for heteroligand species of tetragonal geometry formed by ethylenediamine and glycinephosphonic acid [1], aminoacids [22, 23] or aminohydroxamic acids in the copper(II) solution [8]. Distinctly lower values of $\Delta \log_{10} K$ are observed in the case of heteroligand complexes $[\text{Cu(L}_1)(\alpha\text{-Ala(P))}]$ with dien or Me_5dien (Table 1, row 6). They are not unexpected because such low values of this parameter were attained previously in the case of studied five-coordinate copper(II) heteroligand complexes formed by diethylenetriamine or N,N,N',N',N'' -pentamethyldiethylene triamine with aminoacids or aminohydroxamic acids [5–7, 22, 23] as well as glycinephosphonic acid [1]. This effect of the heteroligand complexes is due to the lower (than six) coordination number of Cu^{2+} .

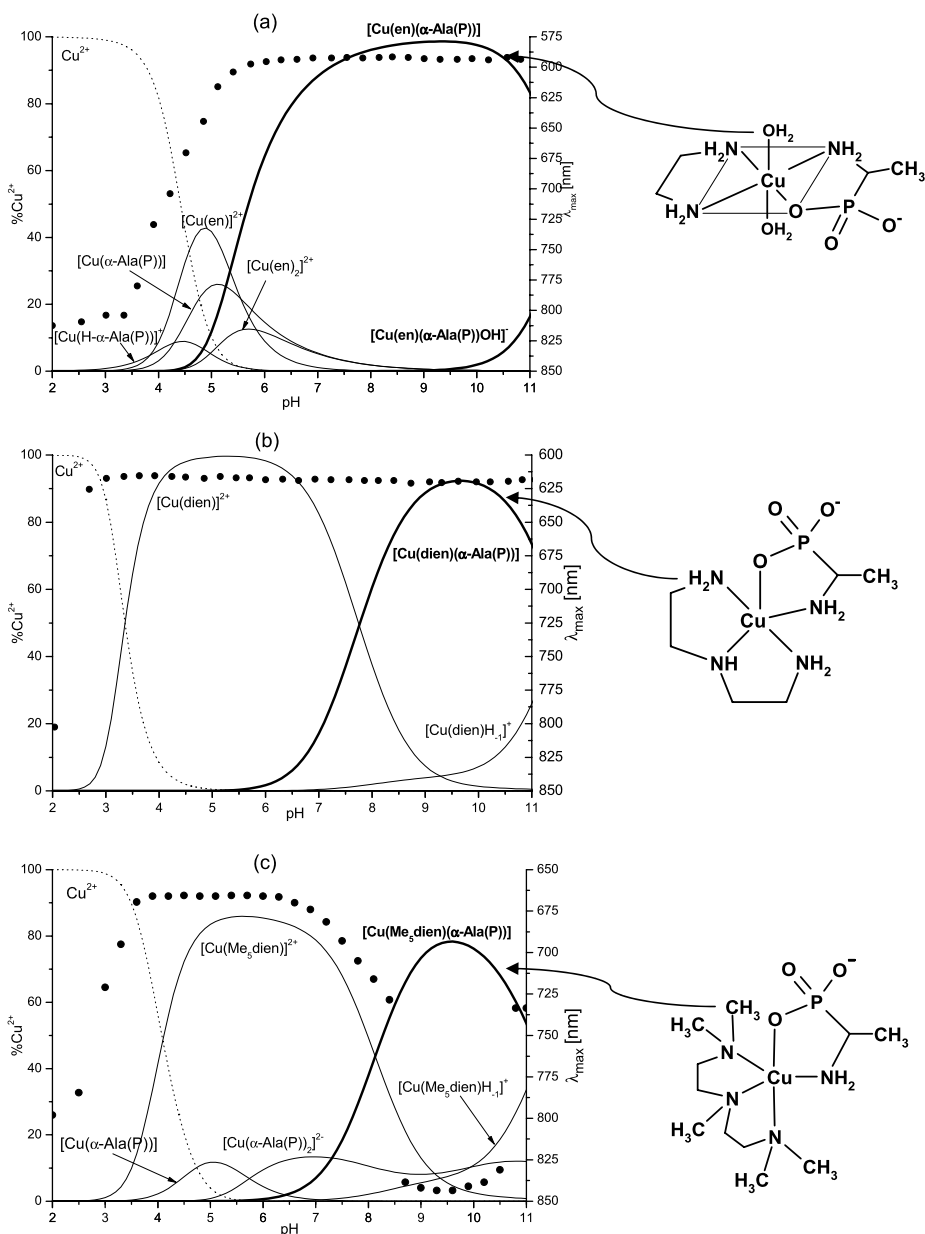


Figure 1 Species distribution curves as a function of pH and variations of visible absorption maximum wavelength (*circle*) for the Cu^{2+} -en- α -Ala(P) system (a), Cu^{2+} -dien- α -Ala(P) system (b) and Cu^{2+} -Me₃dien- α -Ala(P) system (c) at 1:1:2 molar ratio; $c_{\text{Cu}^{2+}} = 4 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

It is noticeable that in the ternary systems studied, the formation of heteroligand complexes is especially favored. The $\log_{10} X_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P))}]}$ values (the constant due to equilibrium: $[\text{Cu}(\text{L}_1)_2] + [\text{Cu}(\alpha\text{-Ala(P))}_2] \rightleftharpoons 2[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P))}]$) calculated for the heteroligand species of α -Ala(P) with polyamines (Table 1, row 7; $\log_{10} X = 2 \log_{10} \beta_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala(P))}]}$ -

$\log_{10} \beta_{[\text{Cu}(\text{L}_1)_2]} - \log_{10} \beta_{[\text{Cu}(\alpha\text{-Ala}(\text{P}))_2]}$ are higher than expected on a statistical basis (0.6) [24]. Furthermore, as was observed for the ternary systems with the same simple polyamines [1, 22, 23], the formation of heteroligand complexes is especially preferred in the system with dien (the $\log_{10} X_{[\text{Cu}(\text{L}_1)(\alpha\text{-Ala}(\text{P}))]}$ is distinctly higher than the value for the system with en). This is a reflection of the ratio of the stepwise formation constants for the binary Cu^{2+} –amine system ($\log_{10}(K_{\text{Cu}(\text{dien})}/K_{\text{Cu}(\text{dien})_2}) = 11.26$ which is significantly greater than $\log_{10}(K_{\text{Cu}(\text{en})}/K_{\text{Cu}(\text{en})_2}) = 1.43$).

3.1 Cu^{2+} –en– α -Ala(P) system

The species distribution curves for Cu^{2+} –en– α -Ala(P) system at 1:1:2 molar ratio as a function of pH, presented in Fig. 1(a), indicate that under these experimental conditions the $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))]$ heteroligand species starts to form above pH = 4.5. Up to this pH only simple species of en or α -Ala(P) are formed. The EPR parameters of the spectra observed at this pH in the liquid and frozen solution ($g_{\text{iso}} = 2.134$, $A_{\text{iso}} = 68 \times 10^{-4} \text{ cm}^{-1}$, $g_{\parallel} = 2.282$, $A_{\parallel} = 182 \times 10^{-4} \text{ cm}^{-1}$) are very similar to those reported for the Cu^{2+} –en binary system in an acid solution [8], what confirms that $[\text{Cu}(\text{en})]^{2+}$ dominates. As the pH of the solution increases up to pH = 6, the spectrum changes distinctly. From pH = 6.5 until 10 the EPR parameters of the spectra observed in the liquid and frozen solution ($g_{\text{iso}} = 2.114$, $A_{\text{iso}} = 79 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\parallel} = 2.235$, $A_{\parallel} = 190 \times 10^{-4} \text{ cm}^{-1}$) are practically unchanged and completely different from those obtained for the binary systems with α -Ala(P) or en (Table 2). They should be assigned to the heteroligand species $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))]$ predicted at this pH range to be predominant. Similarly, the pH dependence of λ_{max} in the visible spectra collected for the Cu^{2+} –en– α -Ala(P) ternary system (Fig. 1(a)) shows that the energy of the absorption bands remains unchanged at this pH range and confirms the formation of the $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))]$ heteroligand species. The obtained energy of $d-d$ transition for this species equal to 595 nm is intermediate between those obtained for the $[\text{Cu}(\alpha\text{-Ala}(\text{P}))_2]^{2-}$ (656 nm) and $[\text{Cu}(\text{en})_2]^{2+}$ (549 nm) species with 2N and 4N coordination, respectively (Figs. 2 and 3, Table 2). It should be mentioned here that the EPR parameters and absorption spectroscopic data are almost identical to those corresponding to the heteroligand species formed by en and glycinephosphonic acid— $[\text{Cu}(\text{en})(\text{Gly}(\text{P}))]$ with the same donor atoms in the coordination sphere of copper(II) (Table 2). So, they clearly support the formation of $(\text{NH}_2, \text{NH}_2)$ and $(\text{NH}_2, \text{PO}_3^{2-})$ chelates in the plane of $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))]$ (Fig. 1(a)).

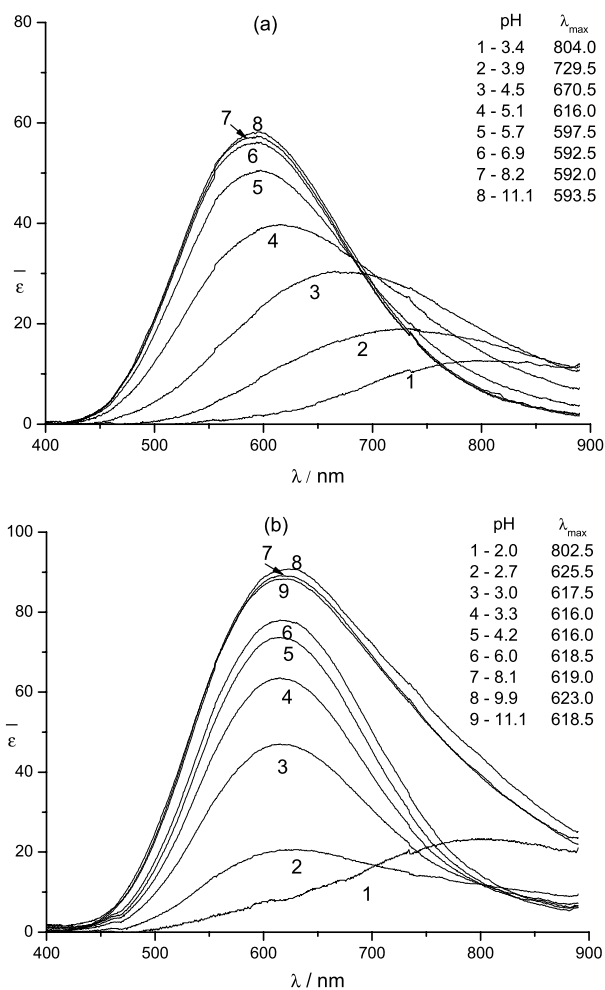
3.2 Cu^{2+} –dien– α -Ala(P) System

The calculated concentrations of the copper(II) complex species for the Cu^{2+} –dien– α -Ala(P) 1:1:2 molar ratio system as a function of pH, presented in Fig. 1b, indicate that under these conditions the complexation of $[\text{Cu}(\text{dien})]^{2+}$ by α -Ala(P) begins above pH = 6. Up to pH = 6 the EPR spectrum typical for the $[\text{Cu}(\text{dien})]^{2+}$ complex ($g_{\text{iso}} = 2.114$, $A_{\text{iso}} = 75 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\parallel} = 2.233$, $A_{\parallel} = 194 \times 10^{-4} \text{ cm}^{-1}$) is observed as dominant in the liquid and frozen solution. As the pH of the solution increases, a distinct change of EPR spectral features can be noticed. The spectrum typical of the $[\text{Cu}(\text{dien})]^{2+}$ complex is still observed as dominant between pH = 6.0–7.0 and in a small extent at pH = 8.0, but at the pH range 7.0–8.0 a new spectrum is also observed at equilibrium. This new spectrum with parameters $g_1 = 2.211$, $g_2 = 2.055$, $g_3 = 2.045$ and $A_1 = 198$, $A_2 = 31$, $A_3 = 11 \times 10^{-4} \text{ cm}^{-1}$, that is only dominant in the pH range 8.5–10.5 in this ternary system, is apparently different from those recorded for Cu^{2+} –dien or Cu^{2+} – α -Ala(P) binary systems in this pH range. The

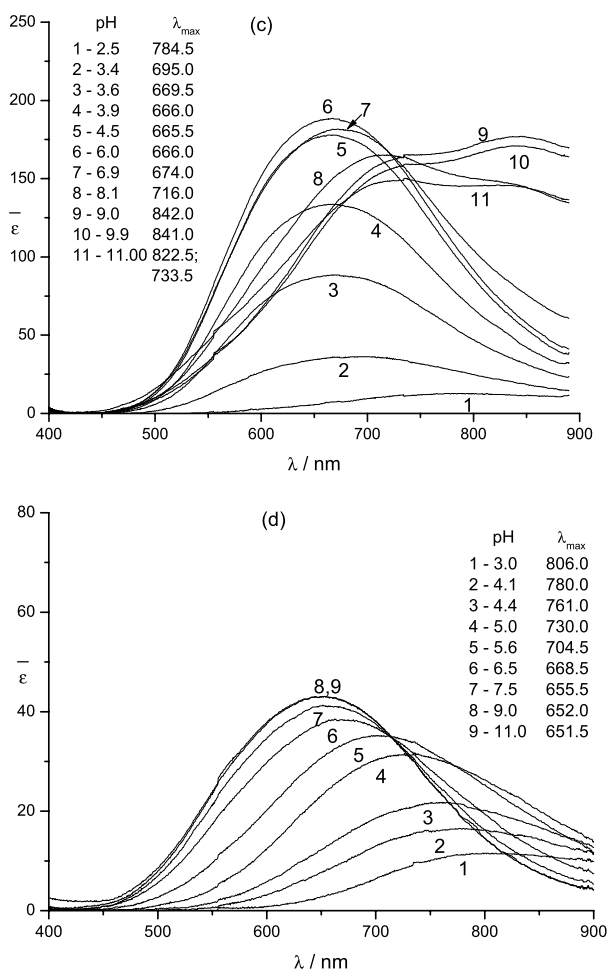
Table 2 Vis and EPR spectral parameters of the copper(II) complexes

Species	EPR				Coordination mode		Vis λ_{max} (nm) ϵ ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	
	g_{iso}	A_{iso} (10^{-4} cm^{-1})	g_{\parallel}	A_{\parallel} (10^{-4} cm^{-1})	g_{\perp}	A_{\perp} (10^{-4} cm^{-1})		
[Cu(α -Ala(P))] [1]	2.158	58	2.328	161	2.070	11	{NH ₂ , PO ₃ ²⁻ }	723 (39)
[Cu(α -Ala(P) ₂) ²⁻]	2.130	67	2.271	167	2.055	14	2 × {NH ₂ , PO ₃ ²⁻ }	656 (43)
[Cu(en)] ²⁺ [8]	2.138	68	2.283	183	2.060	14	{NH ₂ , NH ₂ }	666 (39)
[Cu(en) ₂] ²⁺ [8, 22]	2.100	86	2.207	198	2.040	20	2 × {NH ₂ , NH ₂ }	549 (71)
[Cu(en)(α -Ala)] ⁺ [22]			2.230	190	2.051	18	{NH ₂ , NH ₂ }; {NH ₂ , COO ⁻ }	580 (58)
[Cu(en)(Gly(P))] [11]	2.114	77	2.237	191	2.050	19	{NH ₂ , NH ₂ }; {NH ₂ , PO ₃ ²⁻ }	597 (54)
[Cu(en)(α -Ala(P))] [1]	2.114	79	2.235	190	2.050	19	{NH ₂ , NH ₂ }; {NH ₂ , PO ₃ ²⁻ }	595 (58)
[Cu(dien)] ²⁺ [5, 22]	2.114	75	2.234	192	2.055	20	{NH ₂ , NH, NH ₂ }	614 (78)
[Cu(dien)(α -Ala)] ⁺ [22]	g_1 2.217	g_2 2.054	g_3 2.043	A_1 (10^{-4} cm^{-1}) 190	A_2 (10^{-4} cm^{-1}) 30	A_3 (10^{-4} cm^{-1}) 15	{NH ₂ , NH, NH ₂ }; {NH ₂ , COO ⁻ }	635 (106)
[Cu(dien)(Gly(P))] [1]	2.212	2.054	2.044	199	32	11	{NH ₂ , NH, NH ₂ }; {NH ₂ , PO ₃ ²⁻ }	592 (103)
[Cu(dien)(α -Ala(P))] [1]	2.211	2.055	2.045	198	31	11	{NH ₂ , NH, NH ₂ }; {NH ₂ , PO ₃ ²⁻ }	622 (93)
[Cu(Me ₅ dien)] ²⁺ [6]	2.240	2.065	2.050	183	29	14	{N(CH ₃) ₂ , N(CH ₃), N(CH ₃) ₂ }	665 (225)
[Cu(Me ₅ dien)(α -Ala)] ⁺ [22]	2.208	2.138	2.007	135	20	62	{N(CH ₃) ₂ , N(CH ₃), N(CH ₃) ₂ }; {NH ₂ , COO ⁻ }	777 (275)
[Cu(Me ₅ dien)(Gly(P))] [1]	2.236	2.165	2.01	125	19	66	{N(CH ₃) ₂ , N(CH ₃), N(CH ₃) ₂ }; {NH ₂ , PO ₃ ²⁻ }	~827 (231), 750 (sh)
[Cu(Me ₅ dien)(α -Ala(P))] [1]	2.237	2.160	2.01	128	17	65	{N(CH ₃) ₂ , N(CH ₃), N(CH ₃) ₂ }; {NH ₂ , PO ₃ ²⁻ }	~848 (219), 752 (sh)

Figure 2 pH-varied absorption spectra of the Cu^{2+} -en- α -Ala(P) system (a), Cu^{2+} -dien- α -Ala(P) system (b) at 1:1:2 molar ratio ($c_{\text{Cu}^{2+}} = 4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, 2 cm cells), Cu^{2+} -Me₅dien- α -Ala(P) system (c) at 1:1:2 molar ratio ($c_{\text{Cu}^{2+}} = 4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, 1 cm cells) and Cu^{2+} - α -Ala(P) system at 1:2 molar ratio (d) ($c_{\text{Cu}^{2+}} = 4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, 2 cm cell)



isotropic EPR parameters $g_{\text{iso}} = 2.112$, $A_{\text{iso}} = 76 \times 10^{-4} \text{ cm}^{-1}$ are also different from those for binary $\text{Cu}(\text{dien})$ and $\text{Cu}(\alpha\text{-Ala(P)})$ species. So, the formation of the heteroligand species $[\text{Cu}(\text{dien})(\alpha\text{-Ala(P)})]$ can be supported. The EPR parameters obtained for this species correspond well to a five-coordinate species formed by dien and amino acids or glycinephosphonic acid in the copper(II) frozen solution (Table 2) [1, 22, 23]. The presence of a weak rhombic distortion suggests that the geometry is slightly deviated from square pyramidal towards trigonal bipyramidal [27]. Formation of the heteroligand $[\text{Cu}(\text{dien})(\alpha\text{-Ala(P)})]$ species is also observed in the electronic spectral changes (Figs. 2(b) and 3). The electronic absorption spectra at pH range 9.0–9.5 (Fig. 3) are characteristic for a five-coordinate asymmetric complexes with 4N coordination mode [1, 7, 22, 23]. So, α -Ala(P) completes the coordination number of five by binding with the amine nitrogen in Cu^{2+} plane and the phosphonic oxygen in an axial position.

Figure 2 (Continued)

3.3 Cu^{2+} - Me_5dien - α -Ala(P) System

The concentration distribution curves for the Cu^{2+} - Me_5dien - α -Ala(P) system together with the variation of the visible absorption maximum wavelength are presented in Fig. 1(c). It can be seen that, in this system with 1:1:2 molar ratio, up to pH ~ 7 the simple species with Me_5dien and α -Ala(P) are mainly formed. Moreover, the $[\text{Cu}(\text{Me}_5\text{dien})]^{2+}$ complex predominates in the solution, whereas the simple species with α -Ala(P) is formed in low concentration (ca. 10%). The EPR parameters of the spectra observed below pH = 7 in the liquid solution ($g_{\text{iso}} = 2.120$, $A_{\text{iso}} = 73 \times 10^{-4} \text{ cm}^{-1}$) and frozen solution of this ternary system ($g_z = 2.240$, $g_x = 2.065$, $g_y = 2.050$ and $A_z = 186$, $A_x = 28$, $A_y = 14 \times 10^{-4} \text{ cm}^{-1}$) are very similar to those of $[\text{Cu}(\text{Me}_5\text{dien})]^{2+}$ (Table 2). However, in the pH range 7.0–10.5 a distinct change of EPR spectra can be noticed. A new spectrum that is apparently different from that observed for Cu^{2+} - Me_5dien and Cu^{2+} - α -Ala(P) should be ascribed to the predominance, at this pH range, of the heteroligand species $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala(P)})]$ (maximum concentration nearly 80% at pH = 9–10) (Fig. 1(c)). The values of g parameters and the hyperfine splitting constants A calculated from the separated EPR

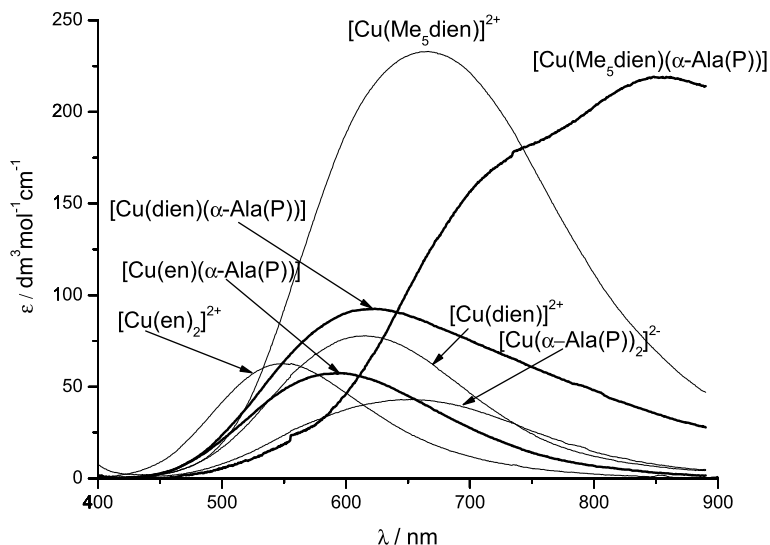


Figure 3 Distribution-corrected absorption spectra for the $[\text{Cu}(\text{en})(\alpha\text{-Ala}(\text{P}))]$, $[\text{Cu}(\text{dien})(\alpha\text{-Ala}(\text{P}))]$, $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala}(\text{P}))]$, $[\text{Cu}(\alpha\text{-Ala}(\text{P}))_2]^{2-}$, $[\text{Cu}(\text{en})_2]^{2+}$, $[\text{Cu}(\text{dien})]^{2+}$, and $[\text{Cu}(\text{Me}_5\text{dien})]^{2+}$ species

spectrum of this heteroligand species in frozen solution are similar to those obtained for $[\text{Cu}(\text{Me}_5\text{dien})(\text{Gly}(\text{P}))]$, $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala})]^+$ (Table 2), $[\text{Cu}(\text{Me}_5\text{dien})(\text{L-proline})]^+$ or $[\text{Cu}(\text{Me}_5\text{dien})(\text{L-valine})]^+$ [19]. Furthermore, they are typical for the “rhombic” spectrum of five-coordinate heteroligand species, with the geometry intermediate between the trigonal bipyramid and the square pyramid [29, 30]. The value of the R parameter calculated for the heteroligand $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala}(\text{P}))]$ species from the EPR spectrum ($R = g_y - g_z / g_x - g_y$), being a measure of the geometry distortion from square pyramid to trigonal bipyramid and the relative contribution of the d_{z^2} and $d_{x^2-y^2}$ orbital in the ground state [30], is equal 1.948. This value is greater than that for heteroligand species with amino acid— $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala})]^+$ ($R = 1.871$), which indicates a greater contribution of the d_{z^2} orbital in the ground state and structure closer to a trigonal bipyramid when $\alpha\text{-Ala}(\text{P})$, with the much larger spatial and electrostatic hindrance, is involved in the heteroligand complex. It is worthwhile to mention that a very strong rhombic distortion in the geometry was also observed for phosphonic derivatives of iminodiacetate or nitrilotriacetate complexes, when the substitution of the COO^- functions by PO_3^{2-} occurred [31, 32]. The increasing contribution of the $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala}(\text{P}))]$ complex between pH = 8.5–10.5 is also accompanied by a change of the absorption spectra. The pH varied absorption spectra of the Cu^{2+} – Me_5dien – $\alpha\text{-Ala}(\text{P})$ ternary system, obtained in basic solution (Fig. 2(c)), are completely different from those of both Cu^{2+} – Me_5dien [6] and Cu^{2+} – $\alpha\text{-Ala}(\text{P})$ binary systems (Fig. 2(d)). In addition, the pH dependence of λ_{max} in the visible spectra collected for the Cu^{2+} – Me_5dien – $\alpha\text{-Ala}(\text{P})$ system clearly shows a significant red shift (the value of λ_{max} increases from ~667 at pH ca. 6.3 to ~844 nm at pH ca. 9–9.5 and then starts to decrease to 733 at pH = 11 because at this pH the hydroxo complex $[\text{Cu}(\text{Me}_5\text{dien})\text{H}_{-1}]^+$ also exists), which parallels the formation and decay of the $[\text{Cu}(\text{Me}_5\text{dien})(\alpha\text{-Ala}(\text{P}))]$ species (Fig. 1(c)). Such effects have been observed several times in copper(II) ternary systems when the transition from a six to distorted five-co-ordination geometry occurs when going from the simple to heteroligand species [1, 6, 20, 22, 23, 28]. Moreover, the energy of the d – d transition for

Table 3 Cumulative formation constants ($\log_{10} \beta$), derived equilibrium constants ($\log_{10} K$) of heteroligand complexes formed in the $\text{Cu}^{2+}\text{-L}_1$ (en, dien, Me_5dien)– L_2 ($\text{L} = \alpha\text{-Ala}$, Gly(P) and $\alpha\text{-Ala(P)}$) at 25.00 °C and $I = 0.2 \text{ mol}\cdot\text{dm}^{-3}$ (KCl) (Charges are omitted for simplicity)

	Compound L_2		
	$\alpha\text{-Ala}$ Ref. [22, 28]	Gly(P) Ref. [1]	$\alpha\text{-Ala(P)}$ This work
$\log_{10} \beta[\text{Cu(en)(L}_2)]$	17.66	17.50	17.929
$\log_{10} K[\text{Cu(en)(L}_2)]$	7.08	6.92	7.349
$[\text{Cu(en)}] + \text{L}_2 \rightleftharpoons [\text{Cu(en)(L}_2)]$			
$\log_{10} K[\text{Cu(en)(L}_2)] - \text{p}K_{\text{NH}_3^+} - \text{p}K_{\text{COOH}}$	−4.96	–	–
$\log_{10} K[\text{Cu(en)(L}_2)] - \text{p}K_{\text{NH}_3^+} - \text{p}K_{\text{PO}_3\text{H}^-}$	–	−8.395	−8.2385
$\log_{10} \beta[\text{Cu(dien)(L}_2)]$	20.16	20.40	20.47
$\log_{10} K[\text{Cu(dien)(L}_2)]$	4.13	4.39	4.46
$[\text{Cu(dien)}] + \text{L}_2 \rightleftharpoons [\text{Cu(dien)(L}_2)]$			
$\log_{10} K[\text{Cu(dien)(L}_2)] - \text{p}K_{\text{NH}_3^+} - \text{p}K_{\text{COOH}}$	−7.89	–	–
$\log_{10} K[\text{Cu(dien)(L}_2)] - \text{p}K_{\text{NH}_3^+} - \text{p}K_{\text{PO}_3\text{H}^-}$	–	−10.925	−11.1275
$\log_{10} \beta[\text{Cu(Me}_5\text{dien)(L}_2)]$	17.33	16.286	16.57
$\log_{10} K[\text{Cu(Me}_5\text{dien)(L}_2)]$	5.13	3.816	4.10
$[\text{Cu(Me}_5\text{dien)}] + \text{L}_2 \rightleftharpoons [\text{Cu(Me}_5\text{dien)(L}_2)]$			
$\log_{10} K[\text{Cu(Me}_5\text{dien)(L}_2)] - \text{p}K_{\text{NH}_3^+} - \text{p}K_{\text{COOH}}$	−6.89	–	–
$\log_{10} K[\text{Cu(Me}_5\text{dien)(L}_2)] - \text{p}K_{\text{NH}_3^+} - \text{p}K_{\text{PO}_3\text{H}^-}$	–	−11.499	−11.4875

$[\text{Cu(Me}_5\text{dien)(}\alpha\text{-Ala(P))}]$ (Fig. 1(c) and Fig. 3, Table 2) is very similar to those for five-coordinate heteroligand species containing Me_5dien and glycinephosphonic acid (Table 2). So, the coordination of $\alpha\text{-Ala(P)}$ to the copper(II) ion is supposed to be the same, with bidentate chelation (NH_2 , PO_3^{2-}).

It is very interesting to compare the relative stabilities of the complexes formed in the ternary systems with phosphonic acids with those of amino acid (Table 3). The data clearly show that the relative stabilities of the heteroligand $[\text{Cu(L}_1)(\text{L}_2)]$ species with $\alpha\text{-Ala}$ are about 3–4 orders of magnitude higher even though amino acid and phosphonic acids form chelate rings of the same size and have a similar mixed-bonding mode (N, O). This can be explained in part by the significantly larger size of the PO_3^{2-} group. Another factor that may influence the relative stability is the difference in charge of PO_3^{2-} and COO^- donor groups. The formation of heteroligand complexes with phosphonic acids is strongly favored by their charge neutralization. The same relative stability decrease of phosphonate complexes in comparison to carboxylates was observed in the cases of binary systems with different metal ions [11, 31–33] and still exists in the ternary system with copper(II) ions.

4 Conclusion

In the studied copper(II)–polyamine–Gly(P) ternary systems, the potentiometric, VIS and EPR results support the formation of the heteroligand complexes with $[\text{Cu(L}_1)(\alpha\text{-Ala(P))}]$ stoichiometry. In the case of the $[\text{Cu(en)(}\alpha\text{-Ala(P))}]$ species, which predominates in the solution at pH range 6.5–10, the formation of (NH_2 , NH_2) and (NH_2 , PO_3^{2-}) chelates in the

equatorial plane of the copper(II) ion is supported. For the [Cu(dien)(α -Ala(P))] species, which predominates in basic solution, a slight deviation from square pyramidal geometry is postulated. In this heteroligand species the binding of Cu²⁺ in the equatorial plane is by three amine nitrogens of dien and the amine nitrogen of α -Ala(P) and phosphonic oxygen completes the coordination number to five by binding in Cu²⁺ in axial position. The co-ordination mode in the [Cu(Me₅dien)(α -Ala(P))] species is the same as in the case of [Cu(dien)(α -Ala(P))], but the geometry of this heteroligand species deviated strongly from square pyramidal towards trigonal bipyramidal due to the steric effect of the two methyl substituents at each nitrogen atom.

Acknowledgements We would like to express our gratitude to Ms Jadwiga Kędzierska for her technical assistance in the EPR measurements.

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