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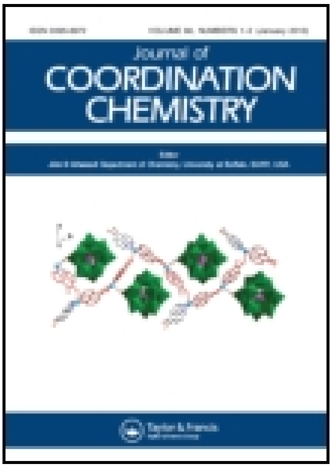

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Review: Solution equilibria of ternary complexes formed from copper(II), aliphatic amines, and bioligands

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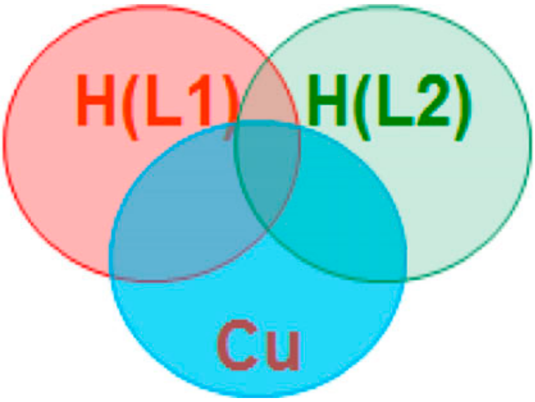

This review provides a summary of the coordination chemistry of ligands in the ternary system: copper(II)–aliphatic amine–bioligand, where amine = ethylenediamine – En, diethylenetriamine – Dien, or N, N, N′, N″, N″-pentamethyldiethylenetriamine – Me$_5$dien, and bioligand = selected amino acid, aminohydroxamic acid, or aminophosphonic acid, in aqueous solution. We would like to show the specific interactions of copper(II) in ternary systems in the context of complex equilibria chemistry.

Keywords: Copper(II) complexes; Amines; Bioligands; Heteroligand complexes; Stability constants; Equilibria

1. Introduction

Heteroligand complex formation occurs commonly in biological fluids, with several potential ligands, including certain amino acids [1, 2], peptides [3], peptide derivatives, or their analogs [4, 5]. The solution speciation of metal–bioligand complexes [6–9] is significant in reaching a more complete understanding of how bioligands interact with the active site of enzymes (e.g. inhibition of metalloenzymes); the reagents constituting ternary systems:

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metal ion–enzyme–bioligand are promising models for investigation of the biological activity and transport processes of metal ions [10–13].

To our best knowledge, there is no review on the ternary systems: metal ion–amine–amino acid/aminophosphonic acid or aminohydroxamic acid in aqueous solution, although amino acids, aminophosphonic acids, and aminohydroxamic acids are very important classes of compounds, which traverse coordination chemistry, chemical biology, and medical science.

We have found only two X-ray structures of the considered copper(II) heteroligand complexes: $[Cu(Me_5dien)(\text{L-val})]ClO_4$ and $[Cu(Me_5dien)(aiba)]ClO_4$ [14] and our efforts to get crystals of this type of complexes with polyamine and bioligands listed below have failed.

On the one hand, we know that: "there is no more basic enterprise in chemistry than the determination of the geometrical structure of a molecule. Such a determination when it is well done, ends speculations and provides us with the starting point for the understanding of every physical, chemical and biological properties of the molecule" [15] and on the other hand, we are aware that probably there are compounds that are unable to be crystallized which warrant solution studies but X-ray structure is a structure in the solid state – no solvent or other types of interactions.

Thus, we have decided to study the ternary systems: copper(II)–aliphatic amine–bioligand in aqueous solution.

Many questions concerning the role of metals in living organisms are still far from solved. Their explanation, first of all, needs full recognition of the character of metal-amines as well as polyamine–bioligand interactions in model binary systems, preceding investigation of ternary systems, in water solutions [16, 17].

We have chosen copper(II) as the metal ion because of its role in biosystems [18–26] and because the coordination sphere of this metal ion is characterized by its plasticity [27]. Apart from that, copper(II) binds quite strongly to studied amine molecules in planar position thus, the $[Cu(amine)]^{2+}$ complex could be an ideal receptor for a given bioligand, offering it vacant binding sites, to form the heteroligand species – [Cu(II)–amine–bioligand]. As primary ligands, we have chosen polyamine L1 because they may introduce geometrical selectivity while, amino acid, aminophosphonic acid, and aminohydroxamic acid played a role as a secondary one, L2.

The history of the phosphonic acids is strongly connected with the discovery of aminophosphonic acids in living organisms in the 1940s [28–30]. Since then, a number of excellent articles on various aspects of the chemistry or biological activity of phosphonates and phosphonic acids have appeared. In 2005, a first review on the solution and solid-state complexation features for two classes of diphosphonic acids, with *gem*-phosphonic–phosphonate groups or with a C–N–C spacer between them, appeared [31]. In particular, the coordination and supramolecular networks in their complexes, the geometrical and charge preferences of the metal ions, and the influence of the counter ions were discussed in this review. In 2012, a review on coordination chemistry of mono-, bis- and polyphosphonates, as well as of their functionalized analogs, their specific interactions with various metal ion complexes and bioapplications were presented [32]. In this review, the binary systems were only presented.

In 1978, a first review on hydroxamic acid complexes appeared [33]. Fourteen years later another review [34] was devoted to chemistry of complex equilibria in aqueous solutions, mainly. In this review, there are two important discoveries: (a) in hydroxamic derivatives of amino acids, the NH_3^+ group of α-derivative is somewhat more acidic than the COONHOH function, while the acidity sequence is opposite for the β-derivative and (b) stable metallacrown with β-alaninehydroxamic acid (β-Alaha) – $[Cu_5(\beta\text{-Alaha})_4H_{-4}]$ exists in

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solution as well as in solid state. In this review, there are only a few examples of ternary systems with aminehydroxamic acids, which exist in solution. In 2007, a review on the different aspects of metallacrown chemistry appeared and the expanse of metallacrown structures has been analyzed [35]. The review [36] discusses briefly the solution chemistry of metal–hydroxamic acid complexes as a prelude to highlighting the roles that hydroxamic acids play in chemical biology. In the review [37], the overall thermodynamic parameters for the formation of a wide number of metallacrown (12-MC-4) species of α-, β-, and γ-aminehydroxamates were discussed. This review includes structural investigations on metallacrowns (15-MC-5) as anion receptors as well as the thermodynamics of host–Quest solution equilibria of metallacrown complexes as receptors for carboxylates, which has been studied only very recently [38–40].

Some hydroxamic acids are effective inhibitors of metalloproteinase, which have been proved to involve the hydroxamate/aminohydroxamate coordination to the nickel [41, 42], copper [43–45] or zinc [46–49] of the enzymes.

This review describes the examination of coordination equilibria in aqueous solution in ternary systems containing copper(II), polyamine, and bioligand. Potentiometric data combined with spectroscopic parameters (electronic absorption spectra and electron paramagnetic resonance) are presented and discussed. Potentiometry enables the detection of different simple and heteroligand species formed in solution as well as the determination of their thermodynamic stability and species distribution relative to solution pH. Spectroscopic data can be used to identify the type and number of donor atoms involved in metal ion coordination as well as geometry of heteroligand complexes.

In the present review:

(1) We collect cumulative formation constants, derived equilibrium constants as well as Vis and EPR spectral parameters for heteroligand complexes formed in the ternary systems containing copper(II), polyamine, and bioligand.
(2) We discuss general properties of the selected ligands, complex equilibria in the ternary systems with these bioligands, stability relations in the ternary systems and factors as well as specific effects occurring in the ternary systems influencing the formation and structure of heteroligand complexes.
(3) We present schematic representations showing the possible structures of the heteroligand complexes formed in the Cu(II) ternary systems. When possible the information obtained in solution has been integrated with structural details of the complexes.

2. General properties of amines and bioligands

The compounds of interest are presented in scheme 1. Aminophosphonic acids and aminohydroxamic acids are broadly defined as amino acid analogs in which the carboxylic function is replaced by a phosphonic function in the former case and a hydroxamic function in the latter one.

The differences in structure, size, basicity, and charge can be easily observed (schemes 1 and 2). These properties are crucial in the complex-forming abilities of these ligands in the binary systems as well as in the ternary ones.

Some of the considered bioligands have been also characterized by X-ray crystallography. In α-amino acids, the configuration of the group H_3N^+–CH–COO^- is similar [50–53]. The nitrogen lies out of the plane formed by carboxylate group. The considered aminophosphonic

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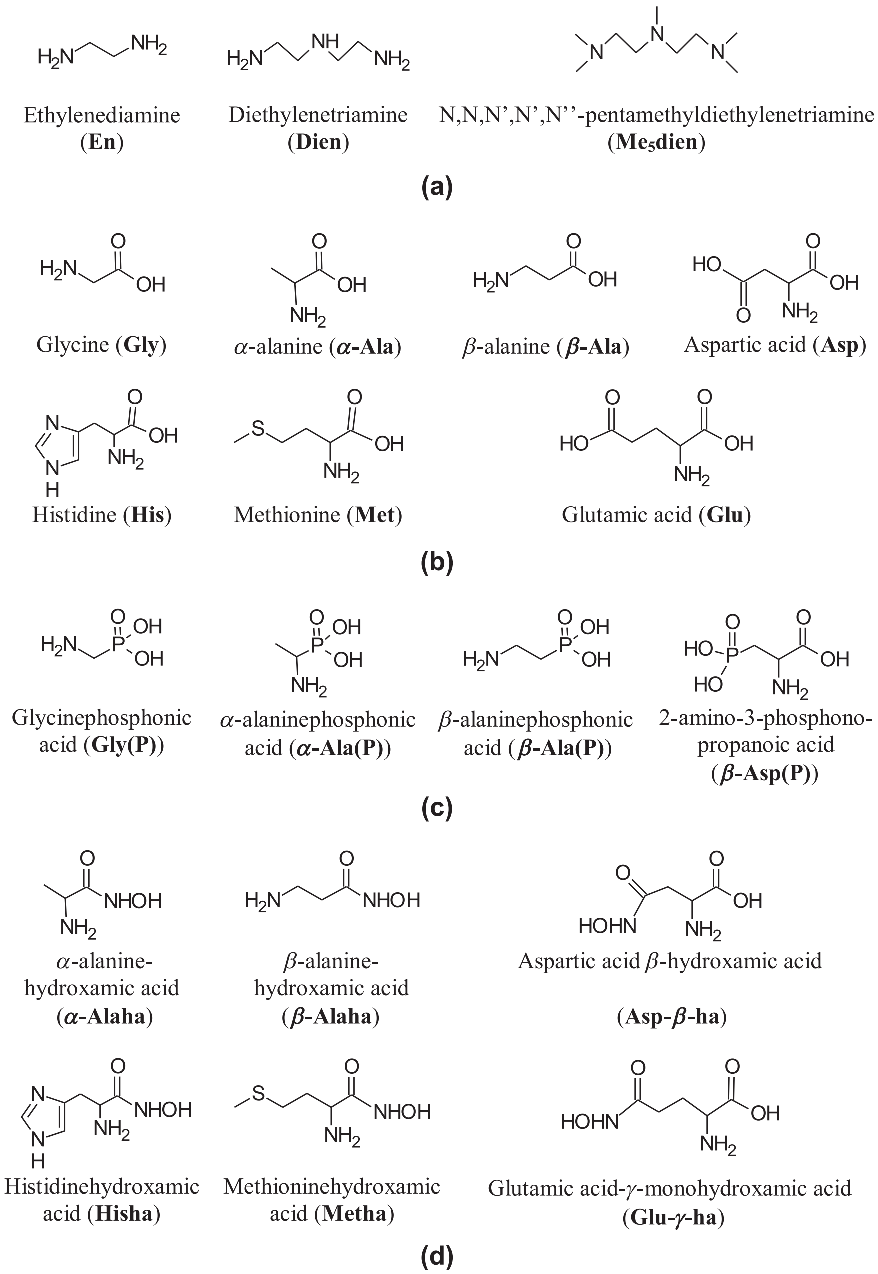

Scheme 1. The compounds under consideration: amines (a), amino acids (b), aminophosphonic acids (c), and aminohydroxamic acids (d).

acids crystallize in their zwitterionic form in which the acidic phosphonate moiety donates one proton to the amino group [54–57]. The phosphonic group is negatively charged, the charge being equally distributed between O(1) and O(3), P–O lengths which are shorter than P–O(2)H bond [the P–O(2)H bond length indicates a single bond]. In the case of

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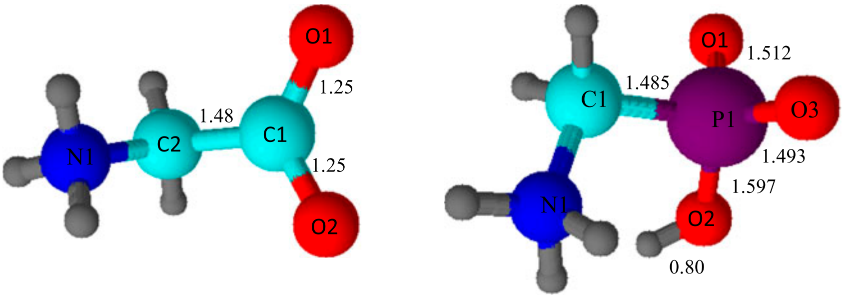
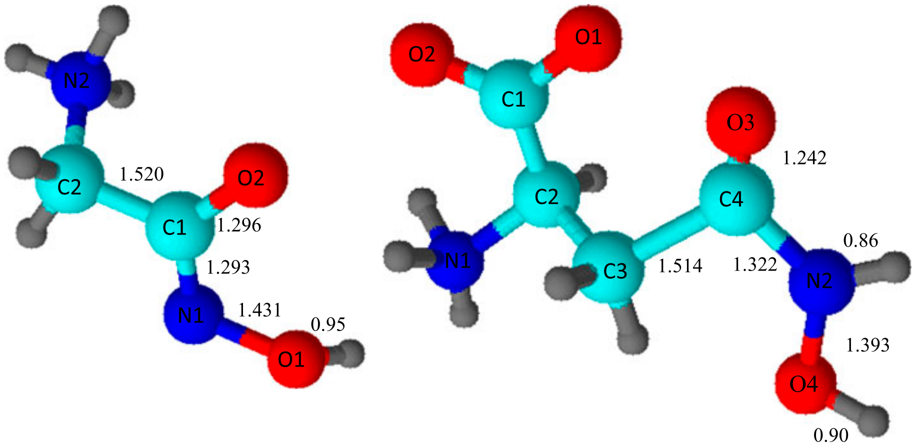


(a) Gly (b) Gly(P)



(c) Glyha (d) Asp-β-ha

Scheme 2. The crystal structures of selected ligand molecules, glycine (Gly) adapted from [53] (a), glycinephosphonic acid (Gly(P)) adapted from [54] (b), glycinehydroxamic acid (Glyha, ionized form) adapted from [58] (c), aspartic acid β-hydroxamic acid (Asp-β-ha) adapted from [59] (d).

aminohydroxamic acids, the bond lengths in the molecule are distinctly different when the hydroxamic moiety is in its completely protonated (like in Asp-β-ha) or ionized form (like in Glyha) [58, 59]. This group forms a planar and rigid structure (scheme 2). In the solid state, Asp-β-ha (β-aminohydroxamic acid) exists in the structure as a zwitterion, $^{-}$OOCCH(NH_3^+) $CH_2C(O)NHOH$ [59].

Extensive work on the acid-base properties of the reviewed ligands has been performed and many references can be found in the literature, e.g. for polyamines [60–70], amino acids [71–85], aminophosphonic acids [68, 86–93], and aminohydroxamic acids [34, 94–103].

There is a distinct difference in acid-base properties of amino acids, amoniphosphonic acids, and aminohydroxamic acids (L2 ligand), playing the role of the secondary ligand in the ternary systems.

The most acidic function is carboxyl group ($pK_{(\alpha\text{-COOH})} \approx 2$ and $pK_{(\beta\text{-COOH})} \approx 3.7$–4 [72]). The phosphonic $-PO_3H^-$ group is more basic than the carboxylic one. The first proton on the phosphonic $-PO_3H_2$ group is very acidic ($pK_{(PO_3H_2)} \leq 1$) [87, 89, 104]. So, only one proton is dissociated from $-PO_3H^-$ in the measurable pH range (2–11.5). The $pK_{(PO_3H^-)}$ values vary from 5.5 to 6.5 [32, 88, 93]. The most basic moieties are amino group and hydroxamic function in the selected ligands. The pK_a values characteristic for the

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dissociation of $–NH_3^+$ group in the amino acids are ≈9–10 and in aminophosphonic acids are ≈10–11 [72, 74, 80, 81, 84, 85, 88–93]. The fully deprotonated carboxyl, phosphonic, and hydroxamic groups are negatively charged ($-COO^-$, $–PO_3^{2-}$ and $–CO–NHO^-$) but the highest negative charge is concentrated on phosphonic function (scheme 2). The fully deprotonated molecules of the presented aliphatic amines (L1 ligand) are neutral.

In the case of histidine and its hydroxamic derivative, an additional donor that can be protonated is imidazole nitrogen. The pK_{im} values characteristic for the proton dissociation from these donor groups of His and Hisha are 6 and 5.4, respectively [81, 100, 102]. The dissociation of the second proton of the imidazole group ($pK_a \sim 14$) is beyond the pH-metric titration range and does not participate in the metal coordination equilibria [105].

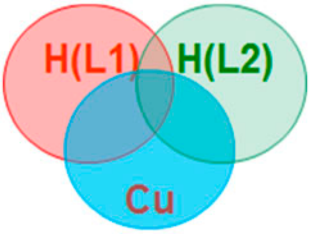
Some information about complexes formed in the binary systems is crucial for analysis of the heteroligand complexes formed in the ternary systems. The results of equilibrium studies of copper(II)–polyamine binary systems are presented in different articles, Cu^{2+}–En [61, 106–109], Cu^{2+}–Dien [64, 65, 100, 110] and Cu^{2+}–Me_5dien [64, 67].

The results of copper(II) equilibrium studies with L2 ligands, i.e. amino acids are presented in articles [64, 71–73, 75, 76, 79, 80, 82, 83, 88, 93, 111–121] and with their structural analogs – aminophosphonic acids [32, 68, 85–88, 91, 93, 122, 123] or aminohydroxamic [34, 36, 37, 98, 100, 101, 103, 123–129].

3. Complexation in the Cu^{2+}–L1–L2 ternary systems

The investigations of complex equilibria in the ternary systems are important in the context of biological systems. Studies of the ternary systems must be preceded by investigation of the binary systems with the same ligands that are involved in the ternary systems in the same experimental conditions (concentrations of the components, ionic strength, and measurement equipment). All complex equilibria that take place in the binary systems have to be also considered in the ternary systems and all possible coordination modes in the binary systems must be known.

Mixed chelation as defined here is the coordination of the same metal ion [copper(II)] by at least one polyamine ligand, L1, and a bidentate or tridentate ligand, L2, which are amino acid, aminophosphonic acid, or aminohydroxamic acid.



For the ternary systems considered in this review, the four-component equilibria can be described as:

$$p\mathrm{Cu} + q(\mathrm{L1}) + r(\mathrm{L2}) + s\mathrm{H} \rightleftharpoons \mathrm{Cu_p(L1)_q(L2)_rH_s}$$

where p, q, r, and s are the stoichiometric coefficients corresponding to Cu^{2+}, polyamine (L1 = En, Dien or Me_5dien), bioligand (L2 = amino acid, aminophosphonic acid, or aminohydroxamic acid) and H, respectively; charges are omitted for simplicity.

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Table 1. Cumulative formation constants (log β), derived equilibrium constants (log K), and characteristic parameters for the stability of $Cu_p(L1)_q(L2)_rH_s$ heteroligand complexes formed in the ternary systems Cu^{2+}-amine (L1 = En, Dien or Me_5dien) – bioligand (L2 = amino acid) at 25 °C. (Charges are omitted for simplicity.)

	Compound L2, I mol·dm^{-3}							
	Gly		α-Ala		β-Ala	Met	His	
Assignments	$I = 0.1$ Ref. [135]	$I = 0.2$ Ref. [106]	$I = 0.2$ Ref. [130]	$I = 0.1$ Ref. [138]	$I = 0.1$ Ref. [135]	$I = 0.2$ Ref. [121]	$I = 0.2$ Ref. [130]	$I = 0.2$ Ref. [136]
Log $\beta_{[Cu(En)(L2)H]}$								24.21
Log $\beta_{[Cu(En)(L2)]}$	17.91	17.69	17.66	17.949	16.58	17.33	19.47	19.46
Log $K_{[Cu(En)(L2)]}$	7.47	7.12	7.08	7.426^a	6.14	6.75	8.89	8.89^b
$[Cu(En)] + L2 \rightleftharpoons [Cu(En)(L2)]$								
Log $K_{[Cu(En)(L2)]} - pK_{NH_3^+} - pK_{COOH}$	−4.54	−4.79	−4.96	−4.734^a	−7.64	−4.59		
Log $K_{[Cu(En)(L2)]} - pK_{NH_3^+} - pK_{im}$							−6.27	
Log $X_{[Cu(En)(L2)]}$	1.03	0.86		1.123^a	0.88	0.66	1.20	1.42^b
ΔLog K	−0.80	−0.95		−0.90	−0.93	−1.01	−1.22	−1.15
	$I = 0.1$ Ref. [64]	$I = 0.1$ Ref. [146]	$I = 0.1$ Ref. [64]		$I = 0.2$ Ref. [131]	$I = 0.2$ Ref. [121]	$I = 0.2$ Ref. [130]	
Log $\beta_{[Cu(Dien)(L2)H2]}$	30.31		31.29					
Log $\beta_{[Cu(Dien)(L2)H]}$	27.57						27.56	
Log $\beta_{[Cu(Dien)(L2)]}$	20.53		20.16		19.41	19.46	20.77	
Log$\beta_{[Cu(Dien)(L2)\ H_{-1}]}$	9.90		9.65					
Log $K_{[Cu(Dien)(L2)]}$	4.50^c	4.42	4.13^c		3.40	3.45	4.76	
$[Cu(Dien)] + L2 \rightleftharpoons [Cu(Dien)(L2)]$								
Log $K_{[Cu(Dien)(L2)]} - pK_{NH_3^+} - pK_{COOH}$	−7.42^c		−7.89^c		−10.23	−7.89		
Log $K_{[Cu(Dien)(L2)]} - pK_{NH_3^+} - pK_{im}$							−10.40	
Log $X_{[Cu(Dien)(L2)]}$						3.89	2.77	
ΔLog K	−3.62		−3.98			−4.31	−5.35	
	$I = 0.1$ Ref. [64]		$I = 0.1$ Ref. [64]		$I = 0.2$ Ref. [131]	$I = 0.2$ Ref. [121]	$I = 0.2$ Ref. [130]	
Log$\beta_{[Cu(Me_5dien)(L2)H2]}$	28.66		28.58					
Log$\beta_{[Cu(Me_5dien)(L2)H]}$	24.43		24.51				24.53	
Log$\beta_{[Cu(Me_5dien)(L2)]}$	17.514		17.331		15.44	16.79	17.09	
Log$K_{[Cu(Me_5dien)(L2)]}$	5.31^c	5.13^c			3.02	4.32	4.62	
$[Cu(Me_5dien)] + L2 \rightleftharpoons [Cu(Me_5dien)(L2)]$								
Log$K_{[Cu(Me_5dien)(L2)]} - pK_{NH_3^+} - pK_{COOH}$	−6.61^c	−6.89^c			−10.61	−7.02		
Log$K_{[Cu(Me_5dien)(L2)]} - pK_{NH_3^+} - pK_{im}$								
ΔLog K	−2.81	−2.98				−3.44	−5.49	

[a] Values calculated basing on data taken from Ref. [138].
[b] Values calculated basing on data taken from Ref. [136].
[c] Values calculated basing on data taken from Ref. [64].

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The cumulative formation constants are defined as:

$$\beta_{\mathrm{pqrs}} = \frac{\left[\mathrm{Cu_p(L1)_q(L2)_rH_s}\right]}{[\mathrm{Cu}]^p[(\mathrm{L1})]^q[(\mathrm{L2})]^r[\mathrm{H}]^s}$$

where [Cu], [L1], [L2], and [H] stand for the concentrations of the free components.

The equilibrium models for the considered ternary systems and the corresponding stability constants for copper(II) heteroligand complexes of amines and amino acids, aminophosphonic acids or aminohydroxamic acids are collected in tables 1–3, respectively. The representative species distribution curves for the selected ternary systems of amino acids [i.e. Cu(II)-polyamine-Met], aminophosphonic acid [i.e. Cu(II)-polyamine-α-Ala(P)], and aminohydroxamic acid [i.e. Cu(II)-polyamine-Metha] are presented in figures 1–3, respectively. Vis and EPR spectral parameters of the considered copper(II) heteroligand complexes formed in the $\mathrm{Cu^{2+}}$–amine–bioligand ternary systems are listed in table 4.

Apart from Cu(II)–En–β-Alaha/Asp-β-ha [101, 107] in all discussed ternary systems, the heteroligand complexes with [Cu(L1)(L2)] stoichiometry are formed (tables 1–3). In many ternary systems, the formation of protonated heteroligand species has been observed, especially for systems with tridentate polyamines – Dien and $\mathrm{Me_5}$dien [64, 67, 68, 90–92, 99–101, 103, 130, 131] or bioligands with an additional coordination site, such as β-Asp(P)

Table 2. Cumulative formation constants (log β), derived equilibrium constants (log K), and characteristic parameters for the stability of $\mathrm{Cu_p(L1)_q(L2)_rH_s}$ heteroligand complexes formed in the ternary systems $\mathrm{Cu^{2+}}$ – amine (L1 = En, Dien or $\mathrm{Me_5}$dien) – bioligand (L2 = aminophosphonic acid) at 25 °C and $I = 0.2$ M dm^{-3} (KCl). (Charges are omitted for simplicity.)

	Compound L2			
Assignments	Gly(P) Ref. [90]	α-Ala(P) Ref. [91]	β-Ala(P) Ref. [92]	β-Asp(P) Ref. [68]
$\mathrm{Log}\,\beta_{[\mathrm{Cu(En)(H\text{-}L2)}]}$				25.29
$\mathrm{Log}\,\beta_{[\mathrm{Cu(En)(L2)}]}$	17.50	17.929	17.37	19.05
$\mathrm{Log}\,\beta_{[\mathrm{Cu(En)(L2)\,H_{-1}}]}$	5.98	6.22	6.17	
$\mathrm{Log}\,K_{[\mathrm{Cu(En)(L2)}]}$	6.92	7.349	6.79	8.47
$[\mathrm{Cu(En)}] + \mathrm{L2} \rightleftharpoons [\mathrm{Cu(En)(L2)}]$				
$\mathrm{Log}\,K_{[\mathrm{Cu(En)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{PO_3H^-}}$	−8.395	−8.2385	−10.29	−8.20
$\mathrm{Log}\,K_{[\mathrm{Cu(En)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{COOH}}$				−4.44
$\mathrm{Log}\,X_{[\mathrm{Cu(En)(L2)}]}$	0.99	1.178	0.47	1.69
$\Delta\mathrm{Log}\,K$	−1.05	−0.945	−1.47	−1.33
$\mathrm{Log}\,\beta_{[\mathrm{Cu(Dien)(H\text{-}L2)}]}$	27.54			28.57
$\mathrm{Log}\,\beta_{[\mathrm{Cu(Dien)(L2)}]}$	20.40	20.47	19.85	21.19
$\mathrm{Log}\,K_{[\mathrm{Cu(Dien)(L2)}]}$	4.39	4.46	3.84	5.18
$[\mathrm{Cu(Dien)}] + \mathrm{L2} \rightleftharpoons [\mathrm{Cu(Dien)(L2)}]$				
$\mathrm{Log}\,K_{[\mathrm{Cu(Dien)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{PO_3H^-}}$	−10.925	−11.1275	−13.24	−11.49
$\mathrm{Log}\,K_{[\mathrm{Cu(Dien)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{COOH}}$				−7.73
$\mathrm{Log}\,X_{[\mathrm{Cu(Dien)(L2)}]}$	5.76	5.23	5.43	5.97
$\Delta\mathrm{Log}\,K$	−3.58	−3.834	−4.42	−4.62
$\mathrm{Log}\,\beta_{[\mathrm{Cu](Me_5dien)(L2)}]}$	16.286	16.57	16.59	17.80
$\mathrm{Log}\,K_{[\mathrm{Cu](Me_5dien)(L2)}}$	3.816	4.10	4.12	5.33
$[\mathrm{Cu(Me_5dien)}] + \mathrm{L2} \rightleftharpoons [\mathrm{Cu(Me_5dien)(L2)}]$				
$\mathrm{Log}\,K_{[\mathrm{Cu](Me_5dien)(L2)}} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{PO_3H^-}}$	−11.499	−11.4875	−12.96	−11.34
$\mathrm{Log}\,K_{[\mathrm{Cu](Me_5dien)(L2)}} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{COOH}}$				−7.58
$\Delta\mathrm{Log}\,K$	−4.154	−4.194	−4.14	−4.47

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Table 3. Cumulative formation constants (log β), derived equilibrium constants (log K), and characteristic parameters for the stability of $Cu_p(L1)_q(L2)_rH_s$ heteroligand complexes formed in the ternary systems Cu^{2+}-amine (L1 = En, Dien or Me_5dien) – bioligand (L2 = aminohydroxamic acid) at 25 °C and $I = 0.2\ M\,dm^{-3}$ (KCl). (Charges are omitted for simplicity.)

	Compound L2					
Assignments	α-Alaha Ref. [107]	β-Alaha Ref. [107]	Metha Ref. [151]	Hisha Ref. [151]	Asp-β-ha Ref. [101]	Glu-γ-ha Ref. [103]
Log $\beta_{[Cu(En)(H\text{-}L2)]}$		Heteroligand species are not formed			Heteroligand species are not formed	26.60
Log $\beta_{[Cu(En)(L2)]}$	20.57		19.81	20.32		21.35
Log $\beta_{[Cu(En)(L2)H_{-1}]}$	9.94					
Log $K_{[Cu(En)(L2)]}$	9.99		9.25	9.76		10.77
$[Cu(En)] + L2L2 \rightleftharpoons [Cu(En)(L2)]$						
Log $K_{[Cu(En)(L2)]} - pK_{NH_3^+} - pK_{NHOH}$	−7.10		−6.50	−6.41		
Log $K_{[Cu(En)(L2)]} - pK_{NH_3^+} - pK_{COOH}$						−1.13
Log $X_{[Cu(En)(L2)]}$	1.48		0.68	0.90		6.00
ΔLog K	−0.86		−1.16			
	Ref. [99]	Ref. [99]	Ref. [100]	Ref. [100]	Ref. [101]	Ref. [103]
Log $\beta_{[Cu(H\text{-}Dien)(H\text{-}L2)]}$				35.73		
Log $\beta_{[Cu(Dien)(H\text{-}L2)]}$	28.33	28.77	27.74	29.39	29.32	29.49
Log $\beta_{[Cu(Dien)(L2)]}$	21.11	19.99	20.57	21.06	20.54	20.58
Log $K_{[Cu(Dien)(L2)]}$	5.10	3.98	4.56	5.05	4.53	4.57
$[Cu(Dien)] + L2L2 \rightleftharpoons [Cu(Dien)(L2)]$						
Log $K_{[Cu(Dien)(L2)]} - pK_{NH_3^+} - pK_{NHOH}$	−11.44	−14.40	−11.18	−11.06	−13.16	
Log $K_{[Cu(Dien)(L2)]} - pK_{NH_3^+} - pK_{COOH}$						−7.28
Log $X_{[Cu(Dien)(L2)]}$	1.35		1.36	1.22		3.25
ΔLog K	−5.75	−8.91	−5.79			
	Ref. [131]	Ref. [67]	Ref. [131]	Ref. [131]	Ref. [101]	Ref. [103]
Log $\beta_{[Cu_2(Me_5dien)(L2)_2H_{-1}]}$	29.78		29.17	30.24		
Log $\beta_{[CuH-(Me_5dien)(H-L2)]}$		34.01			33.51	
Log $\beta_{[Cu(Me_5dien)(H-L2)]}$		27.76		27.23	27.66	27.25
Log $\beta_{[Cu(Me_5dien)(L2)]}$	18.86	18.91	18.42	18.86	18.74	17.61
Log $K_{[Cu(Me_5dien)(L2)]}$	6.39	6.44	5.95	6.39	6.40	5.12
$[Cu(Me_5dien)] + L2 \rightleftharpoons [Cu(Me_5dien)(L2)]$						
Log $K_{[Cu(Me_5dien)(L2)]} - pK_{NHOH}$						−3.30
Log $K_{[Cu(Me_5dien)(L2)]} - pK_{NH_3^+} - pK_{NHOH}$	−10.15	−11.77	−9.80	−9.78	−11.29	
ΔLog K	−4.57	−6.41	−4.46			

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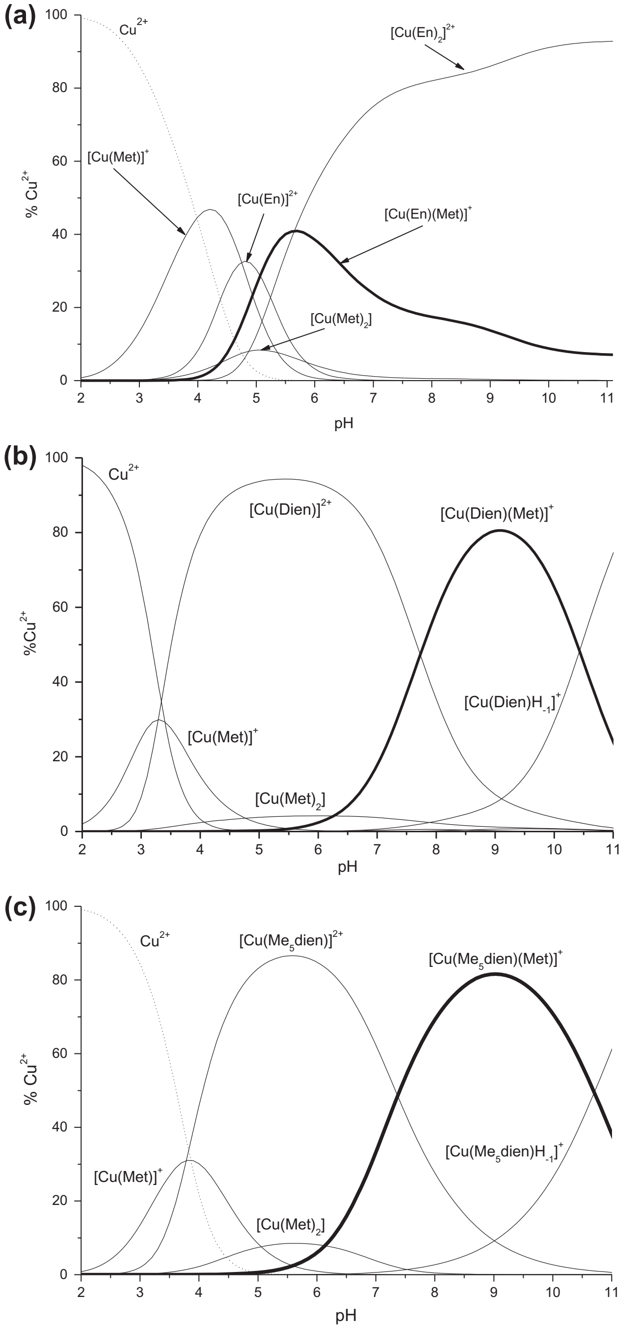

Figure 1. Species distribution curves as a function of pH for the ternary systems: Cu^{2+}–En–Met at 1 : 2 : 1 molar ratio (a), Cu^{2+}–Dien–Met (b), Cu^{2+}–Me_5dien–Met (c); at 1 : 1 : 2 molar ratio; $C_{Cu^{2+}} = 4 \times 10^{-3}$ mol dm^{-3}.

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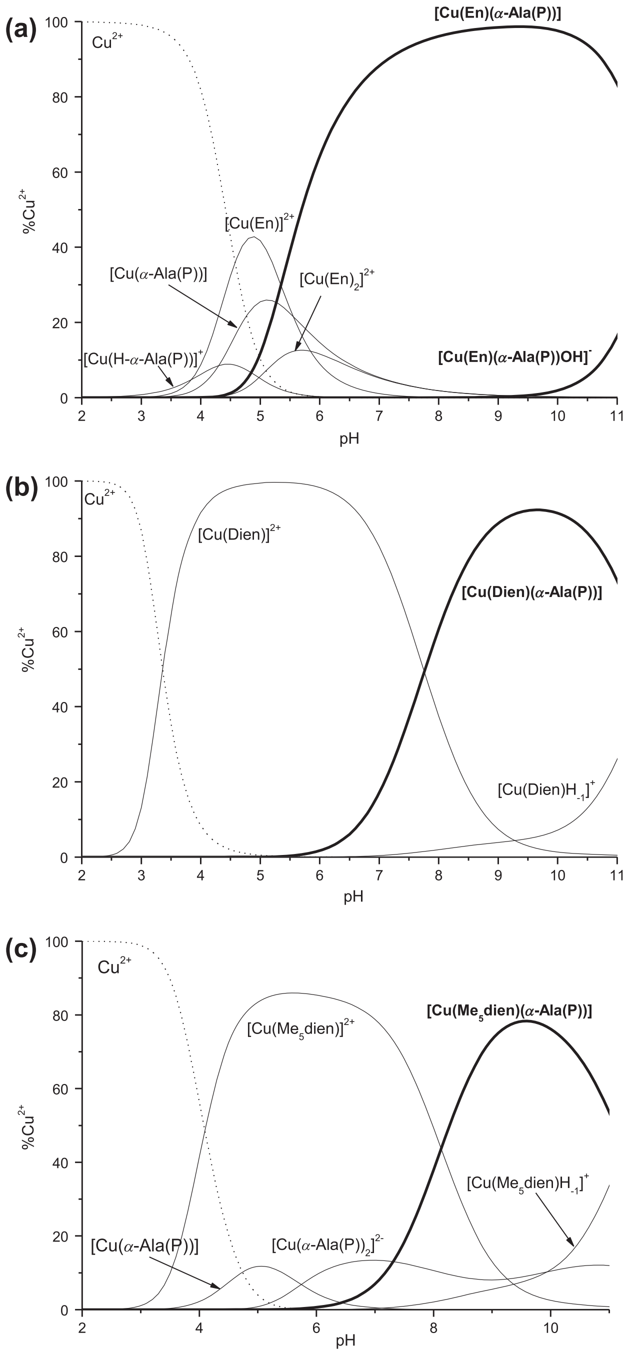

Figure 2. Species distribution curves as a function of pH for the ternary systems: Cu^{2+}–En–α-Ala (P) (a), Cu^{2+}–Dien–α-Ala(P) (b), Cu^{2+}–Me_5dien–α-Ala(P) (c); at 1 : 1 : 2 molar ratio; $C_{Cu^{2+}} = 4 \times 10^{-3}$ mol dm^{-3}.

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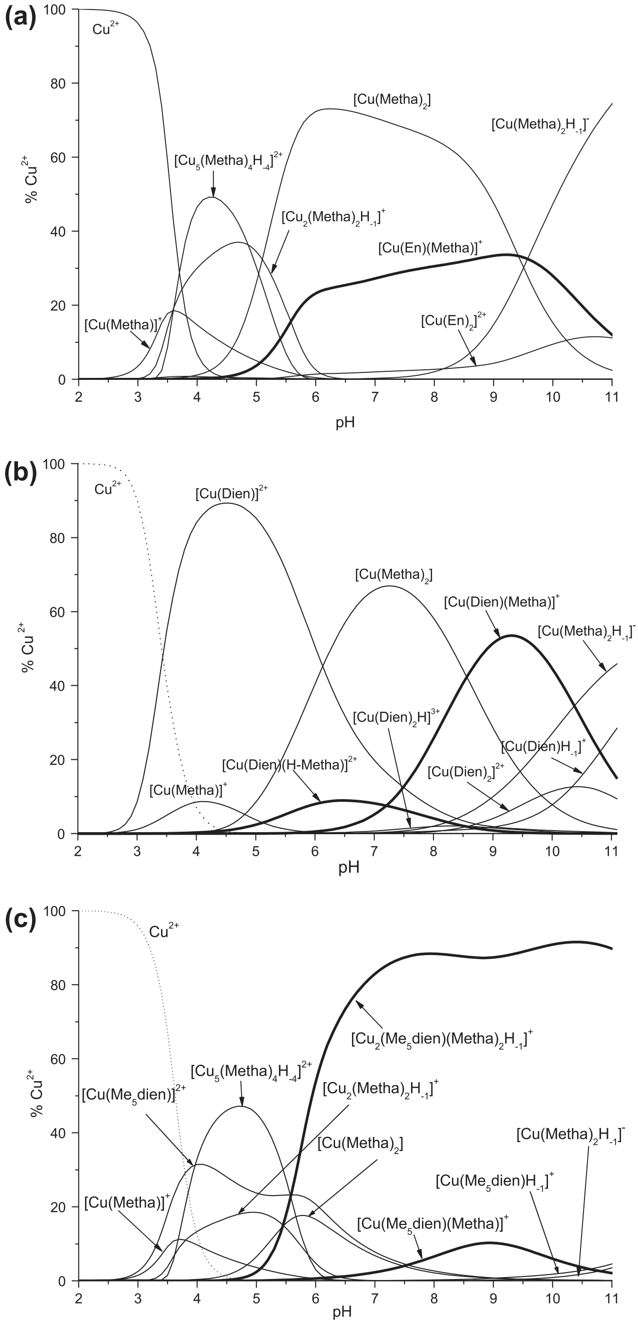

Figure 3. Species distribution curves as a function of pH for the ternary systems: Cu^{2+}–En–Metha at 1 : 1 : 2 molar ratio (a), Cu^{2+}–Dien–Metha at 1 : 1 : 2 molar ratio (b), Cu^{2+}–Me$_5$dien–Metha at 1 : 2 : 1 molar ratio (c); $C_{\mathrm{Cu}^{2+}} = 4 \times 10^{-3}$ mol dm^{-3}.

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Table 4. Vis and EPR spectral parameters of the copper(II) heteroligand complexes formed in the Cu^{2+}-amine (L1 = En, Dien or Me$_5$dien) – bioligand (L2 = amino acid, aminohydroxamic acid or aminophosphonic acid) ternary systems.

	EPR						Vis		
Species	g_{iso}	A_{iso} (10^{-4} cm^{-1})	$g_\parallel$	$A_\parallel$ (10^{-4} cm^{-1})	$g_\perp$	$A_\perp$ (10^{-4} cm^{-1})	λ_{max} (nm) ε (dm^3 mol^{-1} cm^{-1})	Coordination mode	Ref.
[Cu(En)(α-Ala)]$^+$			2.230	190	2.051	18	580 (58)	{NH$_2$, NH$_2$}; {NH$_2$, COO$^-$}	[130]
[Cu(En)(Met)]$^+$			2.234	193	2.050	21	582 (72)	{NH$_2$, NH$_2$}; {NH$_2$, COO$^-$}	[121]
[Cu(En)(His)]$^+$	2.111	81	2.218	196			581 (69)	{NH$_2$, NH$_2$}; {N$_{im}$, NH$_2$}+ ax COO$^-$	[130]
[Cu(En)(Gly(P))]	2.114	77	2.237	191	2.050	19	597 (54)	{NH$_2$, NH$_2$}; {NH$_2$, PO$_3^{2-}$}	[90]
[Cu(En)(α-Ala(P))]	2.114	79	2.235	190	2.050	19	595 (58)	{NH$_2$, NH$_2$}; {NH$_2$, PO$_3^{2-}$}	[91]
[Cu(En)(β-Ala(P))]	2.117	77	2.237	185	2.060	17	612 (85)	{NH$_2$, NH$_2$}; {NH$_2$, PO$_3^{2-}$}	[92]
[Cu(En)(β-Asp(P))]$^-$	2.116	79	2.232	195	2.051	19	595 (58)	{NH$_2$, NH$_2$}; {NH$_2$, COO$^-$, PO$_3^{2-}$}	[68]
[Cu(En)(Metha)]$^+$	2.098	85	2.193	205	2.045	19	547 (93.5)	{NH$_2$, NH$_2$}; {NH$_2$, N$_{ha}$}	[151]
[Cu(En)(Hisha)]$^+$	2.103	87	2.200	204	2.043	19	552(87)	{NH$_2$, NH$_2$}; {NH$_2$, N$_{ha}$}	[151]
[Cu(En)(Glu-γ-ha)]			2.237	194	2.052	20	620 (62)	{NH$_2$, NH$_2$}; {NH$_2$, COO$^-$, N$_{ha}$}	[103]
[Cu(Dien)(H-His)]$^{2+}$			2.213	198				{NH $_2$, NH, NH $_2$}; {N$_{im}$, COO$^-$}	[130]
[Cu(Dien)(His)]$^+$			2.224	180	2.048	15	640 (132)	{NH $_2$, NH, NH $_2$}; {NH$_2$, N$_{im}$}	[130]
[Cu(Dien)(α-Ala)]$^+$	g_1	g_2	g_3	A_1 (10^{-4} cm^{-1})	A_2 (10^{-4} cm^{-1})	A_3 (10^{-4} cm^{-1})	635 (106)	{NH $_2$, NH, NH $_2$};{NH$_2$, COO$^-$}	[130]
	2.217	2.054	2.043	190	30	15			
[Cu(Dien)(Met)]$^+$	2.215	2.054	2.044	193	29	14	635 (107)	{NH $_2$, NH, NH $_2$}; {NH$_2$, COO$^-$}	[121]
[Cu(Dien)(Gly(P))]	2.212	2.054	2.044	199	32	11	592 (103)	{NH $_2$, NH, NH $_2$}; {NH$_2$, PO$_3^{2-}$}	[90]
[Cu(Dien)(α-Ala(P))]	2.211	2.055	2.045	198	31	11	622 (93)	{NH $_2$, NH, NH $_2$}; {NH$_2$, PO$_3^{2-}$}	[91]
[Cu(Dien)(β-Ala(P))]	2.216	2.057	2.047	198	29	11	613 (122)	{NH $_2$, NH, NH $_2$}; {NH$_2$, PO$_3^{2-}$}	[92]
[Cu(Dien)(β-Asp(P))]$^-$	2.216	2.055	2.045	189	30	13	633 (100)	{NH $_2$, NH, NH $_2$}; {NH$_2$, COO$^-$}	[68]
[Cu(Dien)(α-Alaha)]$^+$							651 (119), 750 (sh)	{NH $_2$, NH, NH $_2$}; {NH$_2$, N$_{ha}$}	[99]
[Cu(Dien)(H-β-Alaha)]$^{2+}$	2.244	2.050	2.050	183	18	18	611 (76)	{NH $_2$, NH, NH $_2$}; {CO, O$^-$}	[99]
[Cu(Dien)(β-Alaha)]$^+$	2.212	2.049	2.049	194	18	18	755 (152), 752 (sh)	{NH $_2$, NH, NH $_2$}; {NH$_2$, N$_{ha}$}	[99]
[Cu(Dien)(Metha)]$^+$	2.210	2.055	2.045	180	40	15	634 (122), 750 (sh)	{NH $_2$, NH, NH $_2$}; {NH$_2$, N$_{ha}$}	[100]
[Cu(Dien)(H$_2$-Hisha)]$^{3+}$	2.220	2.055	2.055	194	20	20	586 (78)	{NH $_2$, NH, NH $_2$}; {N$_{im}$}	[100]
[Cu(Dien)(H-Hisha)]$^{2+}$	2.214	2.055	2.055	190	20	20	590 (89)	{NH $_2$, NH, NH $_2$}; {NH$_2$}	[100]
[Cu(Dien)(Hisha)]$^+$	2.215	2.058	2.048	180	40	15	632 (120)	{NH $_2$, NH, NH $_2$}; {NH$_2$, N$_{ha}$}	[100]
[Cu(Dien)(H-Asp-β-ha]$^+$	2.218	2.050	2.050	190	20	25	618 (75)	{NH $_2$, NH, NH $_2$}; {NH$_2$, COO$^-$}	[101]
[Cu(Dien)(Asp-β-ha]	2.215	2.055	2.045	186	35	15	Broad band 600–800 (~80)	{NH $_2$, NH, NH $_2$}; {NH$_2$, N$_{ha}$}	[101]
[Cu(Dien)(Glu-γ-ha)]	2.225	2.046	2.046	193	30	20	650 (86)	{NH $_2$, NH, NH $_2$}; {NH$_2$, COO$^-$}	[103]
[Cu(Me$_5$dien)(Gly)]$^+$							800 (260)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, COO$^-$}	[64]
[Cu(Me$_5$dien)(α-Ala)]$^+$	2.208	2.138	2.007	135	20	62	777 (275)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, COO$^-$}	[130]
[Cu(Me$_5$dien)(Met)]$^+$	2.205	2.140	2.008	132	20	61	784 (294)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, COO$^-$}	[121]
[Cu(Me$_5$dien)(His)]$^+$	2.215	2.130	2.010	141	20	61	772 (286)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{im}$} or {NH$_2$, COO$^-$}	[130]

(*Continued*)

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Table 4. (*Continued*).

	EPR						Vis		
Species	g_{iso}	A_{iso} (10^{-4} cm^{-1})	$g_{\parallel}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$g_{\perp}$	$A_{\perp}$ (10^{-4} cm^{-1})	λ_{max} (nm) ε (dm^3 mol^{-1} cm^{-1})	Coordination mode	Ref.
[Cu(Me$_5$dien)(Gly(P))]	2.236	2.165	2.01	125	19	66	~827 (231), 750 (sh)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, PO$_3^{2-}$}	[90]
[Cu(Me$_5$dien)(α-Ala(P))]	2.237	2.160	2.01	128	17	65	~848 (219), 752 (sh)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, PO$_3^{2-}$}	[91]
[Cu(Me$_5$dien)(β-Ala(P))]	2.225	2.067	2.047	184	31	12	657 (166)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, PO$_3^{2-}$}	[92]
[Cu(Me$_5$dien)(β-Asp(P))]$^-$	2.209	2.139	2.005	133	21	60	794 (238)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, COO$^-$}	[68]
[Cu(Me$_5$dien)(α-Alaha)]$^+$	2.23	2.165	2.040	172	86	20	609, 790	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{ha}$}	[67]
[Cu(Me$_5$dien)(Metha)]$^+$	2.23	2.10	2.03	176	87	17		{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{ha}$}	[131]
[Cu$_2$(Me$_5$dien)(Metha)$_2$H$_{-1}$]$^+$	EPR silent species						624 (254), 780 (268)	{N(CH$_3$)$_2$, N(CH$_3$), N (CH$_3$)$_2$}; {NH$_2$, N$_{ha}$} and {CO, O$^-$} {NH$_2$, N$_{ha}$}	[131]
[Cu(Me$_5$dien)(H-Hisha)]$^{2+}$	2.22	2.08	2.02	173	50	15		{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{im}$}	[131]
[Cu(Me$_5$dien)(Hisha)]$^+$	2.22	2.10	2.02	165	81	19		{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{ha}$}	[131]
[Cu$_2$(Me$_5$dien)(Hisha)$_2$H$_{-1}$]$^+$	EPR silent species						645 (250), 786 (256)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{ha}$} and {CO, O$^-$} {NH$_2$, N$_{ha}$}	[131]
[Cu(Me$_5$dien)(H-β-Alaha)]$^{2+}$	2.33	2.060	2.030	173	40	15	610, 753	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {CO, O$^-$}	[67]
[Cu(Me$_5$dien)(β-Alaha)]$^+$	2.235	2.087	2.030	170	50	20		{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{ha}$}	[67]
[Cu(H-Me$_5$dien)(H-Asp-β-ha]$^{2+}$	2.24	2.055	2.055	175	15	15		{NH$^+$(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, COO$^-$}	[101]
[Cu(Me$_5$dien)(H-Asp-β-ha]$^+$	2.235	2.055	2.030	174	30	15	610 (85), 750 (78)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, COO$^-$}	[101]
[Cu(Me$_5$dien)(Asp-β-ha]	2.233	2.065	2.035	174	50	20	750 (117)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {NH$_2$, N$_{ha}$}	[101]
[Cu(Me$_5$dien)(Glu-γ-ha)]	2.230	2.060	2.050	179	55	20	~600 sh, 769 (197)	{N(CH$_3$)$_2$,N(CH$_3$),N(CH$_3$)$_2$}; {CO, O$^-$}	[103]

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[68] or Glu-γ-ha [103]. For a few ternary systems, the existence of hydroxo heteroligand complexes in solution has been also denoted [90–92, 107, 130]. The formation of completely different heteroligand complexes was reported for copper(II)–Me$_5$dien–α-Alaha/Metha/Hisha ternary systems. In these systems, binuclear heteroligand species of [Cu$_2$(Me$_5$dien)(L2)$_2$H$_{-1}$] type are formed [131, figure 3(c)].

When the stability constants β_{pqrs} for the heteroligand complexes Cu$_\mathrm{p}$(L1)$_\mathrm{q}$(L2)$_\mathrm{r}$H$_\mathrm{s}$ are determined, it is possible to define the stability of this species in relation to those of the parent binary complexes. For instance for the reaction:

$$\mathrm{Cu(L1)_2 + \ Cu(L2)_2 \rightleftharpoons 2Cu(L1)(L2)}$$

the position of this equilibrium and consequently the tendency of heteroligand complex formation are determined by the sign and the value of the $\log X_{[\mathrm{Cu(L1)(L2)}]}$ parameter:

$$\log X_{[\mathrm{Cu(L1)(L2)}]} = 2\log\beta_{[\mathrm{Cu(L1)(L2)}]} - \left(\log\beta_{[\mathrm{Cu(L1)_2}]} + \log\beta_{[\mathrm{Cu(L2)_2}]}\right)$$

The values of this parameter are collected in tables 1–3 for heteroligand complexes formed in the considered ternary systems with amino acids, aminophosphonic acids, and aminohydroxamic acids, respectively. The calculated values of $\log X_{[\mathrm{Cu(L1)(L2)}]}$ are higher than that expected on a statistical basis (0.6) [132]. This indicates that the formation of heteroligand complexes is favored in the ternary systems of En and Dien. For the [Cu(Me$_5$dien)(L2)] heteroligand species the $\log X_{[\mathrm{Cu(Me_5dien)(L2)}]}$ value cannot be calculated, since the complex with 1 : 2 metal to ligand ratio is not formed in the Cu^{2+}–Me$_5$dien binary system.

Despite the fact that the β_{1110} constant expresses the stability of the [Cu(L1)(L2)] heteroligand species, it does not represent directly the binding strength between L2 and copper (II) ions in the presence of polyamine. So, it is interesting to compare the stability of the binary complex with that of the heteroligand complex. The formation of heteroligand complexes from the parent complexes can be the result of two different reactions.

$$\mathrm{Cu\ + (L1) \rightleftharpoons Cu(L1)} \qquad\qquad \mathrm{Cu\ + (L2) \rightleftharpoons Cu(L2)}$$

$$\mathrm{K_{[Cu(L1)]}} = \frac{\mathrm{[Cu(L1)]}}{\mathrm{[Cu][(L1)]}} \qquad\qquad \mathrm{K_{[Cu(L2)]}} = \frac{\mathrm{[Cu(L2)]}}{\mathrm{[Cu][(L2)]}}$$

$$\mathrm{Cu(L1) + (L2) \rightleftharpoons Cu(L1)(L2)} \qquad\qquad \mathrm{Cu(L2) + (L1) \rightleftharpoons Cu(L1)(L2)}$$

$$\mathrm{K^{[Cu(L1)]}_{[Cu(L1)(L2)]}} = \frac{\mathrm{[Cu(L1)(L2)]}}{\mathrm{[Cu(L1)]\cdot[(L2)]}} \qquad\qquad \mathrm{K^{[Cu(L2)]}_{[Cu(L1)(L2)]}} = \frac{\mathrm{[Cu(L1)(L2)]}}{\mathrm{[Cu(L2)]\cdot[(L1)]}}$$

The relation between stability constants $\mathrm{K^{[Cu(L1)]}_{[Cu(L1)(L2)]}}$, $\mathrm{K^{[Cu(L2)]}_{[Cu(L1)(L2)]}}$ and $\log\beta_{[Cu(\mathrm{L1})(\mathrm{L2})]}$ can be given by the formulas:

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$$\log K^{[\mathrm{Cu(L1)}]}_{[\mathrm{Cu(L1)(L2)}]} = \log \beta_{[\mathrm{Cu(L1)(L2)}]} - \log \beta_{[\mathrm{Cu(L1)}]}$$

$$\log K^{[\mathrm{Cu(L2)}]}_{[\mathrm{Cu(L1)(L2)}]} = \log \beta_{[\mathrm{Cu(L1)(L2)}]} - \log \beta_{[\mathrm{Cu(L2)}]}$$

In the presented systems, first $[\mathrm{Cu(L1)}]^{2+}$ is formed and next L2 is coordinated and the heteroligand complex formed. The equilibrium constant, $\log K^{[\mathrm{Cu(L1)}]}_{[\mathrm{Cu(L1)(L2)}]}$, derived from the computed values of $\log \beta_{[\mathrm{Cu(L1)(L2)}]}$, according to above equation (tables 1–3), shows how tightly L2 ligand is bound to the simple $[\mathrm{Cu(L1)}]^{2+}$ complex. The stepwise stability constants of the heteroligand species are much lower for the complexes involving tridentate Dien and $\mathrm{Me_5}$dien than the stability constants of species containing bidentate En. In the case of Dien and $\mathrm{Me_5}$dien only one position in the plane remains available for the coordination of a second ligand.

The relative stability of [Cu(L1)(L2)] can be expressed in terms of $\Delta\log K$ parameter [the constant due to Cu(L1) + Cu(L2) = Cu(L1)(L2) + Cu equilibrium]. This constant can be calculated from the experimentally measured stability constants according to the equation: $\Delta\log K = \log \beta_{[\mathrm{Cu(L1)(L2)}]} - \log \beta_{[\mathrm{Cu(L1)}]} - \log \beta_{[\mathrm{Cu(L2)}]}$. The statistical value of $\Delta\log K$ depends on the geometry of the complex and for the distorted octahedral coordination sphere of Cu^{2+} with two different bidentate ligands was deduced as −0.9 [133, 134] (since more coordination positions are available for bonding of the first ligand to a given metal ion than for the second ligand, the stability constant for the formation of a 1 : 1 complex is usually greater than for the 1 : 2 complex, so $\Delta\log K$ should be negative). The calculated $\Delta\log K$ data for copper(II) heteroligand complexes of aliphatic amines with amino acid, aminophosphonic acids, and aminohydroxamic acids are listed in tables 1–3, respectively.

3.1. *Heteroligand complexes in ternary systems containing copper(II) ions, amines, and amino acids*

The copper(II) ternary systems with ethylenediamine as L1 and amino acids in the function of L2 have been studied by several authors [64, 106, 121, 130, 131, 135–138]. In these ternary systems, generally, one heteroligand species is formed $[\mathrm{Cu(En)(L2)}]^{+}$ (L2 = amino acid, table 1). This heteroligand complex starts to form above pH 4–5 and is present in basic solution at different concentrations depending on the amino acid [figure 1(a)] [121, 130]. The energy of d–d transition (~580 nm) and the EPR parameters ($g_{\|} = 2.230$–2.234, $A_{\|} = 190$–$193 \times 10^{-4}\ \mathrm{cm}^{-1}$) are typical for 3N coordination (table 4). For this type of heteroligand species, the tetragonal geometry around copper(II) and the formation of ($\mathrm{NH_2}$,$\mathrm{NH_2}$) and ($\mathrm{NH_2}$, $\mathrm{COO^-}$) chelates in the plane have been proposed [121] (scheme 3). In the case of $[\mathrm{Cu(En)(Met)}]^{+}$, the involvement of sulfur in the metal ion coordination has been excluded (figure 1) as the S(thioether) → Cu(II) charge transfer (CT) band was not observed in the UV region for this ternary system. The existence of such CT transition around 320–360 nm is generally a good indication of thioether coordination [139–141]. Although there is a wide range of studies focused on Cu(II) binding to a variety of peptides containing methionyl residue that revealed the possibility of S–Cu(II) interaction [141–144], the methionine itself was reported to act as a tridentate ligand for copper(II) ions only at low temperatures and at low pH values [145]. The spectroscopic parameters obtained for $\mathrm{Cu(En)(His)]^{+}}$ species are different (table 4). An apparent decrease of $g_{\|}$ and increase of $A_{\|}$ parameters for $[\mathrm{Cu(En)(His)}]^{+}$ in comparison to the parameters of $[\mathrm{Cu(En)(}\alpha\text{-Ala)}]^{+}$ or

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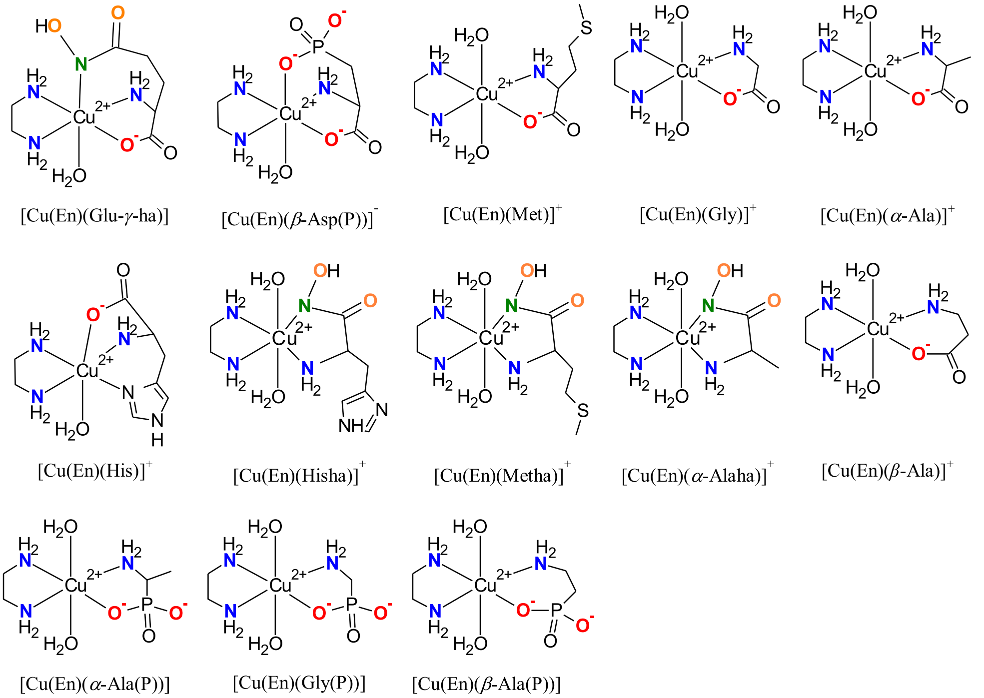
$[Cu(En)(Met)]^+$ supports the presence of a stronger in-plane ligand field [130]. So, it could be concluded that coordination in this heteroligand species is probably realized by amine nitrogen $\{NH_2, NH_2\}$ of En and amine and imidazole nitrogens $\{NH_2, N_{im}\}$ of His in the equatorial plane forming two five-membered chelate rings. A comparison of relative stability constants, which take into account the difference in the basicity of coordinating donor group, for heteroligand complexes of His with Gly or α-Ala (table 1) and His with histamine (−7.97, obtained from data published [106], where coordinating amine and imidazole nitrogens are included) excludes bidentate, histamine-like $\{N_{am}, N_{im}\}$ coordination mode of His in the heteroligand complex. In this species, His coordinates tridentate to copper(II) $\{N_{im}, NH_2, COO^-\}$ and the sixth position is occupied by water [130] (scheme 3).

Investigation of the copper(II) ternary systems with tridentate ligands Dien or Me_5dien and amino acids have been undertaken by a few authors [14, 64, 121, 130, 131, 146, 147]. In these ternary systems, complexation of $[Cu(Dien)]^{2+}$ or $[Cu(Me_5dien)]^{2+}$ by amino acids begins above pH 6 and reaches the maximum concentration at pH 8.5–10 [figures 1(b) and 2(c)] [64, 121, 130]. The effect of the heteroligand species formation is clearly observed in the electronic spectral changes as well as in the EPR spectra. The isolated electronic absorption spectrum for $[Cu(Dien)(L2)]^+$ demonstrates a broad band, asymmetric in the wavelength region 700–900 nm, with poorly noticeable maximum at $\lambda_{max} \sim 635$–640 nm (table 4). Such asymmetry is characteristic of five-coordinate complexes [121, 130]. The presence of a weak rhombic distortion in the EPR spectra obtained suggests that the geometry of these species is slightly deviated from square pyramidal towards trigonal bipyramidal [64, 147, 148].



$[Cu(En)(Glu\text{-}\gamma\text{-}ha)]$ $[Cu(En)(\beta\text{-}Asp(P))]^-$ $[Cu(En)(Met)]^+$ $[Cu(En)(Gly)]^+$ $[Cu(En)(\alpha\text{-}Ala)]^+$

$[Cu(En)(His)]^+$ $[Cu(En)(Hisha)]^+$ $[Cu(En)(Metha)]^+$ $[Cu(En)(\alpha\text{-}Alaha)]^+$ $[Cu(En)(\beta\text{-}Ala)]^+$

$[Cu(En)(\alpha\text{-}Ala(P))]$ $[Cu(En)(Gly(P))]$ $[Cu(En)(\beta\text{-}Ala(P))]$

Scheme 3. Schematic representations showing the possible structures of the selected complex species formed in the water solution of the Cu(II)–L1–L2 ternary systems (L1 – En, L2 – bioligand = amino acid, aminophosphonic acid, or aminohydroxamic acid).

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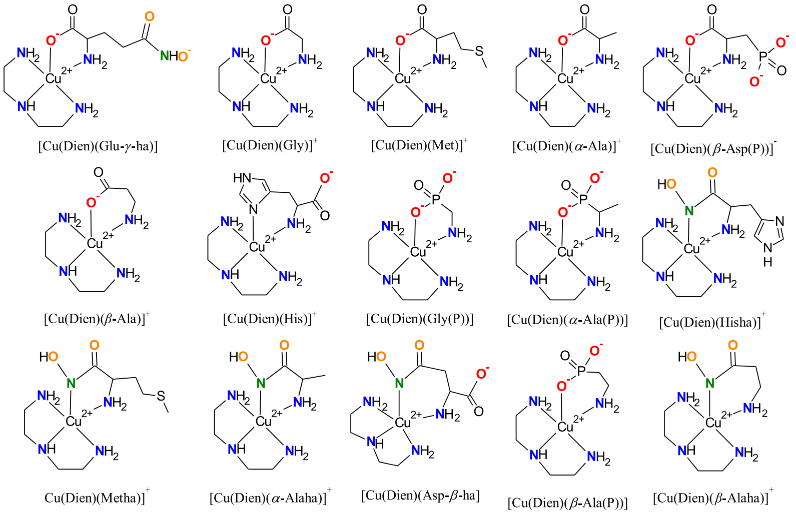
Table 5. Selected crystallographic data for copper(II) heteroligand complexes of Me_5dien and amino acids.

Compound	Space group	Cu–$N(CH_3)_2$	Cu–$N(CH_3)_2$	Cu–$N(CH_3)$	Cu–NH_2	Cu–O (COO^-)	Ref.
				Å			
[Cu(Me_5dien)(L-val)]ClO_4	$P6_5$	2.178	2.075	2.027	2.058	1.96	[14]
[Cu(Me_5dien)(aiba)]ClO_4	$P2_1/c$	2.144	2.110	2.028	2.097	1.918	[14]

Note: L-val = L-valinate and aiba = α-aminoisobutyrate anion.

On the basis of the energy of d–d transitions and EPR parameters (table 4), the [Cu(Dien)(L2)]$^+$ compounds were assigned coordination mode {NH_2, NH, NH_2}{NH_2, COO^-} (scheme 4). The binding of Cu^{2+} in the equatorial plane is realized by three amine nitrogens of Dien and the amine nitrogen of amino acid, whereas the carboxylic oxygen completes the coordination sphere at the axial position, independent of amino acid with the exception of His ligand [130]. In the case of [Cu(Dien)(His)]$^+$, the coordination mode of His is {NH_2, N_{im}} instead of {N_{im}, COO^-} leading to formation of a six-membered chelate ring instead of a five-membered ring like in the case of other amino acids (scheme 4).

Electronic spectral changes in the Cu^{2+}–Me_5dien–amino acid ternary systems are even more resolute. The pH dependence of λ_{max} in the visible spectra collected for these systems clearly shows a significant red shift (the value of λ_{max} increases from ~660 at pH ca. 5.5–6 to 770–775 nm at pH ca. 9 and then starts to decrease) that parallels the formation and decay of the [Cu(Me_5dien)(L2)]$^+$ heteroligand species [121, 130]. This effect is strongly connected with the structural change around the copper(II) ion and transition from a six to distorted five-coordinate geometry while going from the simple to heteroligand species [67, 131]. The coordination mode in [Cu(Me_5dien)(L2)]$^+$ is the same as in [Cu(Dien)(L2)]$^+$, but the geometry of this heteroligand species is strongly deviated from square pyramidal towards trigonal bipyramidal due to the dominant bulky effect of two methyl substituents at each nitrogen (scheme 5) [64, 121, 130]. The coordination mode in the [Cu(Me_5dien)(His)]$^+$ heteroligand species has not been unambiguously explained. A detailed



[Cu(Dien)(Glu-γ-ha)]
[Cu(Dien)(Gly)]$^+$
[Cu(Dien)(Met)]$^+$
[Cu(Dien)(α-Ala)]$^+$
[Cu(Dien)(β-Asp(P))]$^-$
[Cu(Dien)(β-Ala)]$^+$
[Cu(Dien)(His)]$^+$
[Cu(Dien)(Gly(P))]
[Cu(Dien)(α-Ala(P))]
[Cu(Dien)(Hisha)]$^+$
Cu(Dien)(Metha)]$^+$
[Cu(Dien)(α-Alaha)]$^+$
[Cu(Dien)(Asp-β-ha]
[Cu(Dien)(β-Ala(P))]
[Cu(Dien)(β-Alaha)]$^+$

Scheme 4. Schematic representations showing the possible structures of the selected complex species formed in the in the water solution of Cu(II)–L1–L2 ternary systems (L1 – Dien, L2 – bioligand = amino acid, aminohydroxamic acid, or aminophosphonic acid).

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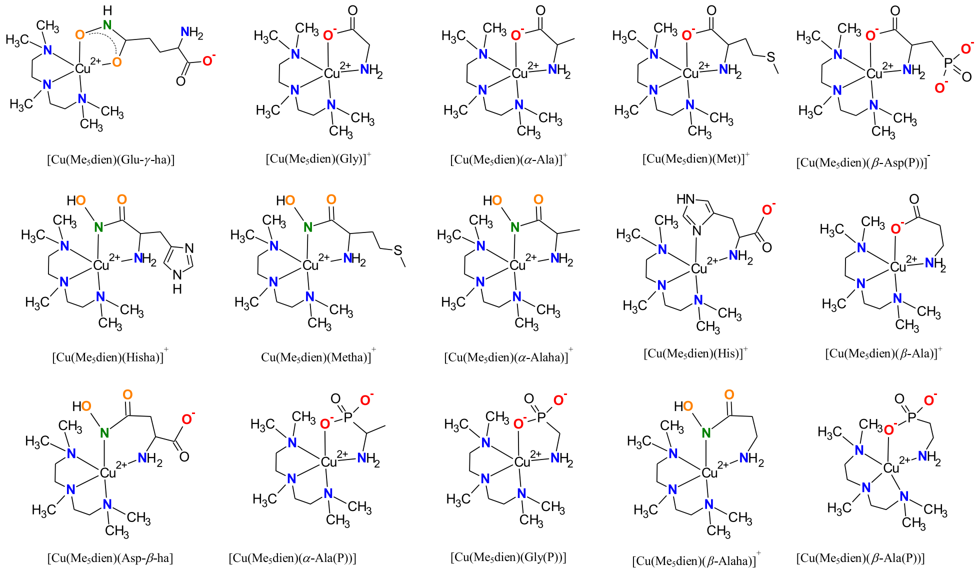
consideration of the equilibrium and spectroscopic results revealed that it can be the same as that proposed for the rest of the amino acids but the participation of the imidazole nitrogen in coordination in the [Cu(Me$_5$dien)(His)]$^+$ species cannot be excluded [130]. The trigonal bipyramidal geometry in the heteroligand complexes of Me$_5$dien is preserved in the solid state. The heteroligand complexes of Me$_5$dien with amino acids (such as L-valinate and *α*-aminoisobutyrate anions) were characterized by X-ray crystallography [14]. In the solid state, the core (CuN$_4$O) geometries of the cations are described as approximately regular trigonal bipyramidal for both [Cu(L-val)(Me$_5$dien)]$^+$ and [Cu(aiba)(Me$_5$dien)]$^+$. Two terminal nitrogens of Me$_5$dien and one nitrogen of the amino acid ligand form a trigonal plane with near-trigonal bond angles of 125.7, 110.5 and 123.8° for the former complex and 118.7, 118.2 and 123.0 for the latter one [14]. The axial Cu–N bond is shorter than any of the in-plane Cu–N bonds [14], typical for trigonal copper(II) geometries [27, 149, 150]. The O–Cu–N group, which defines the axis in the trigonal bipyramidal description, is approximately linear with an angle of 174.4 for [Cu(L-val)(Me$_5$dien)]$^+$ and 174.8 for [Cu (aiba)(Me$_5$dien)]$^+$ [14]. The Cu–NH$_2$ and one of the Cu-N(CH$_3$)$_2$ bond lengths (2.06–2.11 Å, table 5) are in the normal range for Cu-amine in-plane distances of trigonal bipyramidal structures. However, the length of the second Cu–N(CH$_3$)$_2$ bond (2.178 and 2.144 Å, table 5) is quite long. The Cu–O bond length (table 5) is normal for Cu–O (carboxylate) distances. There is no interaction between adjacent complex cations [14].

3.2. *Heteroligand complexes in ternary systems containing copper(II) ions, amines, and phosphonic derivatives of amino acids*

The coordination chemistry of copper(II) ions with aliphatic amines and phosphonic derivatives of amino acids in aqueous solution is interesting due to the differences of phosphonate and carboxylate groups in basicity, charge, and size (scheme 2).



Scheme 5. Schematic representations showing the possible structures of the selected complex species formed in the in the water solution of Cu(II)–L1–L2 ternary systems (L1 – Me$_5$dien, L2 – bioligand = amino acid, aminohydroxamic acid, or aminophosphonic acid).

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In the copper(II) ternary systems of bidentate En and phosphonic acids, the heteroligand species [Cu(En)(L2)] appear in the same pH range as for ternary systems with analogous amino acids [figures 1(a) and 2(a)]. Comparison of the ternary systems with α-phosphonic derivatives [Gly(P) and α-Ala(P)] [90, 91] with that of β-derivative (β-Ala(P)) [92] shows that the concentration of the [Cu(En)(L2)] species formed in the latter ternary system is distinctly lower than the concentration of this heteroligand complex in the former systems. In the case of ternary system with β-Asp(P), which possess an additional coordination site, charge neutralization favors formation of protonated heteroligand complexes, so the protonated [Cu(L1)(H-β-Asp(P))] could be detected [68].

The energies of d–d transition [595–612 nm (table 4)] determined for [Cu(En)(L2)], that predominate in solution at pH 6.5–10, are typical for species with 3 N coordination but they are lower than the energies obtained for this type of heteroligand species formed in the ternary systems with amino acids (580–582 nm). Similarly, the EPR parameters of the spectra observed in the liquid and frozen solution for these species ($g_{\|} = 2.232$–2.237, $A_{\|} = 185$–$195 \times 10^{-4}\ \mathrm{cm}^{-1}$, table 4) support the formation of (NH_2, NH_2) and (NH_2, PO_3^{2-}) chelates in the plane of the tetragonal [Cu(En)(L2)] complexes [68, 90–92] (scheme 3).

Since the formation of six-membered chelate rings generally results in a decrease of thermodynamic stability and distortion of coordination geometry of the complexes, the heteroligand complexes formed with β-Ala(P) are less stable than those formed with Gly(P) or α-Ala(P) although the basicity of the coordinating donors is higher in the case of the former one [92].

The comparative analysis of the equilibrium constants, $\log K_{[\mathrm{Cu(En)(L2)}]}$, obtained for heteroligand species of β-Asp(P) (8.47, table 2) with those calculated for heteroligand species of an amino acid (~7, table 1) and other aminophosphonic acids (~7–7.4, table 2) excludes the pure α-Ala-like or β-Ala(P)-like bidentate coordination mode strongly suggesting that β-Asp(P) coordinates to the copper(II) ion in tridentate manner with the simultaneous presence of five and six-membered chelate rings in $[\mathrm{Cu(En)}(\beta\text{-Asp(P)})]^-$ (scheme 3). This conclusion has been supported by the electronic absorption data for $[\mathrm{Cu(En)}(\beta\text{-Asp(P)})]^-$ (table 4). The obtained energy of d–d transition for $[\mathrm{Cu(En)}(\beta\text{-Asp(P)})]^-$ of 595 nm exhibits a red shift (15 nm) in relation to the d–d absorption band of $[\mathrm{Cu(En)}(\alpha\text{-Ala})]^+$ [68]. The axial coordination of a donor group generally causes a shift of the d–d band towards lower energies [93], therefore the observed effect in the absorption spectrum of $[\mathrm{Cu(En)}(\beta\text{-Asp(P)})]^-$ is further confirmation of tridentate coordination mode of β-Asp(P). The tridentate coordination of β-Asp(P) was also proposed for protonated [Cu(En)(H-β-Asp(P))] species in which PO_3H^- group is weakly coordinated, which consequently becomes more strongly bound to Cu^{2+} in the deprotonated complex. The same values of stability constants, that can be easily observed for the deprotonated ($\log K_{[\mathrm{Cu(En)}(\beta\text{-Asp(P)})]} = 8.47$, table 2) and protonated ones ($\log K_{[\mathrm{Cu(En)(H}\text{-}\beta\text{-Asp(P))}]} = \log \beta_{[\mathrm{Cu(En)(H}\text{-}\beta\text{-Asp(P))}]} - \log \beta_{[\mathrm{Cu(En)}]} - \mathrm{p}K_{\mathrm{PO_3H^-}} = 8.65$), strongly suggest similar coordination mode of these ligands ({NH_2, NH_2} of En and {COO^-, NH_2, PO_3^{2-} or PO_3H^-} of β-Asp(P)) in these two heteroligand species [68].

The interaction of copper(II) ions with aminophosphonic acids in the presence of Dien or Me_5dien led generally to formation of [Cu(Dien)(L2)] and [Cu(Me_5dien)(L2)], respectively [68, 90–92]. The protonated heteroligand complexes of Dien have been detected only in the ternary systems with Gly(P) [90] and β-Asp(P) [68].

For the [Cu(Dien)(L2)] species with aminophosphonic acids, which predominate in basic solution, the EPR parameters correspond well to a five-coordinate species (table 4) and the presence of a weak rhombic distortion suggests that the geometry is slightly deviated from square pyramidal towards trigonal bipyramidal. The electronic absorption spectra at

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pH 9.0–9.5 [e.g. figure 2(b)] are characteristic for five-coordinate asymmetric complexes with 4N coordination mode (table 4). In this heteroligand species, the binding of Cu^{2+} in the equatorial plane is realized by three amine nitrogens of Dien and amine nitrogen of Gly (P), α-Ala(P) or β-Ala(P) and phosphonic oxygen completes the coordination number to five by binding Cu^{2+} in axial position [90–92]. In the case of β-Asp(P), the fifth-axial position can be occupied by one of the remaining groups in the molecule, either phosphonic or carboxylate oxygens. An analysis of basicity-adjusted stability constants obtained for heteroligand complexes of Dien and other phosphonic acids or amino acids (tables 1 and 2) has established that β-Asp(P) reveals the same coordination ability as α-Ala and coordinates to the metal ion in the amino acid manner with the formation of a five-membered chelate ring $\{NH_2, NH, NH_2\}\{NH_2, COO^-\}$ (scheme 4) [68]. Another confirmation of α-Ala-like coordination in the $[Cu(Dien)(\beta\text{-Asp(P)})]^-$ heteroligand species is provided by spectral data. EPR parameters and the energy of d–d transition for this species are almost identical with those obtained for $[Cu(Dien)(\alpha\text{-Ala})]^+$ (table 4).

The coordination mode in $[Cu(Me_5dien)(L2)]$ formed in the ternary systems of aminophosphonic acids is the same as in the case of [Cu(Dien)(L2)] (scheme 4), but the geometry of these heteroligand species is strongly deviated from square pyramidal towards trigonal bipyramidal due to the dominant bulky effect of two methyl substituents at each nitrogen [68, 90, 91]. Similarly as in the ternary systems of Me_5dien and amino acids (see above), the pH dependence of λ_{max} in visible spectra collected for the ternary systems with this polyamine and aminophosphonic acids clearly shows a significant red shift which parallels the formation of the $[Cu(Me_5dien)(L2)]$ species [90, 91]. The absorption spectra for these species exhibit a broad band at 700–900 nm with a characteristic of the five-coordinate asymmetry (like in the case of β-Asp(P) heteroligand species) or even two maxima with shoulder and the latter one more intense (table 4, such as for $[Cu(Me_5dien)(Gly(P))]$ or $[Cu(Me_5dien)(\alpha\text{-Ala(P)})]$). The values of g parameters and the hyperfine splitting constants A calculated from the separated EPR spectrum of these heteroligand species in frozen solution (table 4) are typical for the "rhombic" spectrum of the five-coordinate heteroligand species, with the geometry intermediate between the trigonal bipyramid and the square pyramid. For the $[Cu(Me_5dien)(\beta\text{-Ala(P)})]$ species, stronger geometric distortion was suggested than for the heteroligand species containing Dien but clearly weaker than for $[Cu(Me_5dien)(Gly(P))]$ or $[Cu(Me_5dien)(\alpha\text{-Ala(P)})]$. This difference has been assigned to the dissimilar chelate rings formed by aminophosphonic acids – a five-membered chelate ring in the case of Gly(P) or α-Ala(P) and a six-membered chelate ring in the case of β-Ala(P) [92]. In the five-coordinate $[Cu(Me_5dien)(\beta\text{-Asp(P)})]^-$, the involvement of the carboxylic group together with amino nitrogen in coordination to copper(II) was assumed, resulting in formation of a five-membered chelate ring instead of six-membered like in analogous heteroligand species of β-Ala(P). This binding mode difference resulting from the additional presence of carboxylic group in β-Asp(P) takes effect in a distinct increase of the relative stability of its heteroligand complexes (scheme 5) [68]. Regrettably, there are no data concerning the solid-state chemistry of these ternary systems and no X-ray data on this subject have been found.

3.3. *Heteroligand complexes in ternary systems containing copper(II) ions, amines, and hydroxamic derivatives of amino acids*

The investigations of aminohydroxamic acids in the copper(II) solution with ethylenediamine show that heteroligand complexes form in the ternary systems with α-Alaha, Metha,

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Hisha, and Glu-γ-ha but are not formed in the systems with β-Alaha and Asp-β-ha (table 4) [101, 103, 107, 151].

The formation of the main heteroligand species above pH ~5–6 is preceded mainly by the appearance of simple or polynuclear complexes with aminohydroxamic ligands [e.g. figure 3(a)] [103, 107, 151]. Spectroscopic data made it possible to determine the ligand donors coordinating to copper(II) in the heteroligand species. The distribution-corrected absorption spectra for $[Cu(En)(Metha)]^+$ and $[Cu(En)(Hisha)]^+$ exhibit a band with a maximum at ~547–552 nm (table 4). The energy of this d–d transition corresponds to species with four nitrogen donors in the equatorial position of the metal site (table 4). The formation of heteroligand species in basic solution with 4N coordination in the copper(II) equatorial plane has been confirmed by the EPR results ($g_z = 2.193$–2.200 and $A_z = 204$–$205 \times 10^{-4}\ \mathrm{cm}^{-1}$, table 4). So, on the basis of the EPR and the absorption spectra studies, coordination in the heteroligand species formed in the considered ternary systems is realized by amine nitrogens of En (NH_2, NH_2) and both amine and hydroxamic nitrogen atoms of α-Alaha, Metha, or Hisha (NH_2, N_{ha}) in the equatorial plane with two five-membered chelate rings (scheme 3) [151]. In the Cu-En-Glu-γ-ha ternary system except for [Cu(En)(Glu-γ-ha)] heteroligand species, which dominates in solution above pH 6, also the protonated $[Cu(En)(H\text{-}Glu\text{-}\gamma\text{-}ha)]^+$ complex has been detected [103]. The spectroscopic data made it possible to assign the [Cu(En)(Glu-γ-ha)] species structure in which Glu-γ-ha is a tridentate ligand (scheme 3). The coordination is realized by (NH_2, NH_2) of En and by $\{NH_2, COO^-\}$ in the equatorial position and by N_{ha} of Glu-γ-ha in the axial position; the sixth coordination position is occupied by water [103].

The results of the investigations of the Cu(II)-Dien-L2 (L2 = aminohydroxamic acids) ternary systems are somewhat more dissimilar [99–101, 103]. The potentiometric, Vis and EPR data provide evidence for the presence in all ternary systems protonated [Cu(Dien)(H-L2)] and deprotonated [Cu(Dien)(L2)] heteroligand species (table 4). The absorption curves in the visible spectra for the [Cu(Dien)(L2)] heteroligand species [in 9–10 pH range, e.g. figure 3(b)] exhibit a broad band at 600–800 nm with a poorly shaped maximum (table 4) and a shoulder at about 750 nm. This spectral behavior is distinctive for five-coordinate geometry in heteroligand species [99–101]. The axial rhombic distortion of the EPR spectra in the pH range of the heteroligand complexes existence (table 4) is consistent with the geometry slightly deviated from square pyramid towards trigonal bipyramid. The proposed coordination modes for $[Cu(Dien)(\alpha\text{-}Alaha)]^+$, $[Cu(Dien)(\beta\text{-}Alaha)]^+$, $[Cu(Dien)(Metha)]^+$, $[Cu(Dien)(Hisha)]^+$, and [Cu(Dien)(Asp-β-ha)] are presented in scheme 4. The presence of an additional donor group in Glu-γ-ha gives possibility for two different coordination modes. However, in [Cu(Dien)(Glu-γ-ha)], Glu-γ-ha is a bidentate ligand coordinating through $\{NH_2, COO^-\}$ donors (scheme 4) [103]. The formation and the concentration of protonated heteroligand complexes in the considered ternary systems depend on the type of the aminohydroxamate ligand and the copper(II)–L1–L2 molar ratios [99–101, 103]. The suggested coordination modes for this type of heteroligand complex are very diverse. The $[Cu(Dien)(H\text{-}L2)]^{2+}$ (L2 = α-Alaha and β-Alaha) species was suggested to have a square-based pyramidal geometry in which Dien occupies three equatorial positions and the hydroxamic group forms a $\{CO, O^-\}$ chelate ring involving equatorial and axial positions [99]. In the $[Cu(Dien)(H\text{-}Hisha)]^{2+}$ species, Hisha is coordinated to copper(II) by the amino group in a monodentate manner, whereas in $[Cu(Dien)(H_2\text{-}Hisha)]^{3+}$ this ligand coordinates by nitrogen of the imidazole ring [151]. For $[Cu(Dien)(H\text{-}Asp\text{-}\beta\text{-}ha)]^+$ and $[Cu(Dien)(H\text{-}Glu\text{-}\gamma\text{-}ha)]^+$ a glycine-like coordination mode has been proposed (the neutral hydroxamate group is not coordinated, scheme 4) [101, 103].

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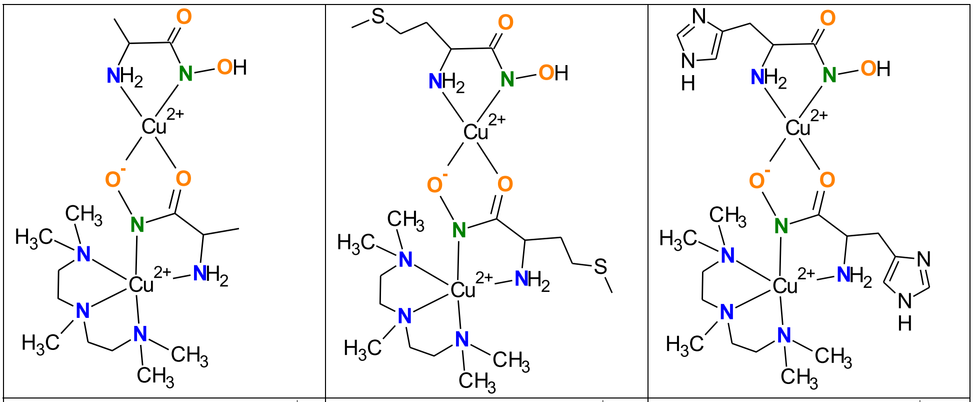
It was reported that the presence of Dien suppresses the formation of binuclear and polynuclear species in the ternary systems [99, 100]. In contrast to Dien, the presence of Me_5dien in solution does not suppress the formation of parent polynuclear species with aminohydroxamic ligand. Furthermore, for the first time, it could be observed that in the Cu(II)-Me_5dien-L2 (L2 = α-Alaha, Metha and Hisha) ternary systems the binuclear heteroligand species are predominant in basic solution. The mononuclear heteroligand species $[Cu(Me_5dien)(L2)]^+$ which have been detected in this type of ternary system are formed in remarkably lower concentrations [131].

The formation of $[Cu_2(Me_5dien)(L2)_2H_{-1}]^+$ predicted by potentiometric studies has been confirmed by EPR spectral data [131]. It has been observed that above pH 6 in the frozen solution of these ternary systems, the intensity of the EPR spectral lines rapidly decreases, associated with a weak Cu(II)–Cu(II) exchange interaction in the $[Cu_2(Me_5dien)(L2)_2H_{-1}]^+$ complexes. The effect of binuclear species formation is observed distinctly in the electronic spectral changes [131]. The absorption spectra exhibit the intense $N^-O^-_{(oxygen)} \rightarrow Cu^{2+}$ CT band in the near-UV region (at about 357 nm), which could be assigned to the transition from hydroxamic oxygen to copper(II) (the $N^-O^-_{(oxygen)} \rightarrow Cu^{2+}$ CT band is expected at wavelengths ca. 350 nm [152–154] (scheme 6). At pH ~ 9 a specific for copper(II) heteroligand species of Me_5dien absorption pattern, two peaks with one more intense being near the IR region, has been observed (table 4). This absorption pattern strongly supports the formation of a five-coordinate heteroligand species with 5N in the coordination sphere in the Cu^{2+}–Me_5dien–L2 ternary systems [155] (scheme 6). The disappearance of the EPR signals in basic solution as a result of polynuclear species formation has allowed observation of the spectrum corresponding to the mononuclear $[Cu(Me_5dien)(L2)]^+$ complex (the concentration of this species is ~10 in the pH range 8.5–9.5) [131]. The EPR spectral parameters (table 4) have suggested that $[Cu(Me_5dien)(L2)]^+$ displays a significant degree of distortion from square pyramid to trigonal bipyramid, similar to that observed for heteroligand species of amino acids and aminophosphonic acids in the copper(II) ternary systems of Me_5dien (see above). Coordination in the Cu^{2+} plane in this heteroligand complex was concluded to be realized by three nitrogens of Me_5dien and NH_2 and N_{ha} donors of α-Alaha, Metha, or Hisha (scheme 5) [131]. In the copper(II) ternary system of Me_5dien and β-Alaha, three



$[Cu_2(Me_5dien)(\alpha\text{-Alaha})_2H_{-1}]^+$ | $[Cu_2(Me_5dien)(Metha)_2H_{-1}]^+$ | $[Cu_2(Me_5dien)(Hisha)_2H_{-1}]^+$

Scheme 6. Schematic representations showing the possible structures of the dimeric species formed in the water solution of Cu(II)–Me_5dien–L2 ternary systems (L2 – α-Alaha, Metha, Hisha).

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heteroligand species are formed: [Cu(H-Me$_5$dien)(H-β-Alaha)]$^{3+}$, [Cu(Me$_5$dien)(H-β-Alaha)]$^{2+}$, and [Cu(Me$_5$dien)(β-Alaha)]$^{+}$ [67]. To summarize, in the first protonated heteroligand species Me$_5$dien occupies two equatorial positions and the hydroxamic group, forming a {CO, O^{-}} type chelate ring, occupies the two remaining ones [67]. For the second protonated heteroligand complex, a structural transformation around copper(II) and the formation of a five-coordinate species was postulated with coordination of the ligands including two nitrogens and two oxygen donors in the copper(II) plane [67]. It was established that total deprotonation β-Alaha allows all the nitrogen donors to participate in the coordination sphere in [Cu(Me$_5$dien)(β-Alaha)]$^{+}$ leading to distortion of the geometry from square pyramidal to trigonal bipyramidal [67] (scheme 5). A quite different coordination mode has been reported for heteroligand complexes formed in the Cu(II)–Me$_5$dien–L2 ternary systems, where L2 is Asp-β-ha or Glu-γ-ha [101, 103]. The presence of the carboxylate in both these ligands causes the changes in the bonding mode of aminohydroxamic ligands in relation to β-Alaha. The analysis of equilibrium and spectral data (tables 3 and 4) established that in the protonated heteroligand species ([Cu(H-Me$_5$dien)(H-Asp-β-ha)]$^{2+}$ and [Cu(Me$_5$dien)(H-Asp-β-ha)]$^{+}$) the protonated H-Asp-β-ha ligand is coordinated via {NH$_2$, COO^{-}} donors in glycine-like mode (the neutral hydroxamate group is not coordinated) [101], whereas in [Cu(Me$_5$dien)(H-Glu-γ-ha)]$^{+}$ hydroxamic acid completes the coordination number is five by binding copper(II) ion through the hydroxamate oxygens [103]. The difference in the binding modes was also reported for the deprotonated heteroligand species of these two ligands. In [Cu(Me$_5$dien)(Asp-β-ha)], the participation of all nitrogen-donors in the coordination sphere was postulated [101] but for [Cu(Me$_5$dien)(Glu-γ-ha)] hydroxamate type {CO, O^{-}} coordination of Glu-γ-ha has been supposed [103].

4. Stability relations

In this section, we shall consider different factors and specific effects occurring in the ternary systems influencing the formation and structure of heteroligand complexes.

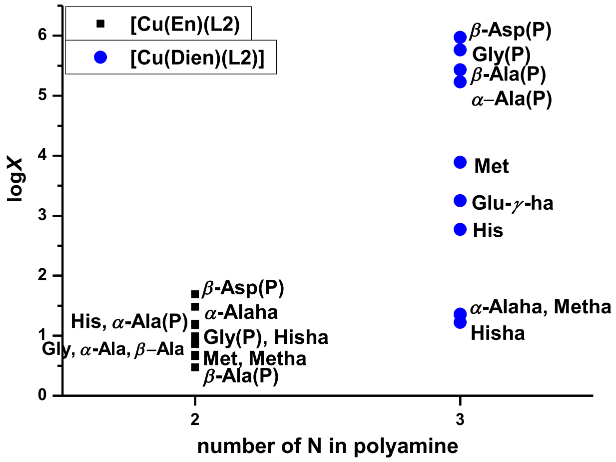

Figure 4. The relations of log *X* parameter with the number of nitrogen donor atoms (*N*) in amine in the ternary systems of En (black square) and Dien (blue circle) (see http://dx.doi.org/10.1080/00958972.2014.950957 for color version).

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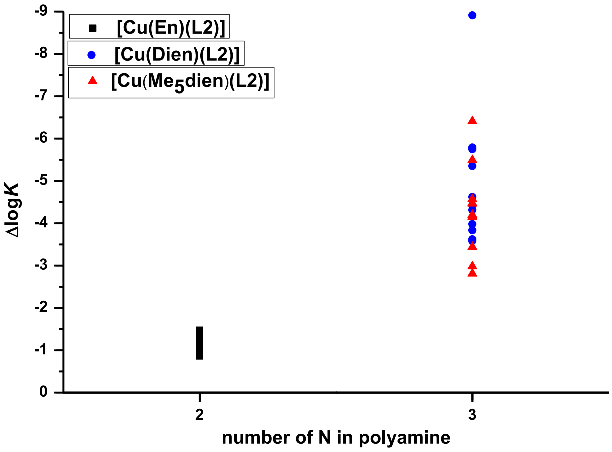

Figure 5. The relations of $\Delta\log K$ parameter with the number of nitrogen donor atoms (N) in amine in the ternary systems of En (black square), Dien (blue circle) and Me_5dien (red triangle) (see http://dx.doi.org/10.1080/00958972.2014.950957 for color version).

It is interesting to compare the values of the $\log X$ parameter calculated for the heteroligand complexes formed in the ternary systems with En and Dien (figure 4). The $\log X_{[Cu(L1)(L2)]}$ values for the system with Dien are distinctly higher than those for the systems with En. This is a reflection of the ratio of the stepwise formation constants for the binary Cu^{2+} polyamine system, $\log(K_{[Cu(Dien)]}/K_{[Cu(Dien)_2]}) = 11.26$ is significantly greater than $\log(K_{[Cu(En)]}/K_{[Cu(En)_2]} = 1.43$ [92] ($\log K_{[Cu(Dien)]} = 16.01$, $\log K_{[Cu(Dien)_2]} = 4.75$ [100], $\log K_{[Cu(En)]} = 10.58$, $\log K_{[Cu(En)_2]} = 9.15$ [107]). In the case of heteroligand species formed with bidentate En, an additional stabilization of $[Cu(En)(\beta\text{-Asp(P)})]^-$ is observed when comparing to other heteroligand complexes of [Cu(En)(L2)] type (figure 4). The clearly higher value of $\log X$ parameter calculated for this complex confirms a tridentate bonding mode of β-Asp(P) [68].

The next parameter is $\Delta\log K$ in relation to the number of nitrogen donors in amine (figure 5). The values of this parameter for heteroligand complexes with bidentate En oscillate close to −1 and this allows the conclusion that all heteroligand complexes formed in these ternary systems possess tetragonal geometry. However, $\Delta\log K$ parameters for the heteroligand complexes with tridentate Dien ($\Delta\log K$ are from −3.58 to −8.91) or Me_5dien (from −2.81 to −6.41) (tables 1–3), more negative than statistical value. Negative $\Delta\log K$ values (figure 5) imply that the heteroligand complexes are less stable than the binary ones. However, this does not mean that the heteroligand complexes are not formed. The negative value may be interpreted in terms of higher stability of the binary complexes and/or reduced number of coordination sites in the ligand. Other electronic and structural factors such as steric hindrance, bond type, and geometrical configuration are also expected to have an effect on $\Delta\log K$ values [133, 134]. It was concluded that the heteroligand complexes of Dien or Me_5dien are less than six coordinate of Cu^{2+} [64, 67, 68, 90–92, 99, 100, 121]. So, the geometry of this type of complex is more or less distorted towards tetragonal pyramid or trigonal bipyramid (see above).

To gather information on the factors influencing the compositions and structures of the complexes and to draw general conclusions, the basicity-adjusted stability constants have to be considered (figure 6 and table 6). These constants have been calculated according to the following equation:

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$$\beta_{[\mathrm{Cu(L1)(L2)}]} = \frac{[\mathrm{Cu(L1)(L2)}]}{[\mathrm{Cu}][(\mathrm{L1})][(\mathrm{L2})]}$$

$$\log K_{[\mathrm{Cu(L1)(L2)}]} = \log \beta_{[\mathrm{Cu(L1)(L2)}]} - \log \beta_{[\mathrm{Cu(L1)}]}$$

Basicity-adjusted stability constants

$\log K_{[\mathrm{Cu(En)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{COOH}}$	$\log K_{[\mathrm{Cu(L1)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{PO_3H^-}}$
L2 = Gly, α-Ala, β-Ala, Met, β-Asp(P), Glu-γ-ha	L1 = En, Dien, Me$_5$dien
$\log K_{[\mathrm{Cu(Dien)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{COOH}}$	L2 = Gly(P), α-Ala(P), β-Ala(P)
L2 = Gly, α-Ala, β-Ala, Met, β-Asp(P), Glu-γ-ha	$\log K_{[\mathrm{Cu(L1)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{pK_{im}}$
$\log K_{[\mathrm{Cu(Me_5dien)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{COOH}}$	L1 = En, Dien, Me$_5$dien
L2 = Gly, α-Ala, β-Ala, Met, β-Asp(P)	L2 – His
$\log K_{[\mathrm{Cu(En)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3{}^+}} - \mathrm{p}K_{\mathrm{NHOH}}$	$\log K_{[\mathrm{Cu(Me_5dien)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3^+}} - \mathrm{p}K_{\mathrm{NHOH}}$
L2 = α-Alaha, Metha, Hisha	L2 = α-Alaha, β-Alaha, Metha, Hisha, Asp-β-ha
$\log K_{[\mathrm{Cu(Dien)(L2)}]} - \mathrm{p}K_{\mathrm{NH_3{}^+}} - \mathrm{p}K_{\mathrm{NHOH}}$	$\log K_{[\mathrm{Cu(Me_5dien)(L2)}]} - \mathrm{p}K_{\mathrm{NHOH}}$
L2 = α-Alaha, β-Alaha, Metha, Hisha, Asp-β-ha	L2 = Glu-γ-ha

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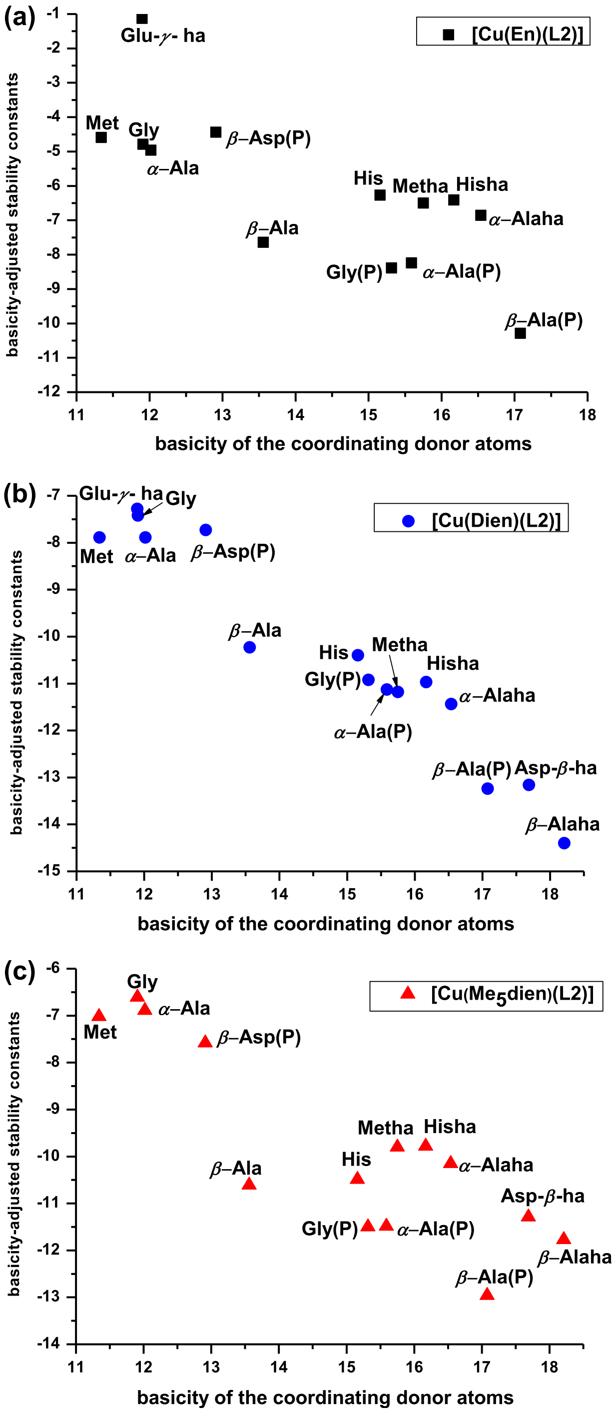

Figure 6. The dependence between the relative stabilities of the heteroligand complexes and the basicity of coordinating donor groups in the copper(II)-En-L2 (a), copper(II)-Dien-L2 (b), and copper(II)-Me$_5$dien-L2 (c) ternary systems.

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Table 6. The basicity values of the coordinating donors ΣpK, the corresponding basicity-adjusted stability constants values, coordination mode, and size of the chelate ring formed by L2 bioligand.

Compound L2	ΣpK,	$\log K_{[Cu(En)(L2)]} - \Sigma pK$	Coordination mode and size of the chelate ring formed by L2 ligand ring	Ref.
Glu-γ-ha	11.90	−1.13	{NH , COO$^-$}+ ax N$_{ha}$ ⬠ ⬡	[103]
β-Asp(P)	12.91	−4.44	{NH$_2$, COO$^-$}+ ax PO$_3^{2-}$ ⬠ ⬡	[68]
Gly	11.91	−4.79	{NH$_2$, COO$^-$}, ⬠	[106]
Met	11.34	−4.59	{NH$_2$, COO$^-$}, ⬠	[121]
α-Ala	12.02	−4.96	{NH$_2$, COO$^-$}, ⬠	[130]
His	15.16	−6.27	{N$_{im}$, NH$_2$}+ ax COO$^-$ ⬡ ⬠	[130]
Hisha	16.17	−6.41	{NH$_2$, N$_{ha}$}, ⬠	[151]
Metha	15.75	−6.50	{NH$_2$, N$_{ha}$}, ⬠	[151]
α-Alaha	16.54	−6.86	{NH$_2$, N$_{ha}$}, ⬠	[107]
β-Ala	13.56	−7.64	{NH$_2$, COO$^-$}, ⬡	[135]
Gly(P)	15.315	−8.39	{NH$_2$, PO$_3^{2-}$}, ⬠	[90]
α-Ala(P)	15.5875	−8.24	{NH$_2$, PO$_3^{2-}$}, ⬠	[91]
β-Ala(P)	17.08	−10.29	{NH$_2$, PO$_3^{2-}$}, ⬡	[92]
		$\log K_{[Cu(Dien)(L2)]} - \Sigma pK$		
Glu-γ-ha	11.90	−7.28	{NH$_2$, COO$^-$}, ⬠	[103]
Gly	11.91	−7.42	{NH$_2$, COO$^-$}, ⬠	[64]
β-Asp(P)	12.91	−7.73	{NH$_2$, COO$^-$}, ⬠	[68]
Met	11.34	−7.89	{NH$_2$, COO$^-$}, ⬠	[121]
α-Ala	12.02	−7.89	{NH$_2$, COO$^-$}, ⬠	[64]
β-Ala	13.56	−10.23	{NH$_2$, COO$^-$}, ⬡	[131]
His	15.16	−10.40	{N$_{im}$, NH$_2$}, ⬡	[130]
Gly(P)	15.315	−10.9225	{NH$_2$, PO$_3^{2-}$}, ⬠	[90]
α-Ala(P)	15.5875	−11.1275	{NH$_2$, PO$_3^{2-}$}, ⬠	[91]
Hisha	16.17	−10.97	{NH$_2$, N$_{ha}$}, ⬠	[100]

(*Continued*)

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Table 6. (*Continued*).

Compound L2	ΣpK,	$\log K_{[Cu(En)(L2)]} - \Sigma pK$	Coordination mode and size of the chelate ring formed by L2 ligand ring	Ref.
Metha	15.75	−11.18	$\{NH_2, N_{ha}\}$, ⬠	[100]
α-Alaha	16.54	−11.44	$\{NH_2, N_{ha}\}$, ⬠	[99]
Asp-β-ha	17.69	-13.16	$\{NH_2, N_{ha}\}$, ⬡	[101]
β-Ala(P)	17.08	-13.24	$\{NH_2, PO_3^{2-}\}$, ⬡	[92]
β-Alaha	18.21	-14.40	$\{NH_2, N_{ha}\}$, ⬡	[99]
		$\log K_{[Cu(Me5dien)(L2)]} - \Sigma pK$		
Gly	11.91	−6.61	$\{NH_2, COO^-\}$, ⬠	[64]
α-Ala	12.02	−6.89	$\{NH_2, COO^-\}$, ⬠	[64]
Met	11.34	−7.02	$\{NH_2, COO^-\}$, ⬠	[121]
β-Asp(P)	12.91	−7.58	$\{NH_2, COO^-\}$, ⬠	[68]
Hisha	16.17	−9.78	$\{NH_2, N_{ha}\}$, ⬠	[131]
Metha	15.75	−9.80	$\{NH_2, N_{ha}\}$, ⬠	[131]
α-Alaha	16.54	−10.15	$\{NH_2, N_{ha}\}$, ⬠	[131]
His	15.16	−10.49	$\{N_{im}, NH_2\}$, ⬡	[130]
β-Ala	13.56	−10.61	$\{NH_2, COO^-\}$, ⬡	[131]
Asp-β-ha	17.69	−11.29	$\{NH_2, N_{ha}\}$, ⬡	[101]
α-Ala(P)	15.5875	−11.4875	$\{NH_2, PO_3^{2-}\}$, ⬠	[91]
Gly(P)	15.315	−11.499	$\{NH_2, PO_3^{2-}\}$, ⬠	[90]
β-Alaha	18.21	−11.77	$\{NH_2, N_{ha}\}$, ⬡	[67]
β-Ala(P)	17.08	−12.96	$\{NH_2, PO_3^{2-}\}$, ⬡	[92]

Analysis of the data presented in figure 6 and table 6 allow us to summarize the most important factors governing heteroligand complex formation:

- The relative stability is higher for the heteroligand complexes with mixed-bonding mode and five-membered chelate rings formed by amino group and planar carboxylic one $\{NH_2, COO^-\}$ [Gly, α-Ala, Met, β-Asp(P)] than for the complexes with pure type of donors and the same type of chelate rings $\{NH_2, NHO^-\}$ (α-Alaha, Metha, Hisha).

- Heteroligand [Cu(En)(L2)] species with amino acids (Gly, α-Ala, β-Ala, Met) are about 2–4 orders of magnitude higher than those for phosphonic analogs (Gly(P), α-Ala(P), β-Ala(P)) even though particular α- and β-derivative of amino acid and phosphonic acids form chelate rings of the same size and involve similar mixed-bonding mode (N, O). This effect results from the difference in size and geometry of both groups: planar COO^- and tetrahedral PO_3^{2-}. The same effect of the relative stability decrease of phosphonates complexes in comparison to carboxylates was observed in the case of binary systems and still exist in the ternary system with copper(II) ions.
- The relative stability is the lowest in the case of heteroligand complexes with the six-membered chelate ring formed by amino group and tetrahedral phosphonic one $\{NH_2, PO_3^{2-}\}$ (β-Ala(P)) or hydroxamic one $\{NH_2, NHO^-\}$(β-Alaha).
- Additional stabilization of heteroligand complexes is observed when coordinating L2 possess an extra donor group (Glu-γ-ha, β-Asp(P), His).
- In contrast to systems with En, the relative stabilities of five-coordinate heteroligand complexes with Dien and phosphonic acids $\{NH_2, PO_3^{2-}\}$ (Gly(P), α-Ala(P)) are similar to the relative stabilities of the heteroligand complexes with Dien and hydroxamic acids $\{NH_2, NHO^-\}$ (α-Alaha, Metha, Hisha). The coordination of tetrahedral phosphonic group in axial position is more favored than in the equatorial one like in the heteroligand complexes of ethylenediamine.

5. Concluding remarks

This review shows a summary of the complex equilibria and the heteroligand complex formation in the ternary systems preceded by a short analysis of the structure, size, basicity, and charge of the aliphatic amines and bioligands.

This review also demonstrates that a comprehensive correlation of the potentiometric data with spectroscopic parameters (UV–Vis and EPR) obtained in solution comes to conclusions about stability of the complexes, their coordination modes, and structures in spite of the lack of suitable crystals for X-ray characterization. In the presented ternary systems, the heteroligand complexes are usually formed and predominate in neutral and basic solution. The presented results indicate the tetragonal geometry for the [Cu(En)(L2)] heteroligand species. If ligand L1 is Dien or Me_5dien, five-coordinated heteroligand copper(II) complexes are supported. For the [Cu(Dien)(L2)] complexes, the geometry slightly deviated from square pyramidal is postulated, whereas for the [Cu(Me_5dien)(L2)] heteroligand species the geometry is usually strongly deviated from square pyramidal towards trigonal bipyramidal due to the dominant bulky effect of two methyl substituents at each nitrogen.

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