

Determination of Equilibrium Constants of Some Novel Antioxidant Compounds and Study on their Complexes with Some Divalent Metal ions in Ethanol-water Mixed

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Abstract

This study aims to investigate the nature and type of complexes formed in solution, between novel antioxidant compounds [P1(4-(1-(3-hydroxy-4-methoxyphenyl)propyl)benzene-1,2-diol) and P2(4-(1-(3-hydroxy-4-methoxyphenyl)propyl)benzene-1,3-diol)] and the ions Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} . Potentiometric titration technique was used to follow the formation of complexes during the course of coordination. The stability of the complexes formed was controlled through the determination of stability constants in aqueous ethanol solution at $25 \pm 0.1 \text{ }^\circ\text{C}$ and ionic strength of 0.1 M NaCl. Basicity of the ligand was also assessed by the determination of the dissociation constants of the ligand. All the constants were computed by computer refinement of pH–volume data using the SUPERQUAD program. The species distribution diagram of each type of complex has been obtained after computer calculation process.

Keywords: Antioxidant, Potentiometric titration, Phenolic compounds, proton affinity

1. Introduction

Radicals and active oxygen species play a role in cancer, aging,^{1–4} and some diseases. Antioxidants are chemical compounds that can quench reactive radical intermediates formed during the oxidative reactions. Phenolic derivatives are one of the groups of antioxidants.⁷ Phenolic antioxidants have good antioxidant capacity.^{8–13} For example, butylated hydroxytoluene, butylated hydroxyanisole or butylated hydroxyquinone have been utilized in the food preservation. Additionally, many phenolic antioxidants such as caffeic acid,¹⁴ gallic acid,¹⁵ resveratrol¹⁶ and hydroxytyrosol^{17–20} are well known in literature. However; development, characterization, synthesis or isolation of new and safer antioxidants is very important and necessary.

Recently, Ceylan et al.²¹ have synthesized two new phenolic compounds (4-(1-(3-hydroxy-4-methoxyphenyl)propyl)benzene-1,2-diol (P1) and (4-(1-(3-hydroxy-4-methoxyphenyl)propyl)benzene-1,3-diol (P2) from the reaction of isoeugenol with pyrocatechol and resorcinol, respectively. In addition, they have determined that the P1 and P2 showed the significant ferric ion reducing power, lipid peroxidation inhibition and radical scavenging activity on DPPH, ABTS⁺, and O_2^- radicals.

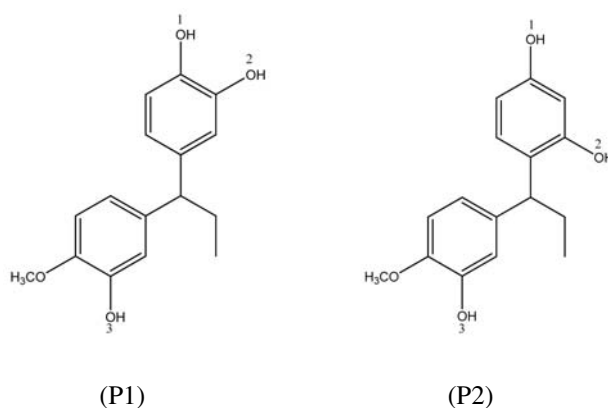


Figure 1. Chemical structures of P1 and P2.

Anti-oxidant and free radical scavenging activity of phenolic derivatives is due to phenolic hydroxyl group. As known, phenols prevent the free radical formed with ionizing of the hydrogen atom in the phenolic OH group during the oxidation process.²² The dissociation of phenolic compounds plays an important role in the antioxidant activity and their complexation.²³ So, the determination of

dissociation and stability constants are very important in the explaining of the antioxidant behaviour and interaction with the transition metal ions of phenolic compounds and many study have been published in literature.^{24–29}

In the present study, the dissociation constants of novel antioxidant compounds P1 and P2 and stability constants of their complexes with Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} were investigated using potentiometric titration method that is a powerful electro analytical technique.^{30–34}

2. Experimental and Methods

2.1. Apparatus and Materials

P1 and P2 ligands were synthesised and characterized according to the reported procedure by Ceylan et.al.²¹ Ethanol, NaCl, CuCl_2 , ZnCl_2 , NiCl_2 and CoCl_2 were purchased from Merck, potassium hydrogen phthalate (KHP) and borax ($\text{Na}_2\text{B}_4\text{O}_7$) from Fluka, 0.1 M NaOH and 0.1 M HCl as standard from Aldrich. All reagents were of analytical quality and were used without further purification. Solutions of metals ions ($1 \cdot 10^{-3}$ M) were prepared from CuCl_2 , ZnCl_2 , NiCl_2 and CoCl_2 as received and standardized with ethylenediaminetetraacetic acid (EDTA).³⁵ 1.0 M NaCl (Riedel-de Haën) stock solution was prepared. For the solutions, CO_2 -free double-distilled deionized water was obtained from an aquaMAX™-Ultra water purification system (Young Lin Inst.). Its resistivity was $18.2 \text{ M}\Omega \text{ cm}^{-1}$. pH-metric titrations were performed using the Molspin pH meter™ with a Orion 8102BNUWP ROSS ultra combination pH electrode. The temperature in the double-wall glass titration vessel was constantly controlled using a thermostat (DIGITERM 100, SELECTA) and kept at 25.0 ± 0.1 °C.

2.2. Potentiometric Measurements

0.05 mol kg^{-1} potassium hydrogen phthalate (KHP) and 0.01 mol kg^{-1} borax ($\text{Na}_2\text{B}_4\text{O}_7$) were prepared for calibration of electrode systems. An automatic burette was connected to Molspin pH-mV-meter. The pH electrode was calibrated according to instructions of the Molspin Manuel³⁶ with buffer solutions of pH 4.005 (KHP) and pH 9.180 ($\text{Na}_2\text{B}_4\text{O}_7$) at $25.0 (\pm 0.1)$ °C.³⁷ $2 \cdot 10^{-3}$ M phenols in ethanol-water mixture (20%) and 0.025 M NaOH were prepared. NaOH concentration (0.025 M) was standardized with primer standard KHP solution by pH-metric titration. Nitrogen gas (99.9%) was purged trough the cell solutions to exclude atmospheric CO_2 . All potentiometric pH measurements were carried out in a 100 mL double-walled glass vessel. The titration cell was equipped with magnetic stirrer. The system was maintained at an ionic strength of 0.1M by NaCl as a supporting electrolyte. For each measurement, 0.01 mmol of ligand and the required amount of 1.0 M NaCl and 0.1M HCl were added into the titration cell. The final volume of the titration solutions

was completed to 50 mL by deionised water and the volume increments were adjusted as 0.03 mL. The pH data points were collected after each addition of 0.03 mL of the standardised NaOH solution. Additionally, the same titrations were performed for metal (Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}) ligands complexes. In this study, metal:ligand molar ratios were 2:1 and 1:1 and each titration were repeated for the three times. The SUPERQUAD computer program was used for the calculation of both protonation and stability constants.³⁸

3. Result and Discussion

3.1. Dissociation Constants

Theoretical calculation assists the sequencing of the dissociation steps of the ligands and determination of coordination side or sides of the ligands. Therefore, the theoretical calculations have been used in some potentiometric studies.^{39,40} In this study, semi-empirical methods such as Parametric Model 3 (PM3) and Parametric Model 6 (PM6) are used for calculating of proton affinity of donor atoms of the ligands. The formation heats (H_f) and the total energies (TE) of the ligands and mono-protonated species were calculated by PM3 and PM6 methods. In addition, the proton affinity of each oxygen atom (PA) in the ligands was found using formation heats in the following equation and given in Table 1.

$$\text{PA} = 367.2 + \Delta H_f^\circ(\text{B}) - \Delta H_f^\circ(\text{BH}^+)$$

Where, PA is the proton affinity of B types; $\Delta H_f^\circ(\text{B})$ is the formation heat of B molecule; $\Delta H_f^\circ(\text{BH}^+)$ is the for-

Table 1. The calculated H_f , TE and PA values with PM3 and PM6 methods for P1 and P2 and their mono-protonated forms.

Species	PM3		
	T.E. (kcal/mol)	H_f	PA
P1	-77196.94	-128.79	-
1 O-H ₂ ⁺	-77353.88	67.85	170.56
2 O-H ₂ ⁺	-77355.13	66.60	171.81
3 O-H ₂ ⁺	-77360.01	61.73	176.68
P2	-77198.84	-130.79	-
1 O-H ₂ ⁺	-77344.66	77.07	159.34
2 O-H ₂ ⁺	-77354.20	67.53	168.88
3 O-H ₂ ⁺	-77357.95	63.78	172.63
Species	PM6		
	T.E. (kcal/mol)	H_f	PA
P1	-3369.41	-130.70	-
1 O-H ₂ ⁺	-3381.57	-99.55	336.05
2 O-H ₂ ⁺	-3381.57	-99.72	336.22
3 O-H ₂ ⁺	-3381.74	-103.38	339.88
P2	-3369.73	-137.86	-
1 O-H ₂ ⁺	-3381.72	-103.09	332.43
2 O-H ₂ ⁺	-3381.75	-103.80	333.14
3 O-H ₂ ⁺	-3381.95	-108.22	337.56

mation heat of BH^+ molecule, and 367.2 is the formation heat of H^+ .⁴¹

Proton affinity gives information about the degree of basicity of donor atoms and protonation order. The proton affinity of oxygen atom in 3 positions is higher than the other oxygen atoms in P1 and P2 in Table 1. In other words, the oxygen atoms in 3 positions of ligands are the most basic atom. This can be explained by the hydrogen bonding between the hydroxyl group in 3 positions and the methoxy group. Therefore, the first protonated step is oxygen atom in 3 positions in both of P1 and P2. The other protonation steps are oxygen atoms in 2 and 1 positions in the ligands. But, proton affinities of 1O and 2O in P1 are higher than 1O and 2O in P2. 1O and 2O atoms in P1 are more basic than that of P2. This case can be explained by different inductive effects in ligands. While the oxygen atoms (1O and 2O) in P1 are located *o*-positions, they are located *m*-positions in P2 to each other. Although there is a hydrogen bond between 1O and 2O in P1, it is not formed in P2. According to the calculation results, the protonation order for both ligands is as 3O, 2O and 1O. In other

words, the dissociation order for both ligands is as 1O, 2O and 3O.

Dissociation constants were potentiometrically obtained from several series of independent measurements. The titration and species distribution curves for P1 and P2 are shown in Fig. 2a-d.

According to Fig. 2b and d, all species of the ligands are observed between pH 8–12. All species starts to form at pH 8. While LH_3 form exist a maximum concentration (95 %) at pH 8, L is dominant 98 % at pH 12. If LH_3 is shown as the fully protonated form of the P1 and P2, its deprotonation equilibria is as following:

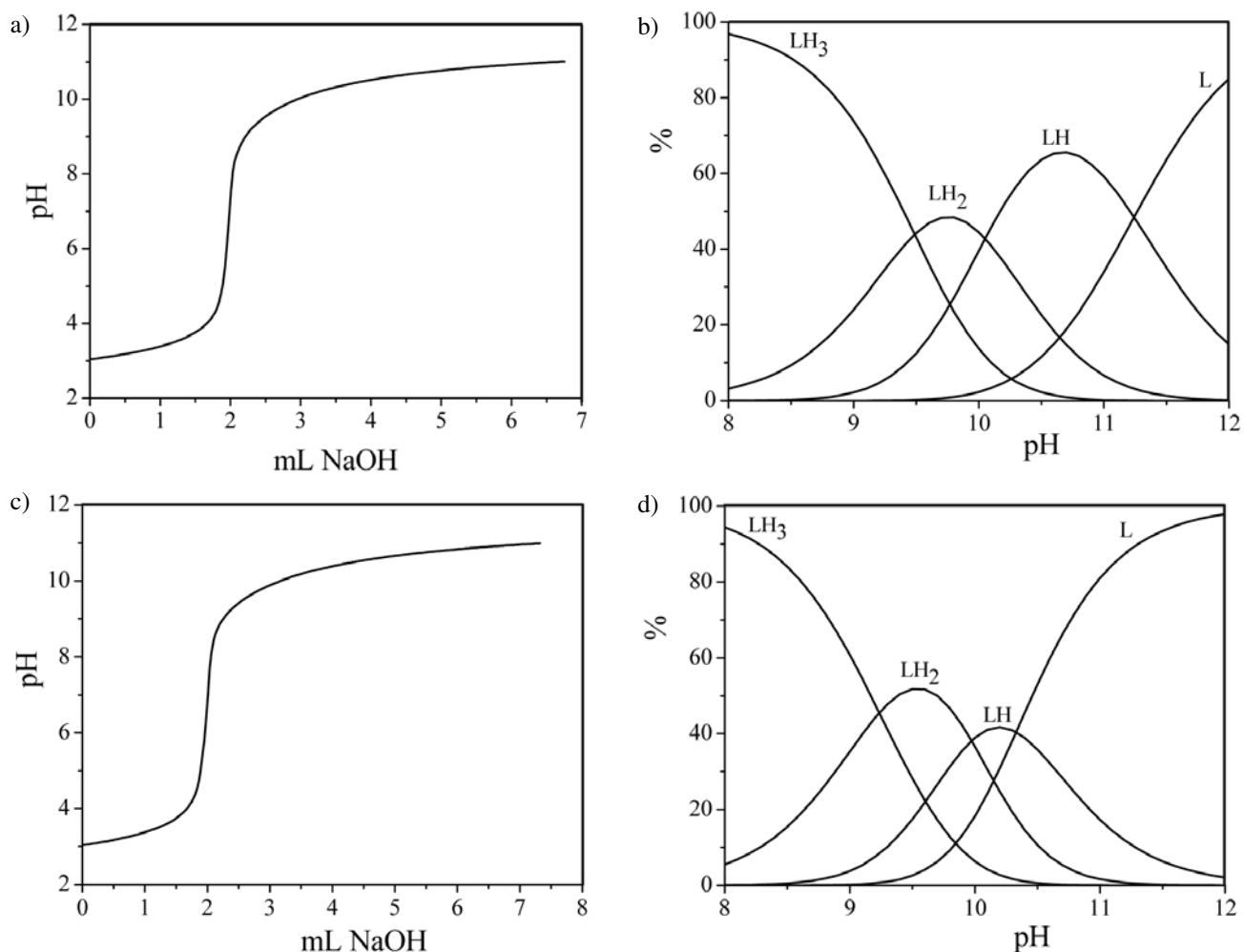
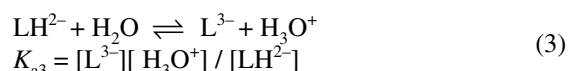
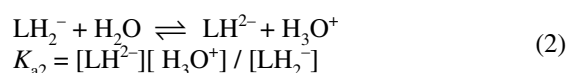
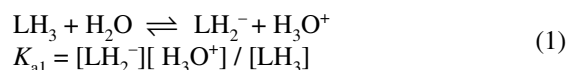


Figure 2. Titration curve for P1 and P2 [(a) P1 (c) P2, 0.05 mmol HCl] and the species distribution curves of P1 and P2 [(b) P1, (d) P2, (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl, 0.05 mmol HCl)]

Hence,

$$pK_a = -\log K_a \quad (4)$$

According to Eq. 4, the negative logarithms of equilibrium constants (K_{a1} , K_{a2} and K_{a3}) of species (LH_3 , LH_2^- and LH^-) describes as pK_{a1} , pK_{a2} and pK_{a3} and these values which was calculated using SUPERQUAD computer program for the P1 and P2 in under the experimental conditions are given in Table 2.

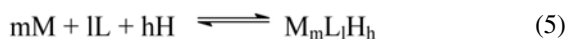
Table 2. Dissociation constants of P1 and P2 (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl)

ligands	species	$\log\beta$	pK_a
P1	LH_3	11.24 ± 0.05	9.49 ± 0.03
	LH_2^-	21.29 ± 0.01	10.05 ± 0.05
	LH^-	30.78 ± 0.01	11.24 ± 0.08
P2	LH_3	10.33 ± 0.06	9.24 ± 0.04
	LH_2^-	20.30 ± 0.08	9.97 ± 0.06
	LH^-	29.54 ± 0.09	10.33 ± 0.07

Although P1 should be evaluated as two moieties: *o*-methoxy and *o*-dihydroxy phenol, P2 evaluated as *o*-methoxy and *m*-dihydroxy phenol. Theoretical calculations and experimental studies are shown that 3O atom in *o*-methoxy phenol of both P1 and P2 is the more basic centre that of the others. Thus, pK_{a3} values (11.24 and 10.33) are related to hydroxyl group in 3 positions in both ligands. pK_{a1} and pK_{a2} values belong to hydroxyl groups in 1 and 2 positions *o*- and *m*-dihydroxy phenol in the ligands. As expected, pK_a 's values of P1 are higher than that of P2 because of intermolecular hydrogen bonding in P1. In addition, this might be explained as returning capability of *o*-dihydroxy phenol to the quinone form. Since the *o*-dihydroxy phenols are generally known to be very efficient systems to delocalize electrons, but not for *m*-dihydroxy phenol systems. Additionally, this situation leads to becoming higher capability antioxidant property of P1 than that of P2.²¹

3. 2. Stability Costants

The stability constants of binary complexes of P1 and P2 with some divalent metal ions in aqueous solution were determined following refinement of data by SUPERQUAD computer program. The cumulative stability constants (β_{mlh}) are defined by Eq. (3–4).



$$\beta_{mlh} = \frac{[M_mL_lH_h]}{[M]^m[L]^l[H]^h} \quad (6)$$

Where M is metal ions (Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}), L is ligand and H is proton and m, l and h subscripts are the respective stoichiometric coefficients. Because of unknowing the ligand and complexes activity coefficients, the β_{mlh} values are defined as concentrations. The titration curves of the metal-ligand complexes for the ions used in this work are given in Fig.3a and b.

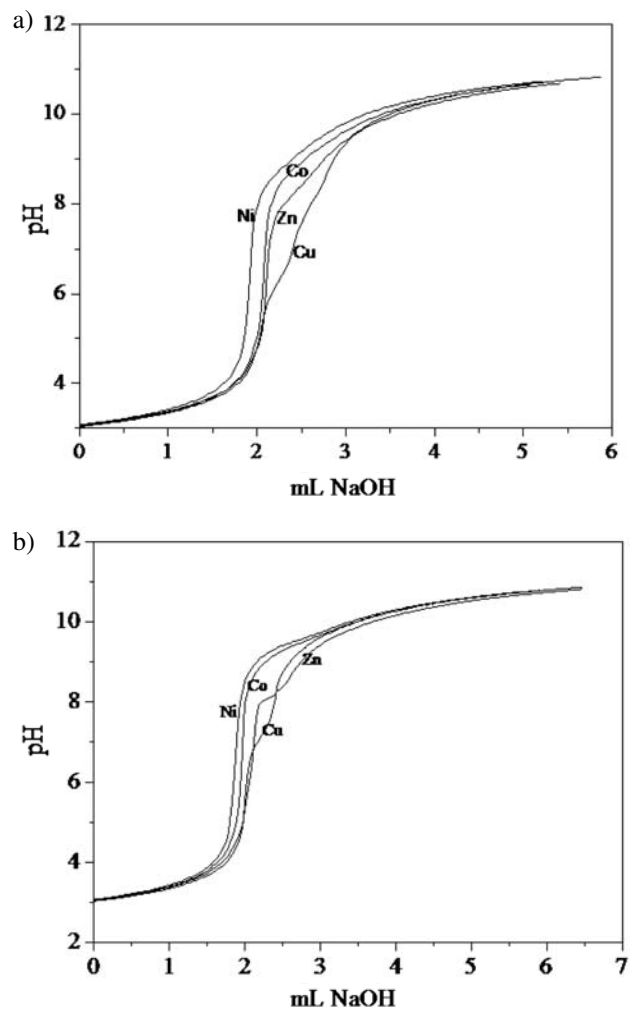


Figure 3. Titration curves for P1(a) and P2 (b) with Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} complexes (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl, 0.05 mmol HCl)

Potentiometric titration of complexes system of Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+} ions with P1 and P2 in aqueous solution were carried out to evaluate their stoichiometry and stability constants. The complexes are formulated for P1 as M_2L , M_2HL , MH_2L and for P2 as ML , MHL , MH_2L , MH_2L depending on pH and their distribution curves are given in Fig.4–6.

The ligand (P1) consists of two units: *o*-dihydroxy phenol and *o*-methoxy phenol. Each of them includes two oxygen donor atoms. The oxygen donor atoms are hard base. Therefore each part behaviours as bidantate ligand

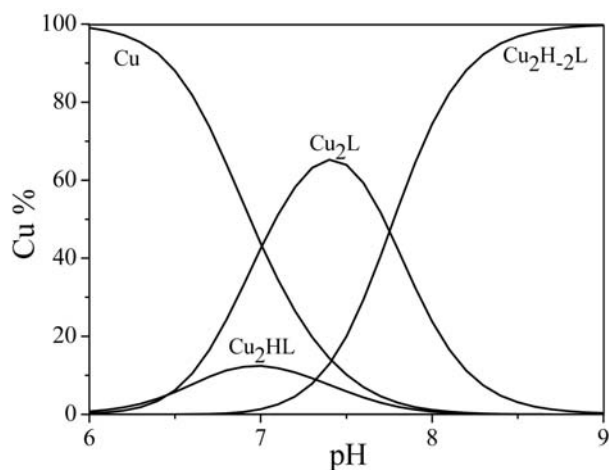


Figure 4. Species distribution curves for P1 with Cu^{2+} complexes (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl)

and they have capable of occurring five membered chelat with all metal ions. In this case, P1 includes four oxygen donor atoms and it occurs polynuclear complexes with all metal ions at 2:1 metal-ligand ratio.

According to the species distribution diagrams of Cu^{2+} -P1 system (see Fig. 4); Cu_2L , Cu_2HL , CuH_2L complexes forms are seen between pH 6–9. CuH_2L which is hydrolyzed species form is the main complex and it takes place a maximum concentration (approx. 100 %) at pH 9. All the Cu^{2+} ions turn to $\text{Cu}_2\text{H}_2\text{L}$ form in this region. Crystal structure (ORTEP diagram⁴²) of this complex species is given Fig. 5.

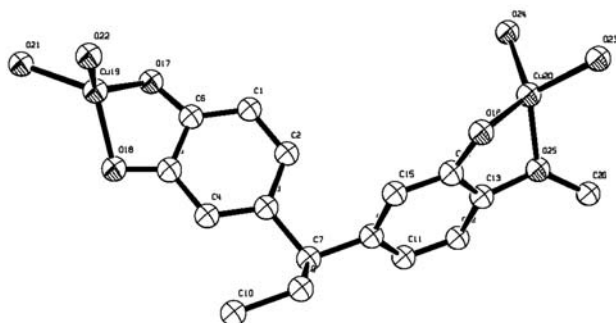


Figure 5. Crystal structure of $\text{Cu}_2\text{H}_2\text{L}$ species of Cu^{2+} -P1 complexes (Thermal ellipsoids at 50% probability)

Complexation between the metal ions and the ligands start with losing of the proton of the ligands. Therefore, all complex species are generally obtained in basic region. However, because of not having enough electrons in the donor atoms of the ligand, the coordination of the metal ions is not completed. Therefore, coordination of the metal ions is completed with the hydrolysis of the metal ions. Consequently, our experimental results are shown that the hydrolysis species are more stable than the others under the experimental conditions.

P2 also contains two moieties as the same P1. But one of units is *m*-dihydroxy phenol. In other words, positions of hydroxyl group of P2 are different from P1. This point is very important respect to coordination properties of the ligand. Because, the hydroxyl groups in the *m*-position can not attempted coordination with the metal ions. Therefore, this part of P2 acts as mono-dentate and it can not be formed the stable chelate complexes with the metal ions. In this case, P2 forms at ratio of 1:1 metal-ligand complexes with all metal ions from side of *o*-methoxy phenol.

Cu^{2+} -P2 complex system is shown in Fig. 6. CuL , CuHL , CuH_2L and CuH_2L complex forms are obtained between pH 4–11. Two main complexes form such as CuL and CuH_2L which is the hydrolyzed species are observed.

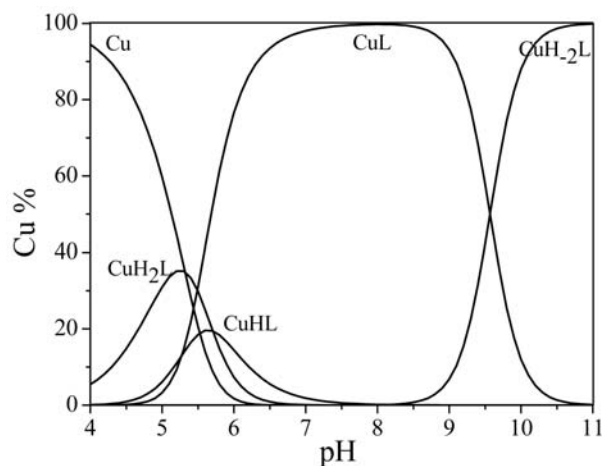


Figure 6. Species distribution curves for P2 with Cu^{2+} complexes (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl)

Cu^{2+} ions turn to CuL at pH 8 (approx. 99%) and this species is the main complex. Besides, all Cu^{2+} ions are hydrolyzed at pH 11 and turn to the CuH_2L complex species. Crystal structure (ORTEP diagram⁴²) of this complex species is illustrated Fig. 7.

Hydrolysis species of complexes are more stable than other complexes species at pH 11 in metal-P2 sys-

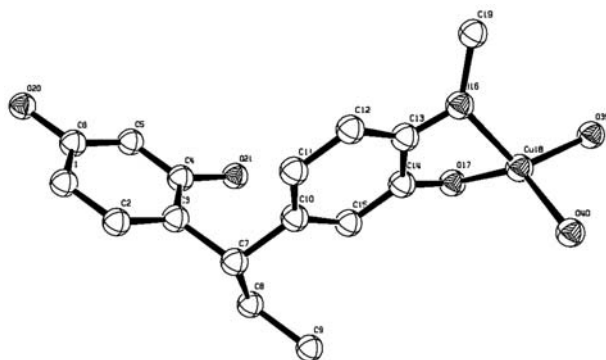


Figure 7. Crystal structure of CuH_2L species of Cu^{2+} -P2 complexes (Thermal ellipsoids at 50% probability)

tems same as P1. Thus, in this paper, crystal structures of hydrolysis species of complexes are given Fig.5 and Fig 7. Also, the overall stability constants of all complexes species of P1 and P2 are given in Table 3–4.

Table 3. Overall stability constants in M^{2+} – P1 system (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl)

metal	m	h	l	$\log\beta$
Cu ²⁺	2	0	1	20.08±0.04
	2	1	1	26.54±0.05
	2	-2	1	4.57±0.32
Ni ²⁺	2	0	1	22.12±0.09
	2	1	1	29.60±0.10
	2	-2	1	5.10±0.16
Zn ²⁺	2	0	1	20.93±0.09
	2	1	1	27.46±0.10
	2	-2	1	4.60±0.16
Co ²⁺	2	0	1	21.66±0.06
	2	1	1	28.58±0.05
	2	-2	1	4.82±0.09

Table 4. Overall stability constants in M^{2+} – P2 system (25.0 ± 0.1 °C, $I = 0.1$ M by NaCl)

Metal	m	h	l	$\log_{10}\beta$
Cu ²⁺	1	0	1	18.14±0.01
	1	1	1	25.47±0.09
	1	2	1	32.34±0.07
	1	-2	1	-0.77±0.02
Ni ²⁺	1	0	1	20.95±0.08
	1	1	1	26.55±0.07
	1	2	1	32.12±0.09
	1	-2	1	1.79±0.04
Zn ²⁺	1	0	1	14.91±0.04
	1	1	1	23.42±0.03
	1	2	1	29.13±0.04
	1	-2	1	-0.99±0.13
Co ²⁺	1	0	1	18.12±0.06
	1	1	1	26.81±0.07
	1	2	1	31.71±0.07
	1	-2	1	-0.78±0.04

4. Conclusion

Consequently, Proton affinities of P1 and P2 were calculated using PM3 and PM6 semi-empirical methods theoretically. According to the calculation results, the protonation order for both ligands is as 3O, 2O and 1O. In ot-

her words, the dissociation order for both ligands is as 1O, 2O and 3O. Dissociation constants of P1 and P2 were calculated as 9.49, 10.05, 11.24 and 9.24, 9.97, 10.33 respectively. Also, Stability constants of complexes of P1 and P2 with some divalent metal ions including Cu²⁺, Ni²⁺, Zn²⁺ and Co²⁺ have been studied in ethanol-water mixed in 0.1 M ionic strength and at 25.0 ± 0.1 °C, using glass electrode potentiometrically. The dissociation constants and overall stability constants were calculated using SUPERQUAD and these values are given Table 1–4. P1 includes four oxygen donor atoms and it occurs polynuclear complexes with all metal ions at 2:1 metal-ligand ratio. P2 forms at ratio of 1:1 metal-ligand complexes with all metal ions from side of *o*-methoxy phenol. The complexes are formulated for P1 as M₂L, M₂HL, MH₂L and for P2 as ML, MHL, MH₂L, MH₂L depending on pH and their distribution curves are given in Fig.4–6.

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Povzetek

S pomočjo potenciometričnih titracij smo zasledovali tvorbo kompleksov med antioksidatoma [P1(4-(1-(3-hidroksi-4-metoksifenil)propil)benzen-1,2-diol) in P2(4-(1-(3-hidroksi-4-metoksifenil)propil)benzen-1,3-diol)] ter Cu^{2+} , Ni^{2+} , Zn^{2+} in Co^{2+} ioni. V mešanica h vode in etanola smo pri 25 ± 0.1 °C ter ionski moči 0.1 (NaCl) določili konstante stabilnosti proučevanih kompleksov, ki smo jih preverili s pomočjo UPERQUAD programa. Izkazalo se je, da se izračunana porazdelitev kompleksov dobro ujema z eksperimentalno dobljenimi rezultati.