J Solution Chem (2010) 39: 909–919
DOI 10.1007/s10953-010-9558-1

Stability and Coordination Mode of Complexes of Polyphosphates and Polymetaphosphates with Copper(II) Ions in Aqueous Solution—Potentiometric, Spectral and Theoretical Studies

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Received: 4 November 2009 / Accepted: 31 January 2010 / Published online: 14 July 2010
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Abstract Complexes of copper(II) with a number of polyphosphate and polymetaphosphate anions have been studied in aqueous solutions by potentiometric, spectroscopic and theoretical methods. Stability constants of the complexes have been determined as well as their coordination modes. Results of the equilibrium studies provided evidence for the formation of ML, MHL and $ML(OH)_x$ type complexes with the ligands studied. The length of the polyphosphate chain was found to affect the oxygen atom charge that is reflected in the stability constants of the ML type complexes. Moreover, the stability of the complex is also influenced by the spatial arrangement of the phosphate groups in phosphates and metaphosphates. The spectral parameters observed for certain complexes have permitted us to deduce the inner coordination sphere of the studied complexes.

Keywords Polyphosphates · Polymetaphosphates · Copper complexes · Potentiometric studies · Spectroscopic studies · DFT calculations

1 Introduction

Polyphosphates are defined as compounds that contain anions with PO_4^{3-} tetrahedra linked together by shared corners. The P–O bond has a length of 1.62 Å, with bond angles of 130° at the O atoms and 102° at the P atoms [1]. Polyphosphates are stable in neutral aqueous solutions at room temperature but hydrolysis occurs in acidic media. The hydrolysis of polyphosphates can be followed by Raman spectroscopy, which allows monitoring of the –O–P–O– band. Triphosphates are less stable than diphosphates, and tetraphosphates are less stable than triphosphates [2]. Polymetaphosphoric acid and two well-known cyclic phosphoric acids (trimetaphosphoric and tetrametaphosphoric acid), their salts, and their capabilities for complexing transition metals have been the object of numerous studies [3–5]. It should be noted that chain phosphates are relatively more effective in complexation metal ions than cyclic phosphates [4].

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To study the mechanisms of biochemical reactions, it is necessary to know as accurately as possible the speciation of polyphosphates. Owing to their high charge, polyphosphates are mainly present in biological fluids as ion pairs or as complexes with different metal ions that can be of great importance in biochemical processes, e.g., pyrophosphates (diphosphates, $P_2O_7^{4-}$) are involved in many neutral reactions. Additionally, esters of the chain phosphates play important roles in biology. Perhaps the best known of these esters are adenosine mono-, adenosine di- and adenosine triphosphates, which are derivatives of the ortho-, pyro- and tripolyphosphate ions, respectively. ATP is known for its ability to hydrolyze its α-phosphoryl group and to lose the pyrophosphate group at alkaline pH [6], but at acidic pH ATP loses the orthophosphate group [7, 8]. On the other hand, one of the most important processes for protein modification and signal transmission in the cells is phosphorylation. It is assumed that about 30% of the proteins encoded by the human genome contain covalently bound phosphate. Phosphorylation and dephosphorylation control almost every aspect of the cell metabolism and can modify the functioning of proteins [9].

The tendency for complex formation between alkali or alkaline earth metal ions and the lower condensed phosphates in aqueous solutions, in particular pyrophosphates, $P_2O_7^{4-}$, and tripolyphosphates, $P_3O_{10}^{5-}$, was studied earlier [4, 10–16]. Recently, it has been reported that pyrophosphate forms quite stable complexes with protonated polyamines [14], and it has been suggested, from kinetic studies [17], that polyamines can substitute for Mg^{2+} ions as activators in vitro [18]. Copper is a trace metal in the human organism, where it plays important roles (e.g., in electron transport, antioxidant defense, and lipoprotein metabolism). Toxic accumulation of copper can be deleterious to human health (e.g. Wilson and Menkes disease genes [19, 20]).

This paper presents the results of potentiometric, spectroscopic and theoretical studies of the formation of complexes between Cu(II) and polyphosphates and with metaphosphates. Moreover, the relation is analyzed between the charge at the oxygen atom of the phosphate group and the stability of the complexes formed. In the earlier studies, the reactions for copper ion complexation with phosphates (monoP, diP, triP and trimetaP and tetrametaP) were investigated, but without a computer-aided analysis of the pH-metric data and spectroscopic methods (determination of coordination mode) [5, 21–23]. Moreover, no reliable spectroscopic data are yet available on the structure of the complexes. The data obtained in this study could also permit understanding of the mode of coordination in the metal complexes with bioligands containing phosphate groups.

2 Experimental

Sodium monophosphate (NaH_2PO_4) and sodium pyrophosphate ($Na_2H_2P_2O_7$) were purchased from Fluka, whereas sodium triphosphate ($Na_5P_3O_{10}$) and sodium trimetaphosphate ($Na_3P_3O_9$) were purchased from Sigma. Sodium tetrametaphosphate ($Na_4P_4O_{12}$) was prepared by first making the copper salt and then metathesizing it with sodium sulphide according to the procedure described by Barney et al. [3]. Structural formulae of the studied phosphates are given in Fig. 1.

Copper(II) nitrate (from Merck) was purified by recrystallization from water. The concentration of copper ions was determined by inductively coupled plasma optical emission spectrometry (ICP OES). The potentiometric measurements were carried out using a Titrino 702 Metrohm (signal drift 2 $mV \cdot min^{-1}$ and equilibrium time 300 s) equipped with an autoburette, and a glass electrode (ROSS Ultra Orion) calibrated according to a method described in the literature [24]. All potentiometric titrations (pH range 2.2 to 11.0) were made under

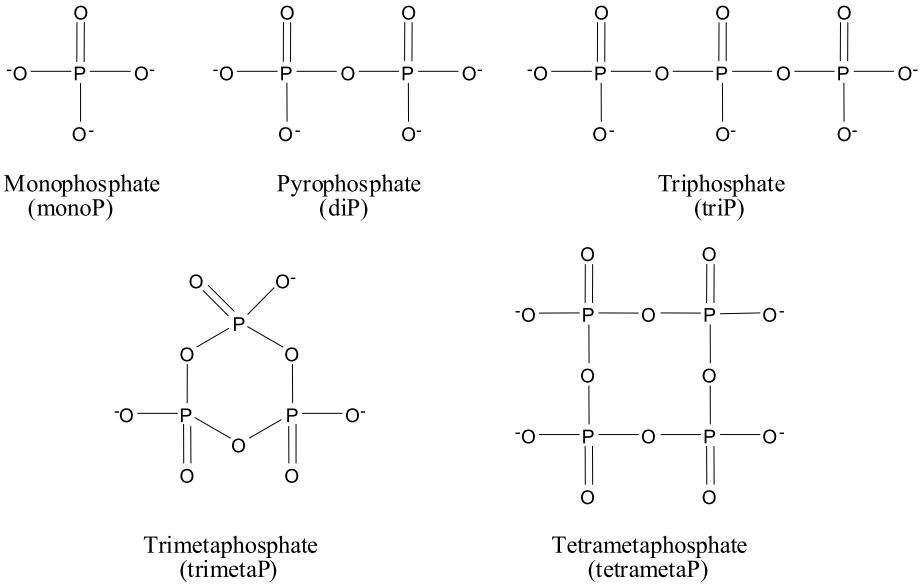

Fig. 1 Totally deprotonated forms of the ligands studied

a helium atmosphere at the constant ionic strength of 0.1 mol·L^{-1} (KNO_3) and temperature (20 ± 1) °C, using CO_2-free sodium hydroxide solution (concentration 0.1827 mol·L^{-1}) as the titrant. The concentrations of the various phosphates were 2×10^{-3} mol·L^{-1}, and the metal-to-ligand ratios were 2:1, 1:1 and 1:2. The determination of stability constants of the complexes, and protonation constants of ligands, was carried out using the SUPERQUAD program [25] (the value of the ionic product of water, determined here, is $pK_w = 13.78$), whereas the distribution of chemical forms was obtained by the HALTFALL program [26]. The calculations were performed using 150 to 350 points for each experiment, taking into account only those parts of the titration curves where no precipitate was present. The correctness of the speciation models was confirmed by verification of the results obtained (standard deviations, the convergence of the experimental and simulated titration curves, the Hamilton and chi squared tests) [27]. The iteration procedure allows one to determine stoichiometric composition and thermodynamic stability constants ($\log_{10}\beta$) of the complexes formed in the studied systems:

$$pM + qL + rH^+ \leftrightarrows M_pL_qH_r \tag{1}$$

$$\beta = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \tag{2}$$

In all cases the speciation testing began with the simplest hypothesis and then, in following steps, the models were expanded to include progressively more species, and the results were scrutinized to eliminate those species that were rejected by the refinement processes. Moreover, the correctness of the selected model was confirmed by the coincidence of experimental and simulated curves such as presented in Fig. 2.

For solution structure determinations, UV-VIS and EPR measurements were performed. Samples for visible spectroscopic studies were prepared in H_2O at M:L ratios of 1:1 and 1:2 while the Cu(II) concentration was held at 0.005 mol·L^{-1}. The spectra were recorded at

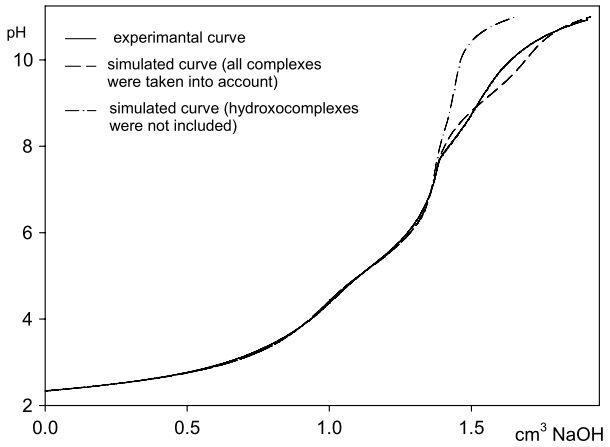

Fig. 2 Experimental and theoretical titration curves for the Cu/diP system

20 °C in a PLASTIBRAND PMMA cell with 1 cm optical path length using an Evolution 300 UV-VIS ThermoFisher Scientific Spectrometer equipped with a xenon lamp (measurement accuracy of 0.2 nm, sweep rate of 120 nm·min^{-1}, range of measurement from 450 to 950 nm). EPR studies were carried out at −196 °C using glass capillary tubes. The concentration of Cu(II) was 0.005 mol·L^{-1} in a water + glycol mixture (3:1), and the M:L ratios were 1:1 and 1:2. The spectra were recorded on a SE/X 2547 Radiopan instrument.

Full optimization of the isolated structures of each totally deprotonated phosphate was performed with the GAUSSIAN 03 program (Ground State DFT and B3LYP/Set lanL2DZ level). Structures, pre-optimized semi-empirically with HYPERCHEM-7.52 (PM3 Hamiltonian) [28, 29], were used as starting points.

3 Results and Discussion

The measured protonation constants as well as the stability constants of Cu(II) complexes with the ligands studied are given in Table 1. These results are in good agreement with literature data, and some deviations can be explained by different measurement conditions of [5, 21–23]. As far as we know, stability constants for the hydroxocomplexes determined in our study were not reported previously.

In a comparative analysis of equilibrium parameters for complexes of different composition, values of the equilibrium constants ($\log_{10} K_e$) have been taken into consideration, rather than the stability constants ($\log_{10} \beta$). For instance, the equilibrium constant for Cu(HmonoP) formation is $\log_{10} K_e = \log_{10} \beta_{Cu(HmonoP)} - \log_{10} K_{HmonoP}$, and this value corresponds to the efficiency of the protonated phosphate ligand to react with Cu(II) ions.

3.1 Protonation of Ligands

The successive $\log_{10} K$ protonation constants of the series of polyphosphates (Table 1) decrease with increasing chain length. On the other hand, an increase is observed in the $\log_{10} K$ values with increasing number of phosphate groups in the cyclic metaphosphates. According to our experience, the highest value of $\log_{10} K$ for which the potentiometric method can be applied is about 1.5. Carefully performing the experiments with appropriate acidification allowed us to determine $\log_{10} K$. In some systems studied the complexation reaction begins

Table 1 The overall ($\log_{10}\beta$) and successive ($\log_{10}K$) protonation constants of the mono-, di-, tri-, trimeta- and tetrametaphosphates, and the overall stability ($\log_{10}\beta$) and equilibrium ($\log_{10}K_e$) constants of the Cu(II) complexes (values in the parentheses refer to standard deviations (σ) obtained by SUPERQUAD)

System	Σ	Chi^2	Equilibrium	$\log_{10}\beta$	$\log_{10}K$
monoP	4.52	15.12	$monoP + H^+ \leftrightarrows HmonoP$	11.65 (3)	11.65
			$HmonoP + H^+ \leftrightarrows H_2monoP$	18.41 (3)	6.76
			$H_2monoP + H^+ \leftrightarrows H_3monoP$	20.12 (4)	1.71
diP	4.66	10.18	$diP + H^+ \leftrightarrows HdiP$	8.38 (1)	8.38
			$HdiP + H^+ \leftrightarrows H_2diP$	14.48 (2)	6.10
			$H_2diP + H^+ \leftrightarrows H_3diP$	16.15 (4)	1.67
			$H_3diP + H^+ \leftrightarrows H_4diP$	Not determined	
triP	5.12	14.15	$triP + H^+ \leftrightarrows HtriP$	7.90 (2)	7.90
			$HtriP + H^+ \leftrightarrows H_2triP$	13.40 (2)	5.50
			$H_2triP + H^+ \leftrightarrows H_3triP$	14.98 (5)	1.58
			$H_3triP + H^+ \leftrightarrows H_4triP$	Not determined	
			$H_4triP + H^+ \leftrightarrows H_5triP$	Not determined	
trimetaP	4.98	13.82	$trimetaP + H^+ \leftrightarrows HtrimetaP$	1.48 (3)	1.48
tetrametaP	5.50	17.06	$tetrametaP + H^+ \leftrightarrows HtetrametaP$	2.38 (4)	2.38
Cu(II)/monoP	6.54	17.33	$Cu^{2+} + HmonoP \leftrightarrows Cu(HmonoP)$	15.63 (3)	3.98
			$Cu^{2+} + monoP \leftrightarrows Cu(monoP)$	10.59 (2)	10.59
			$Cu(monoP) + H_2O \leftrightarrows Cu(monoP)(OH) + H^+$	−0.24 (8)	−10.83
Cu(II)/diP	7.12	13.45	$Cu^{2+} + HdiP \leftrightarrows Cu(HdiP)$	13.74 (2)	5.36
			$Cu^{2+} + diP \leftrightarrows Cu(diP)$	8.46 (3)	8.46
			$Cu(diP) + H_2O \leftrightarrows Cu(diP)(OH) + H^+$	−0.75 (3)	−9.21
Cu(II)/triP	5.98	16.26	$Cu^{2+} + HtriP \leftrightarrows Cu(HtriP)$	13.04 (4)	5.14
			$Cu^{2+} + triP \leftrightarrows Cu(triP)$	7.80 (6)	7.80
			$Cu(triP) + H_2O \leftrightarrows Cu(triP)(OH) + H^+$	−0.79 (6)	−8.59
			$Cu(triP) + 2H_2O \leftrightarrows Cu(triP)(OH)_2 + 2H^+$	−10.74 (7)	−18.54
Cu(II)/trimetaP	5.25	14.54	no complex formation	–	–
Cu(II)/tetrametaP	5.47	17.57	$Cu^{2+} + (tetrametaP) \leftrightarrows Cu(tetrametaP)$	3.34 (9)	3.34

at a pH of about 2, in the range of ligand deprotonation, so the first protonation constant needs to be considered for computer-added calculations.

For fully protonated ligands, the charge distribution on their molecules was calculated with the GAUSSIAN package, see Fig. 3. With increasing length of the polyphosphate chain, the –P–O bond length and the negative charge on the oxygen atoms were calculated to decrease in the order: PO_4^{3-} (−1.08) > $P_2O_7^{4-}$ (−0.99) > $P_3O_{10}^{5-}$ (−0.98).

For metaphosphates, the charges were observed to be higher than that for analogous chain forms (for $P_3O_{10}^{5-}$ it is −0.98, and for $P_3O_9^{3-}$ is −0.82), and an increase in the metaphosphate ring size resulted in an increase in the negative charge of the phosphate group (for $P_3O_9^{3-}$ it is −0.82, and for $P_4O_{12}^{4-}$ is −0.85).

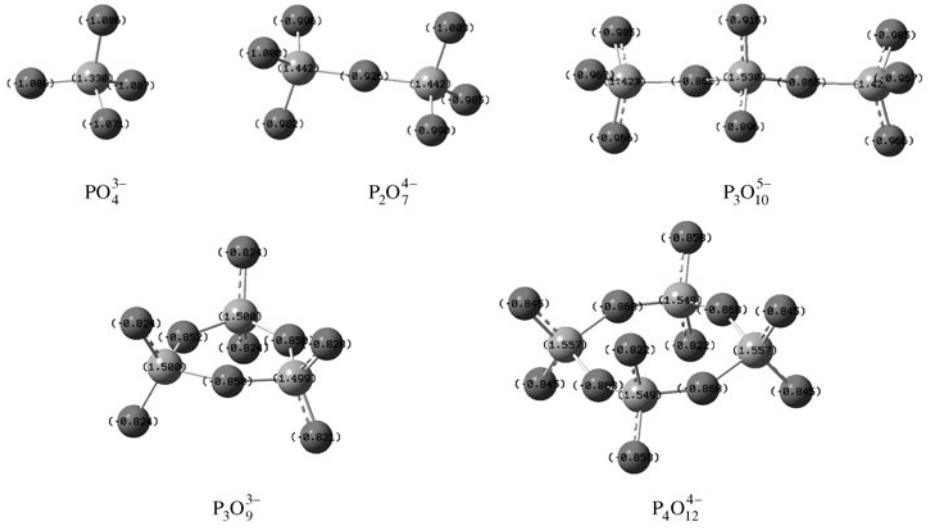

Fig. 3 Optimized totally deprotonated ligand solution structures

3.2 Complexation in the Cu(II)/Phosphate Systems

Computer-aided analysis of potentiometric titration data for the system Cu(II)/phosphates revealed the formation of MHL and ML complexes, along with ML(OH) and $ML(OH)_2$ (hydroxocomplexes were not observed in previous potentiometric studies). The only exception was the Cu/trimetaphosphate system, in which no complex was formed (at least in detectable amounts) in the studied pH range. However, this type of complex was found under different experimental conditions [5, 21–23]. Computer-aided analysis of the potentiometric titration data was performed by taking into account the protonation constants of the ligands and the known constants for Cu(II) hydrolysis {Cu(OH), $\log_{10}\beta = -7.73$; $Cu(OH)_2$, $\log_{10}\beta = -14.15$}. No detectable amounts of $Cu(OH)_x$ complexes have been found in the systems studied at the applied experimental conditions [30]. Taking into account the literature data and our experience, a relation was found between the d–d transition energy and the $g_{||}$, as $A_{||}$ parameters obtained from our EPR study and the number of coordinated donor atoms. Then, structures were proposed for the complexes formed in the investigated systems [31–33]. Additionally, results of DFT calculations, aimed at verifying the proposed coordination mode, were in all cases in agreement with the chromophore type established on the basis of the spectroscopic measurements. For instance, spectral parameters determined for the complex Cu(triP), discussed below ($\lambda_{max} = 819$ nm, $g_{||} = 2.398$, $A_{||} = 135 \times 10^{-4}$ cm^{-1}), indicate that only one oxygen atom is located in the inner coordination sphere, although several other oxygen atoms are present. It is worth noting that DFT calculations point to the highest stability for the model where only one donor atom is bound to the metal ion. Only when such agreement was found was the type of chromophore postulated.

3.2.1 ML Type Complexes

Simple ML type complexes occur in the all systems with chain and cyclic polyphosphates. In the systems with chain polyphosphates, the formation of ML complexes begins at pH about

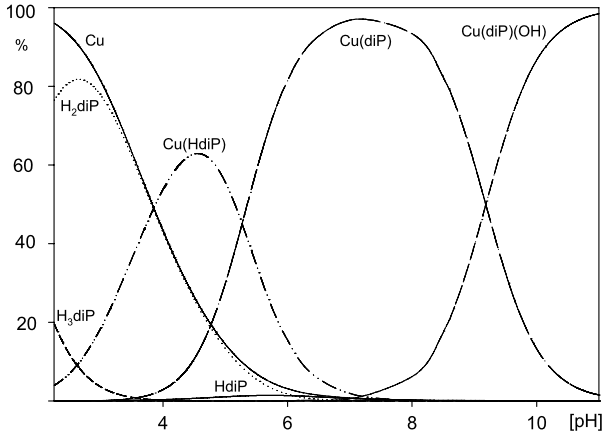

Fig. 4 Distribution curves of the species formed in the system Cu/diP ($c_{diP} = c_{Cu} = 0.002$ mol·L^{-1}), where percentages refer to the total amount of ligand

4.0 and vanishes at pH = 10.5 (the maximum relative concentrations, over 90%, occurs at pH ∼ 7.5, see Fig. 4). The complex Cu(tetrametaP) appears already at pH = 2.0 and binds 55% of the Cu(II) at pHs of about 4.0 and higher.

Comparison of equilibrium constants of ML type complexes formed in these systems shows that, with increasing length of the phosphate chain, the $\log_{10} K_e$ values decrease ($\log_{10} K_e = 10.59$, $\log_{10} K_e = 8.46$, $\log_{10} K_e = 7.80$ for Cu(monoP), Cu(diP), Cu(triP), respectively, see Table 1). A similar relation has been described by Crea et al. for chain polyphosphate species with Ca(II) and for non-covalent bonds with polyamines [34]. For cyclic polyphosphates, the complex forming ability increases with increasing size of the phosphate ring. Equilibrium constants of complexes with chain polyphosphates are much higher than those of complexes with cyclic polyphosphates (e.g., $\log_{10} K_e = 7.8$ and $\log_{10} K_e = 3.34$ for Cu(triP) and Cu(tetrametaP), respectively, Table 1), which indicates that structural factors have a significant effect on complex stability.

Analysis of the charge on oxygen atoms of the phosphate groups of fully deprotonated ligands, calculated using GAUSSIAN (Fig. 3), shows that $\log_{10} K_e$ of a ML complex is strongly related to the increase in the electron density of the donor atom. The charges on oxygen atoms and the corresponding $\log_{10} K_e$ values (below in parentheses) for the studied ligands are as follows:

$$\underset{(-1.08,\ \log_{10} K_e = 10.59)}{PO_4^{3-}} > \underset{(-0.99,\ \log_{10} K_e = 8.46)}{P_2O_7^{4-}} > \underset{(-0.98,\ \log_{10} K_e = 7.80)}{P_3O_{10}^{5-}}$$

$$> \underset{(-0.85,\ \log_{10} K_e = 3.34)}{P_4O_{12}^{4-}} > \underset{(-0.82)}{P_3O_9^{3-}}$$

The Vis and EPR spectral data for the ML complex (Table 2) indicate that the coordination arrangements are {2O}, {2O} and {1O} for the mono- di- and triphosphate complexes, respectively (the EPR spectrum of the system with monophosphate was not recorded because of a problem with turbidity). With increasing number of oxygen donor atoms, a characteristic shift is observed in the position of Vis band: {1O} ∼ 800 nm, {2O} ∼ 775–750 nm, and {3O} ∼ 720 nm (Fig. 5).

The conclusions about the solution structure were confirmed using DFT calculations (GAUSSIAN). It was found that the most probable model is that based on the spectroscopic study (Fig. 6). An analogous mode of coordination was established by Kruger et al. for the

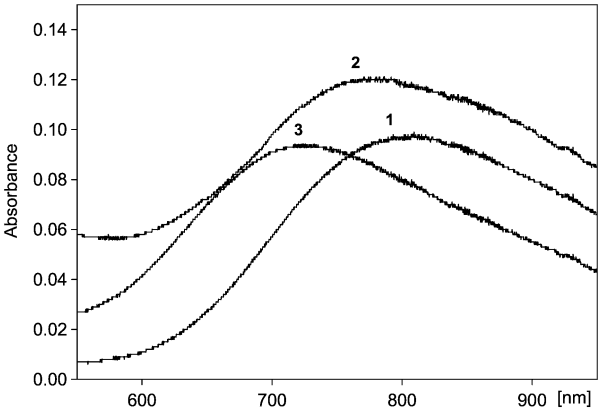

Fig. 5 Vis spectra of: 1—the Cu(II)/triP system (pH = 4.0), coordination mode {1O}; 2—the Cu(II)/monoP system (pH = 4.5), coordination mode {2O}; and 3—the Cu(II)/triP system (pH = 10.5), coordination mode {3O}; $c_{Cu(II)} = 0.005$ mol·L^{-1}

Table 2 Spectral data for the complexes investigated

Species	pH	$\log_{10}\beta$	Vis		EPR		Chromophore
			λ_{max} [nm]	ε [L·mol^{-1}·cm^{-1}]	$g_{\|\|}$	$A_{\|\|}$ [10^{-4} × cm^{-1}]	
Cu(HmonoP)	4.5	15.63	776	24.0	–	–	{2O}
Cu(monoP)	8.0	10.59	762	47.8	–	–	{2O}
Cu(monoP)(OH)	10.5	−0.24	720	23.1	–	–	{3O}
Cu(HdiP)	4.5	13.74	771	29.6	2.359	143	{2O}
Cu(diP)	7.5	8.46	767	28.8	2.358	144	{2O}
Cu(diP)(OH)	10.5	−0.75	719	22.6	2.359	145	{3O}
Cu(HtriP)	4.0	13.04	803	19.4	2.402	135	{1O}
Cu(triP)	7.0	7.80	810	22.4	2.398	135	{1O}
Cu(triP)(OH)	9.5	−0.79	753	17.6	2.380	139	{2O}
Cu(triP)$(OH)_2$	10.5	−10.74	719	18.8	2.244	195	{3O}
Cu(tetrametaP)	6.0	3.34	769	13.0	2.378	139	{2O}

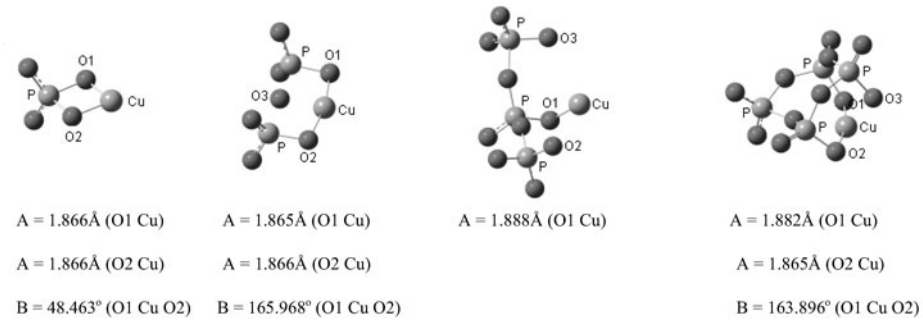

Fig. 6 Optimized structures of investigated ML complexes

copper pyrophosphate crystal in which a pyrophosphate bridge is formed [35]. Together with results obtained by the spectroscopic methods, the calculations permitted us to determine the interaction characteristics of Cu(II) with simple polyphosphate ligands (as yet not fully explained).

3.2.2 MHL Type Complexes

The protonated MHL type complexes are formed only in the systems of Cu(II) with chain polyphosphates, and their stability constants are given in Table 1. The formation of protonated complexes starts at pH close to 2.0 and the maximum amount of Cu(II) complexing occurs at pH close to 4.5 (50–75%), see Fig. 4. The equilibrium constant for Cu(HmonoP) complex formation ($\log_{10} K_e = 3.98$ for Cu(HmonoP)) is the lowest among those of the analogous species with di- and triphosphates, for which the $\log_{10} K_e$ values are similar ($\log_{10} K_e = 5.36$ for Cu(HdiP), $\log_{10} K_e = 5.14$ for Cu(HtriP)). Analysis of the EPR spectral parameters of Cu(HmonoP), Cu(HdiP) and Cu(HtriP) complexes and their Vis spectra, taken at a pH at which the protonated complex dominates, indicate {2O}, {2O} and {1O} coordinations, respectively (Table 2).

3.3 $ML(OH)_x$ Type Complexes

Hydroxocomplexes of the ML(OH) type were detected only in complexes with chain polyphosphates. Complexation starts at pH $>$ 7.0 and these species dominate at pH $\sim$ 10.5 where the complexes bind the maximum amount of Cu(II) (Fig. 4). The equilibrium constants ($\log_{10} K_e$) for formation of hydroxocomplexes are given in Table 1. Values of formation constants for the hypothetical $ML + OH \leftrightarrows MLOH$ reactions, $\log_{10} K'_e = \log_{10} K_e - \log_{10} K_w$, are 2.95, 4.57 and 5.19 for Cu(II) hydroxocomplexes with monoP, diP and triP, respectively. The above values correspond to the energy of binding of hydroxo groups to the anchoring ML complexes formed at lower pH values.

Analysis of the Vis and EPR spectroscopic data of the complexes (Table 2) testifies to the formation of {3O}, {3O} and {2O} chromophores for Cu(monoP)(OH), Cu(diP)(OH) and Cu(triP)(OH), respectively. Monofunctional coordination found in binary Cu(triP) complexes results in higher efficiency for OH group binding (lower spatial hindrance).

The $CuL(OH)_2$ complex is formed only in systems with a chain triphosphate. This species starts forming at pH close to 8.0 and binds a maximum 90% of the Cu(II) at pH = 10.5 and above. The spectral parameters λ_{max}, $g_{||}$ and $A_{||}$ for the complexes indicate {3O} type of coordination (one oxygen atom from triphosphate and two oxygen atoms from hydroxyl groups).

4 Conclusions

In the systems of Cu(II) ions with phosphates, formation of MHL, ML and $ML(OH)_x$ type complexes was established. ML type complexes were observed in the systems with chain and cyclic phosphates. The effectiveness of metal ion binding to the phosphate group in ML complexes decreases with increasing length of the chain, and with decreasing –P–O bond length and charges of oxygen atoms from phosphates. Moreover, the chain polyphosphates were found to have much higher reaction equilibrium constants than those of the polymetaphosphates, although they have similar inner coordination spheres ($\log_{10} K_e = 8.46$ for Cu(diP) and $\log_{10} K_e = 3.34$ for Cu(tetrametaP). This observation indicates that structural

factors have a significant effect on the complex's stability. As it was concluded from spectral studies, only one oxygen atom from the β group of triphosphate is involved in coordination (despite the fact that there are three possible donor groups). This mode of coordination has been confirmed by DFT calculations.

The above conclusions can be used in discussion on more complicated systems including metal ions with bioligands containing phosphate groups.

Acknowledgements This work has been supported by the Ministry of Science and Higher Education (Poland), Grant No. N N204 001736.

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