

**POTENTIOMETRIC STUDY OF THE NEW SYNTHESIZED 1-BENZYL-4-PIPERAZINEGLYOXIME AND 1-METHYL-4-PIPERAZINEGLYOXIME AND THEIR DIVALENT METAL COMPLEXES**

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**Abstract**

The deprotonation constants of 1-benzyl-4-piperazineglyoxime (BPGO) and 1-methyl-4-piperazineglyoxime have been determined in 0.1 mol dm<sup>-3</sup> NaCl at 25 °C potentiometrically (Molspin). The pK<sub>a</sub> values have been found as 9.79, 7.04 and 3.19 for BPGO and 9.56, 7.62 and 3.01 for MPGO in acidic medium. Protonation order of nitrogen atoms in the ligands has been determined by theoretical calculation (Semi-empirical AM1 method). In various pH conditions, the different complexes, which are formulated as MH<sub>6</sub>L<sub>2</sub>, MH<sub>5</sub>L<sub>2</sub>, MH<sub>4</sub>L<sub>2</sub>, MH<sub>3</sub>L<sub>2</sub>, MH<sub>2</sub>L<sub>2</sub>, MHL<sub>2</sub>, ML<sub>2</sub>, MH<sub>1</sub>L<sub>2</sub> and MH<sub>2</sub>L<sub>2</sub> have been formed by titration of the transition metal ions (Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>) and ligands mixtures with NaOH. The stability constants of each complex have been calculated by SUPERQUAD computer program and general mechanisms have been proposed with regard to the formation of these complexes (MH<sub>2n</sub>L<sub>2</sub> and MH<sub>2n-1</sub>L<sub>2</sub>).

**Introduction**

There has recently been a great deal of interest in coordination compounds containing vic-dioximes ligands. It is reported that vic-dioximes have three isomers, syn, anti, and amphi forms, depending on the position of –OH groups in molecule.<sup>1-5</sup> The syn-isomer does not constitute complex with metals but anti- and amphi forms give two different colored complexes with the same metals.<sup>2-5</sup> The transition metal complexes of anti-dioximes are essentially square-planar structures with the four nitrogen atoms of two vic-dioxime molecules coordinating to the metal ion.<sup>1,6</sup> The stable complexes prepared with vic-dioxime ligands have been used extensively for different purposes such as analytical and medicinal chemistry, pigments and biochemistry. Schrauzer<sup>7</sup> has found that this kind of complexes exhibits semiconductor property. Aydogdu et al

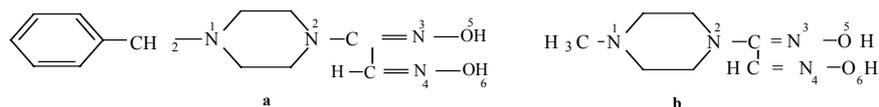
have also synthesized new Ni-glyoxime complexes and found that these complexes have inorganic semiconductor behaviors.<sup>8</sup> In the literature, the numerous vic-dioximes and their transition metal complexes have been investigated for a long period of time.<sup>1,2,9,10</sup> However, potentiometric and spectrophotometric characterizations of their protonation and stability constants have not been investigated so far.

Thus, the purpose of this work is to investigate the deprotonation constants of 1-benzyl-4-piperazineglyoxime and 1-methyl-4-piperazineglyoxime and the stability constants of their complexes with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  potentiometrically.

## Results and discussion

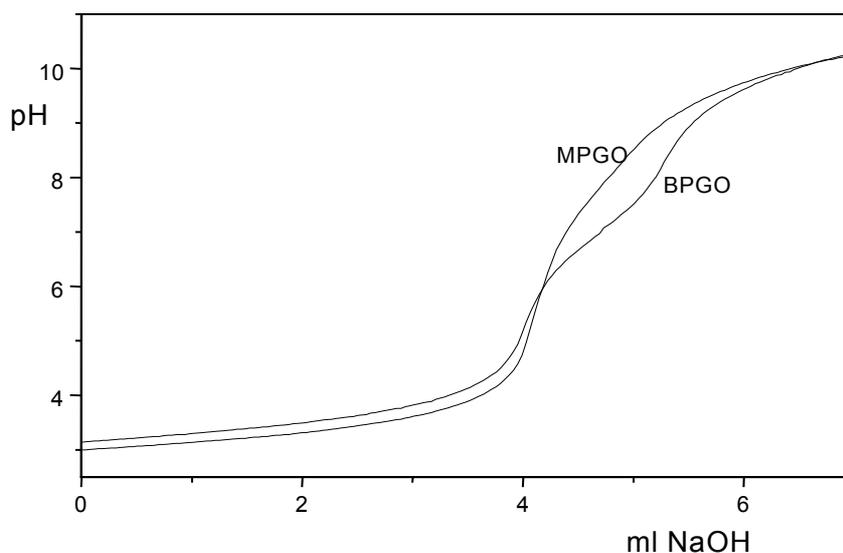
### Protonation Constants

The structures of the ligands investigated have been shown in Scheme 1a and b.



Scheme 1

The potentiometric titration curves of the ligands, BPGO and MPGO, have been shown in Figure 1. As seen in Figure 1, there are two sharp end points for BPGO. In the MPGO (Figure 1), although the first end point is sharp, the second end point is not. The deprotonation constants calculated by SUPERQUAD for the ligands have been given in Table 1. As can be seen in this Table, three  $\text{pK}_a$  values for each ligand have been calculated. The  $\text{pK}_a$  values of the ligands are similar to each other, because their chemical structures consist of the same groups except for benzyl and methyl groups. As known, if the difference between two  $\text{pK}_a$  values is higher, the end points of the titration curves are sharper. When  $\text{pK}_{2a}$  and  $\text{pK}_{3a}$  are compared for each ligand, it is seen that there are differences between two  $\text{pK}_a$  ( $\Delta\text{pK}_a$ ) values, which are 2.75 log unit for BPGO and 1.94 log unit for MPGO. Since this difference in the MPGO is lower than that of BPGO, the second end point belonging to MPGO is not sharp. The difference between  $\text{pK}_{a2}$  and  $\text{pK}_{a1}$  values of MPGO and BPGO are 4.61 log unit and 3.85 log unit respectively. Thus, the first end point for MPGO is sharper than it is for BPGO.



**Figure 1:** Potentiometric titration curves for BPGO and MPGO.

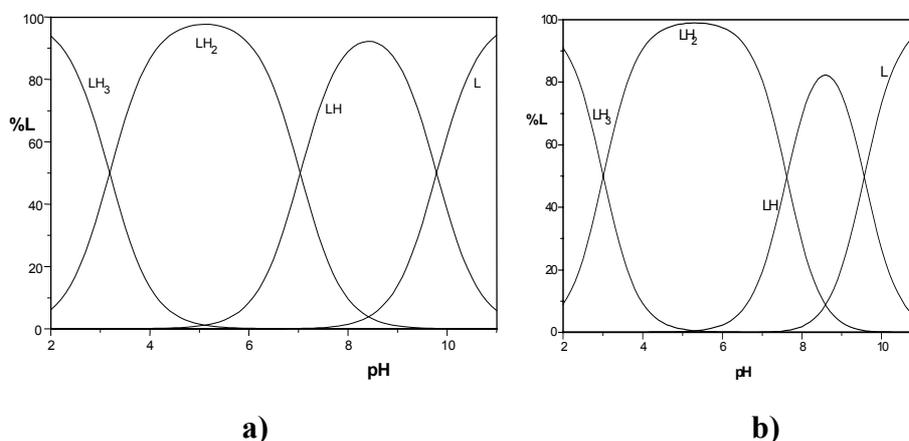
**Table 1.** Deprotonation constants of MPGO and BPGO studied at 25 °C in aqueous NaCl ( $I = 0.100 \text{ mol dm}^{-3}$ ).

Ligands	Species	$\log \beta$	$\text{pK}_a$
MPGO	LH <sub>3</sub>	$20.191 \pm 0.032$	3.007
	LH <sub>2</sub>	$17.184 \pm 0.025$	7.620
	LH	$9.564 \pm 0.017$	9.564
	LH <sub>3</sub>	$20.012 \pm 0.012$	3.187
BPGO	LH <sub>2</sub>	$16.825 \pm 0.008$	7.035
	LH	$9.790 \pm 0.006$	9.790

The species distribution curves of BPGO and MPGO have been shown in Figures 2a and 2b. As can be seen from the species distribution diagram, three groups on each ligand protonate at pH 2, and their three-protonated form is LH<sub>3</sub>. When pH is increased, the ligands lose gradually the protons and convert to the other various forms, LH<sub>2</sub>, LH and L. The formation of free ligand (L) starts at pH 7.80 and reaches maximum concentration at pH 10.5 (95%). The formation rates of all other species (LH<sub>3</sub> at pH 2, LH<sub>2</sub> at pH 5 and LH at pH 8) are quite high (above 80%).

There are four nitrogen and two hydroxyl groups in the BPGO and MPGO as seen in Scheme 1. The  $\text{pK}_a$  value belonging to hydroxide group (=N-O-H) has been obtained as 2.81 by only Akay et al.<sup>11</sup> However, in some studies,<sup>12-14</sup> there are no

definitions about  $pK_a$  value for hydroxide groups of glyoximes. The  $pK_a$  values calculated in this work are 3.19, 7.04 and 9.79 for BPGO and 3.01, 7.62 and 9.56 for



**Figure 2:** Distribution curves of BPGO (a) and MPGO (b) Species

MPGO and in acidic media. All these values defined as macro dissociation constants probably belong to nitrogen atoms in the ligands. In this case, three nitrogen atoms in each ligand can be protonated, but one nitrogen and hydroxyl groups can not. So, three equilibrium equations can be written for deprotonation of nitrogen atoms in the ligands. ( $LH_n$  and  $n=3$ ). The deprotonation equilibrium is as seen in the following equations (Ligand charges are omitted for clarity).



and the deprotonation constants ( $K_n$   $n=1,2$  and  $3$ ) are given as

$$K_n = \frac{[LH_{n-1}][H^+]}{[LH_n]}$$

### Theoretical Calculation

The determination of the protonation order of BPGO and MPGO are not possible with experimental methods such as NMR, IR, and UV. So, in this study, theoretical calculations have been made in order to examine the structure of the species and to determine protonation order of nitrogen atoms in the ligands. The formation heats ( $H_f$ ) and the total energies (TE) of the ligands and mono-protonated species were calculated by Semi-Empirical AM1 method. In addition, the proton affinity of each nitrogen atom

(PA) in the ligands was found using formation heats in the following equation and given in Table 2.

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

Where, PA is the proton affinity of B types;  $\Delta H_f^\circ(B)$  is the formation heat of B molecule;  $\Delta H_f^\circ(BH^+)$  is the formation heat of  $BH^+$  molecule, and 367.2 is the formation heat of  $H^+$ <sup>15</sup>.

**Table 2.** The Calculated  $H_f$ , TE and PA Values with AM1 Method for BPGO and MPGO and Their Monoprotonated Forms.

a)	$H_f$	TE	PA
BPGO	51.25	-77879.61	-
1 N-H <sup>+</sup>	197.57	-78048.01	220.88
2 N-H <sup>+</sup>	206.57	-78039.20	211.88
3 N-H <sup>+</sup>	199.35	-78046.41	219.10
4 N-H <sup>+</sup>	221.57	-78024.20	196.89
5 OH <sub>2</sub> <sup>+</sup>	236.81	-78008.96	181.65
6 OH <sub>2</sub> <sup>+</sup>	251.46	-77994.30	166.99
b)			
MPGO	23.23	-58905.84	-
1 N-H <sup>+</sup>	174.38	-59069.60	216.05
2 N-H <sup>+</sup>	178.65	-59065.33	211.78
3 N-H <sup>+</sup>	172.20	-59071.77	218.22
4 N-H <sup>+</sup>	194.03	-59049.95	196.40
5 OH <sub>2</sub> <sup>+</sup>	208.88	-59035.10	181.95
6 OH <sub>2</sub> <sup>+</sup>	222.73	-59021.25	167.70

Proton affinity gives information about protonation order. Since the nitrogen atom having the highest PA is 1N in BPGO, it has more basic characters than the others. Thus, the first protonated nitrogen is 1N in this ligand. According to the calculated results (TE,  $H_f$  and PA), protonation orders of nitrogen atoms in the BPGO are 1N, 3N and 2N. Whereas, the first protonated nitrogen is 3N as seen in the calculated values for MPGO. The reason for fact that the first protonated nitrogen 1N in the BPGO and 3N in the MPGO is that the inductive effect of benzyl group is higher than that of methyl group. That is, though BPGO and MPGO have similar protonation trends in the pH range investigated, 1N atom in BPGO shows more basicity property than 1N atom in the MPGO, because benzyl group increases the electron density on 1N atom by inductive effect. Thus, as a difference from BPGO, the protonation orders of nitrogen atoms in the MPGO are 3N, 1N and 2N, according to the calculated PA. Since the most acidic nitrogen atoms in both ligands are 4N atoms in terms of PA, their protonations are not

performed. The TE and  $H_f$  values also confirm that protonation arrangement is 1, 3, 2 for BPGO and 3,1 and 2 for MPGO.

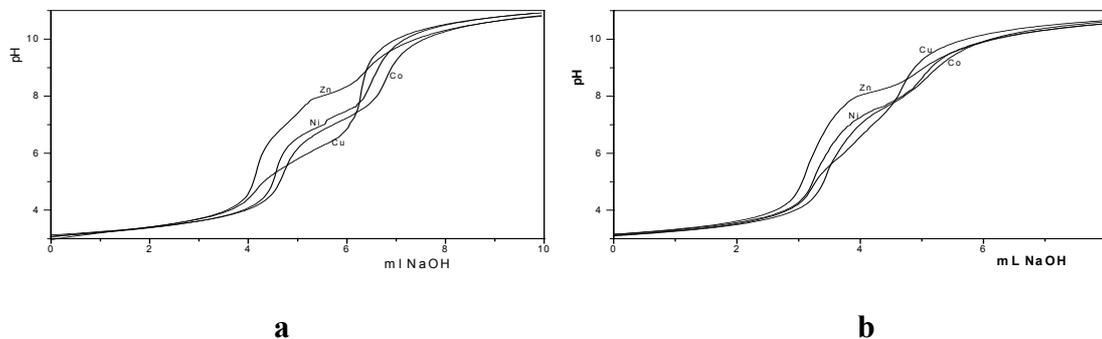
In conclusion, according to the data obtained from theoretical calculation, 9.79 ( $pK_{a3}$ ), 7.04 ( $pK_{a2}$ ), and 3.19 ( $pK_{a1}$ ) values belong to 1N, 3N and 2N in BPGO and 9.56 ( $pK_{a3}$ ), 7.62 ( $pK_{a2}$ ), and 3.01 ( $pK_{a1}$ ) values belong to 3N, 1N and 2N in MPGO respectively (Table 2). For piperazine rings in the BPGO, the calculated  $pK_a$  values for 1N is approximately similar to the literature values. Frenna et al<sup>16</sup> have found  $pK_a$  values of –N1 in piperazine as 9.85 and the  $pK_a$  of 1N value found by Astrom<sup>17</sup> is 10.00. The  $pK_a$  value belonging to 2N in the piperazine is different from in the literature values. In this work, the calculated  $pK_a$  values for 2N in the piperazine ring are 3.18 for BPGO and 3.00 for MPGO. These values are more acidic than literature values<sup>16,17</sup> because of the first performing protonation of 1N (in BPGO) and 3N (in MPGO) atoms, and repulsion of two positive charges on each ligand occurring as a results of protonation of 1N and 2N atoms in BPGO and 3N and 2N atoms in MPGO.

### Stability Constants of Metal Complexes

To determine the stoichiometry and stability constants of complex, which take place between the ligand and various metal ions (Zn, Ni, Co and Cu), the solutions including metal ions, the ligands (1:2 ratio) and certain amount acid have been titrated with standard NaOH solution. The titration curves obtained from these titrations have been given in Figure 3. As seen in Figure 3, there are two end points in all titration curves, but their end points are different from each other because of the various degree of hydrolysis of the metal ions. The change in the end point is proportional with the hydrolysis degree. This case has been seen in the solution including various concentrations of Cu ion clearly.<sup>18</sup> By increasing the hydrolysis degree, the end point shifts to right.

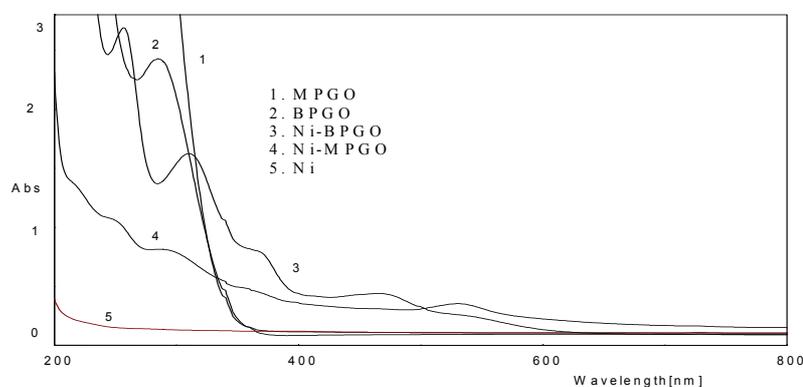
It was observed that the interactions of the ligand with metals ions (at 2:1 ratios) lead to mainly one kind of complexation (See Scheme 2). Ni-BPGO (pink), Ni-MPGO (pink), Cu-BPGO (brown), Co-BPGO (brown) insoluble complexes have been obtained in alkali media (over pH 10). Since the others complexes are soluble, their insoluble complexes have not been obtained but, the titration solutions were collared. Since crystallization of these complexes could not be performed, their structures have not been

determined by X-Ray studies. But, the UV-Vis spectra of Ni-BPGO and Ni-MPGO solutions have been obtained and given in Figure 4.



**Figure 3:** Titration Curves for M-BPGO (a) and M-MPGO (b)

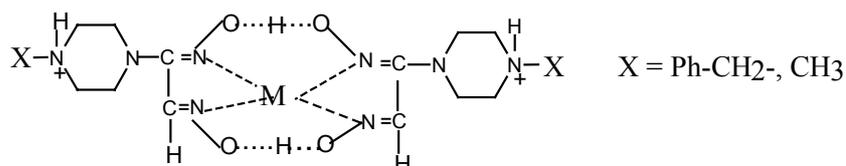
As seen in Figure 4, although there are no absorption bands in the spectra of ligands and Ni ions, there are some broad absorption bands belonging to soluble Ni-BPGO and Ni-MPGO complexes at 370, 470 and 535 nm. Also, the same broad bands have been observed in the UV-spectra of the other metal-ligand complexes.



**Figure 4:** The UV-spectra registered for the M-MPGO and MPGO

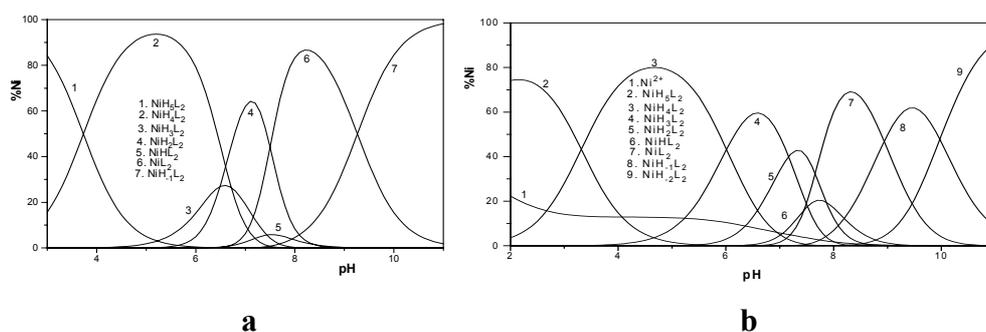
In the literature, there are similar studies with regard to the synthesis of transition metal ion- glyoxime complexes. Dincer et al<sup>9</sup> have synthesized a complex on form of  $ML_2$  between Ni and bis-N-2,6-dimethylphenyl-amino-glyoxime, and its structure has been characterized by X-Ray method. Aydogdu et al. and Özcan et al. have also synthesized some new complexes between Ni(II) and proposed vic-dioximes at the

same structures.<sup>8,19</sup> All ligands investigated by researchers consist of the same group except for benzyl and methyl groups. Therefore, the possible structure of M-BPGO and M-MPGO are as below (Scheme 2). Hydrogen bonds form between hydroxyl groups of the ligands as proposed in the literature.



Scheme 2

The data obtained from Ni<sup>2+</sup>-BPGO and MPG O titrations have been evaluated using SUPERQUAD program and the species distribution curves obtained from calculations have been given in Figure 5. The ligands and the metal ions form various complexes formulated as MH<sub>5</sub>L<sub>2</sub>, MH<sub>4</sub>L<sub>2</sub>, MH<sub>3</sub>L<sub>2</sub>, MH<sub>2</sub>L<sub>2</sub>, MHL<sub>2</sub> and MH<sub>1</sub>L<sub>2</sub>, depending on pH. It has also been observed that the similar complexes form between Cu<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> ions and the ligands.



**Figure 5:** Species Distribution Curves for Ni-BPGO (a) and MPG O (b) systems

At the pH < 2, LH<sub>3</sub> specie occurs. With the formation of LH<sub>2</sub> at above pH 2, complexes in the various forms (1-9 in Figure 5) start to form. The formation of intermediate complexes such as MH<sub>5</sub>L<sub>2</sub>, MH<sub>3</sub>L<sub>2</sub> and MHL<sub>2</sub> (or LH<sub>n</sub>MLH<sub>n-1</sub> type complex) has also been observed because titrant volume added in these titrations is very

little (0.04 mL). If the species distribution curves in Figure 5 are examined, it has been seen that the complexes such as  $MH_{2n}L_2$ ,  $MH_{2n-1}L_2$  and  $MH_2L_2$  occur and in addition, free Ni(II) ions exist in the titration solution until pH 8. Theoretical calculations have shown that protonation of 3N atom in MPGO firstly performs. With deprotonation of 3N at pH 7,  $NiL_2$  complex starts to form and after pH 7, all Ni ions coordinate on side of 3N and 4N atoms of the ligands. At between pH 2-8 in the titration solution, since there are only protonated ligands ( $1NH^+$ ,  $3NH^+$  and  $2NH^+$ ) and water molecules, metal atoms are coordinated from two ligands on 4N atoms and n mol water molecules or two ligands and hydroxyl groups belonging to ligands and  $MH_5(L_2)(n.H_2O)$  or  $MH_5L_2$  complexes can occur. After pH 8, hydroxide groups added as titrant or forming by hydrolysis of metal ions bound to metal ions instead of water molecule and so,  $M(OH)_2L_2$  (or  $MH_2L_2$ ) specie complex forms, as seen in Figure 5.

For Ni(II)-BPGO and MPGO systems, the first interaction appeared at pH 2-6, and the complexes initially formed in considerable concentration are five protonated mononuclear chelates ( $NiH_5L_2$ ). The calculated concentrations are around 80% at the same pH range. These species ratios are similar for both ligands. Other stable complex of Ni(II) ions is  $NiH_4L_2$  (95% for BPGO and 85% for MPGO) at pH 2-8. At pH 5-8, the formation rate of  $NiH_3L_2$  is 30% for Ni-BPGO, 60% for Ni-MPGO system. By the increasing of pH, the other species,  $NiH_2L_2$ ,  $NiHL_2$  and  $NiL_2$ , form. Intermediate complex ( $NiHL_2$ ) is at the lowest level (5%) among them. This specie is 20% for MPGO. As the pH is increased above 7, the unprotonated mononuclear species [ $ML_2$ ] starts to form, then becomes the predominant species in the solution. This case can be explained with deprotonation of all amino and imino groups of the ligands.

For the Cu(II)-BPGO and MPGO systems,  $CuHL_2$  and  $CuL_2$  exist as major components in solution. At pH 8, this chelates reach maximum level (95%), then above pH 8 hydroxide group is bound to the metal ions and species of  $Cu(OH)L_2$  and  $Cu(OH)_2L_2$  form. Mathematical analysis of the titration points reveals that the  $CuH_2L_2$ ,  $CuH_3L_2$  and  $CuH_4L_2$  form at the same time and are found to be in considerable amount. The formation of protonated mononuclear complexes undergoes simple deprotonation reactions at high pH.

For the Co-Ligand system, the pentaprotonated mononuclear cobalt complex is  $\text{CoH}_5\text{L}_2$  between pH 2 and 5 and reaches its highest percentage (75%) at pH 2. The main complex formed is  $\text{CoH}_4\text{L}_2$  at pH 2-7 and it reaches 90% at pH 5. The other species are the same as the Cu-Ligand systems. The predominant species is tetraprotonated complexes,  $\text{CoH}_4\text{L}_2$ . The maximum rates of Co-BPGO system for  $\text{CoH}_2\text{L}_2$ ,  $\text{CoHL}_2$  and  $\text{CoL}_2$  are 40%, 42% and 30% respectively between pH 4 and 9. After pH 7, the hydroxide complexes form and which are also similar to Co-MPGO system.

Finally, in the Zn(II) system, the main complex forms in the type of  $\text{ZnH}_5\text{L}_2$  and it reaches 95% at pH 5 and finishes at pH 7.5. From pH 5 to 10, the other species ( $\text{ZnH}_4\text{L}_2$ ,  $\text{ZnH}_3\text{L}_2$ ,  $\text{ZnH}_2\text{L}_2$ ,  $\text{ZnHL}_2$ , and fully protonated  $\text{ZnL}_2$  chelate) form in the lower concentrations. Their formation percentages change from 10% ( $\text{ZnH}_2\text{L}_2$ ) to 70%. After pH 8, as seen in the titration curve (Figure 3) for this system, Zn (II) ions start to hydrolyse and form only hydroxide complexes with hydroxide ions. Both distributions curves are similar to each other.

Obtaining the protonation constants for BPGO and MPGO using SUPERQUAD, overall stability constants have been calculated at the same way and the  $\log\beta$  values obtained from these calculations for all metal ions-ligand complexes have been given in Table 3. The stability constants of the mononuclear complexes for M(II)-MPGO system decrease in the order  $\text{Zn(II)}(\log K_{\text{ZnL}_2} = 20.82) > \text{Cu(II)} > \text{Co(II)} > \text{Ni(II)}$  and for M(II)-BPGO system in the order  $\text{Co(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)}$ . The reason for the orders being different is that the inductive effect between benzyl and methyl groups is different as reported above. A comparison of stability constants of the Ni(II) complexes with these two ligands ( $\log \beta[\text{ML}_2]$ ),  $\log \beta[\text{Ni-(BPGO)}_2] = 23.22$   $\log \beta[\text{Ni-(MPGO)}_2] = 17.88$ ) indicates that the imino groups (=N-OH) in the ligand plays an important factor on the stability of mononuclear complex formation. Benzyl group in BPGO causes the imino groups to gain more basic property. So, a more stable complex forms between Ni and BPGO above pH 7.

**Table 3.** Stability constant data for the complexation of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> with MPGO and BPGO at 25 °C in aqueous NaCl (*I* = 0.100 mol dm<sup>-3</sup>)  $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$ 

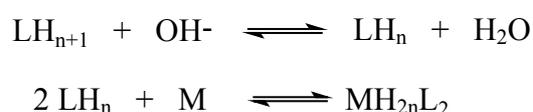
	<i>pqr</i> <sup>*</sup>	Ni(II)	Cu(II)	Co(II)	Zn(II)
M(II)-MPGO complexes	102	17.884 ± 0.014	18.279 ± 0.016	18.034 ± 0.006	20.823 ± 0.027
	112	25.334 ± 0.043	25.616 ± 0.009	25.811 ± 0.043	28.794 ± 0.070
	122	33.198 ± 0.012	32.458 ± 0.006	33.488 ± 0.036	36.832 ± 0.110
	132	40.361 ± 0.027	38.231 ± 0.011	40.512 ± 0.081	45.540 ± 0.019
	142	46.372 ± 0.027	43.808 ± 0.012	46.390 ± 0.100	52.997 ± 0.012
	152	49.687 ± 0.013	–	9.508 ± 0.121	59.009 ± 0.017
	162	–	–	–	62.156 ± 0.031
	1-12	8.946 ± 0.015	8.954 ± 0.027	9.286 ± 0.064	11.375 ± 0.035
	1-22	-1.025 ± 0.022	-1.638 ± 0.034	-0.423 ± 0.151	1.916 ± 0.033
M(II)-BPGO complexes	102	23.218 ± 0.014	20.885 ± 0.046	23.716 ± 0.014	20.757 ± 0.019
	112	29.839 ± 0.025	30.545 ± 0.033	31.032 ± 0.017	28.907 ± 0.056
	122	38.219 ± 0.025	37.237 ± 0.025	38.417 ± 0.021	36.781 ± 0.079
	132	44.707 ± 0.022	43.552 ± 0.034	45.147 ± 0.022	45.266 ± 0.031
	142	51.423 ± 0.030	49.151 ± 0.030	51.453 ± 0.018	52.350 ± 0.027
	152	55.154 ± 0.05	54.864 ± 0.023	55.242 ± 0.041	58.736 ± 0.034
	162	57.895 ± 0.076	58.600 ± 0.021	58.691 ± 0.035	–
	1-12	13.955 ± 0.013	9.590 ± 0.030	14.401 ± 0.024	11.163 ± 0.038

\*(*p*: number of metal, *q*: number of hydrogen (positive values) or hydroxide (negative values), *r*: number of ligand in the complex).

### Conclusions

The deprotonation constant (p*K<sub>a</sub>*) values determined are 9.79 (p*K<sub>a3</sub>*), 7.04 (p*K<sub>a2</sub>*) and 3.19 (p*K<sub>a1</sub>*) for BPGO and 9.56 (p*K<sub>a3</sub>*), 7.62 (p*K<sub>a2</sub>*) and 3.01 (p*K<sub>a1</sub>*) for MPGO in acidic medium. When the solution including the ligand and Ni<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> at 2:1 ratio are titrated with the alkali, various complexes (MH<sub>6</sub>L<sub>2</sub>-MH<sub>2</sub>L<sub>2</sub>) occur. It has been seen that the first protonations of 1N atom in the BPGO and 3N atom in the MPGO occur. The reason for this difference was explained as the presence of different inductive effect between benzyl and methyl groups. This effect can also have an effect in the order of stability constants.

The general mechanisms given below have been proposed with regard to the formation of complexes (MH<sub>2n</sub>L<sub>2</sub> and MH<sub>2n-1</sub>L<sub>2</sub>); for the formations of MH<sub>6</sub>L<sub>2</sub>, MH<sub>4</sub>L<sub>2</sub> and MH<sub>2</sub>L<sub>2</sub> complexes,



and for the formation of intermediate complexes ( $MH_5L_2$ ,  $MH_3L_2$  and  $MHL_2$ ),



### Experimental

1-Benzyl-4-piperazineglyoxime (BPGO) and 1-Methyl-4-piperazineglyoxime (MPGO) have been synthesized according to the literature<sup>9</sup> and their stock solutions ( $2.00 \times 10^{-3}$  mol dm<sup>-3</sup>) used in the titrations have been prepared. The purities and the exact concentrations of stock solutions of the ligands and titrant have pH-metrically been confirmed using the Gran method.<sup>20</sup> Solutions of metals ions ( $0.001$  mol dm<sup>-3</sup>) have been prepared from CuCl<sub>2</sub>, ZnCl<sub>2</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O and CoCl<sub>2</sub>·6H<sub>2</sub>O (Fluka) as received. Potassium hydrogen phthalate (KHP) has been prepared from Fluka reagent as buffer solution (0.05 molal) and used for the calibration of the combination pH electrode according to the method of MOLSPIN<sup>21</sup>. Carbonate-free standard NaOH solution (ca.  $0.025$  mol dm<sup>-3</sup>) has been used as titrant. HCl stock solutions used for obtaining pH 3.0 have been prepared from concentrated HCl (Merck) and its concentration has been determined by pH-metric titrations. The pH-metric and spectrophotometric measurements have been carried out at an ionic strength of  $0.100$  mol dm<sup>-3</sup> (NaCl). The pH has been measured with MOLSPIN automatic titration system,<sup>21</sup> which interfaces to a PC, with a  $10$  cm<sup>3</sup> syringe, a SenTix 20 pH combination electrode (WTW, Weilheim). All titrations have been carried out between pH 3.0–11.0 and under nitrogen atmosphere. The ligands concentrations have varied in the range  $1.00 \times 10^{-4}$  -  $2.00 \times 10^{-4}$  mol dm<sup>-3</sup>. The pH-metric data have been used to find the stoichiometry, deprotonation and stability constants using the SUPERQUAD computer program.<sup>22</sup> The standard deviations ( $\sigma$  values) computed by SUPERQUAD refer to random errors.

A JASCO V-530 UV/VIS spectrophotometer has been used to record the spectra in the region 200–800 nm. In the UV studies, the concentrations of the ligands and metal ions were  $2.00 \times 10^{-4}$  and  $1.00 \times 10^{-4}$  mol dm<sup>-3</sup> respectively.

The theoretical calculations have been performed by Semi-empirical (AM1) method.<sup>23–25</sup> This method is used to study some complex structures such as polymers<sup>26</sup>

and similar study.<sup>27</sup> Total energy and heats of formation have been calculated and the protonation order in the ligands was determined according to the results. Summary of experimental parameters used in this work have been given in Table 4.

**Table 4.** Summary of the experimental parameters for the potentiometric stability constants measurements.

System	: MPGO or BPGO with H <sup>+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> and Zn <sup>2+</sup> in water
Solution composition	: [L] range/mol dm <sup>-3</sup> 0.001-0.002 [M] range/mol dm <sup>-3</sup> 0.001 ionic strength/mol dm <sup>-3</sup> 0.1 electrolyte NaCl
Experimental Method	: pH-metric titration in range pH 3-11 log $\beta_{0-1}$ -13.78
T/°C	: 25.0
n <sub>tot</sub> <sup>a</sup>	: 250
n <sub>tit</sub> <sup>b</sup>	: 3
Method of calculation	: SUPERQUAD
Titration system	: MOLSPIN

<sup>a</sup> Number of titration points per titration

<sup>b</sup> Number of titrations per metal ligand system

M: Metal ion, L: ligand,  $\beta$ : overall stability constant

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### Povzetek

Potenciometrično smo določili deprotonacijske konstante 1-benzil-4-piperazinglioksima (BPGO) in 1-metil-4-piperazinglioksima (MPGO) pri 25 °C, v 0.1 mol dm<sup>-3</sup> NaCl. Za BPGO so bile določene pKa vrednosti 9.79, 7.04 in 3.19, za MPGO pa 9.56, 7.62 in 3.01. Vrstni red protonacije dušikovih atomov liganda je bil določen s teoretičnim izračunom (semi-empirična AM1 metoda). Pri različnih vrednostih pH, v raztopinah nastanejo različni kovinski kompleksi z ligandoma. Pri titracijah so bili uporabljeni ioni kovin prehoda (Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> in Zn<sup>2+</sup>), predvidoma pa nastanejo zvrsti MH<sub>6</sub>L<sub>2</sub>, MH<sub>5</sub>L<sub>2</sub>, MH<sub>4</sub>L<sub>2</sub>, MH<sub>3</sub>L<sub>2</sub>, MH<sub>2</sub>L<sub>2</sub>, MHL<sub>2</sub>, ML<sub>2</sub>, MH<sub>1</sub>L<sub>2</sub>, MH<sub>2</sub>L<sub>2</sub>. Konstante stabilnosti kompleksov so bile izračunane z računalniškim programom SUPERQUAD, predlagani so tudi splošni mehanizmi tvorbe kompleksov v opisanih sistemih.