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Potentiometric Study of the Coordination Tendency of 1,2-Bis(4-benzylpiperidine)glyoxime Toward Some Transition Metal Ions

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A potentiometic study has been carried out to reveal the coordination properties of 1,2-bis(4-benzylpiperidine)glyoxime (BPG), via its reaction with certain transition metal ions, Ni^{2+}, Cu^{2+}, and Zn^{2+}, and to determine the stability constants of the complexes formed. The experimental conditions were arranged to achieve all of the measurements and coordination in aqueous solution (mixed ethyl alcohol (10 %) and water (90 %)) at (25 ± 0.1) °C and an ionic background of 0.1 $mol\cdot dm^{-3}$ NaCl. The overall stability constants log β_n values of all species formed in solution together with the dissociation constants of the ligand were calculated by use of the SUPERQUAD computer program. The dissociation constants of the ligand BPG are 2.830, 6.066, 6.966, and 9.510. The chemical species present in the solution under our experimental conditions were demonstrated by the use of speciation diagrams.

Introduction

The *vic*-dioxime ligands and their complexes have been the subject of detailed research for many years.[1−3] They are of immense significance in the field of coordination chemistry, and their complexes with transition metal ions are of considerable importance.[4−10] Their applications encompass an array of areas, from using them as catalysts in chemical processes[2,11] as well as their usage in analytical chemistry[12] and biochemistry.[13] They also have other applications in the field of medicine,[14] bioorganics, and electrochemistry.[15,16] The similarity between the *vic*-dioxime complexes and vitamin B_{12} is an important issue which attracts much research.[17] *vic*-Dioximes may be of interest with regards to the photophysical and photochemical properties exhibited by some of their complexes with certain metal ions.[15,18−20]

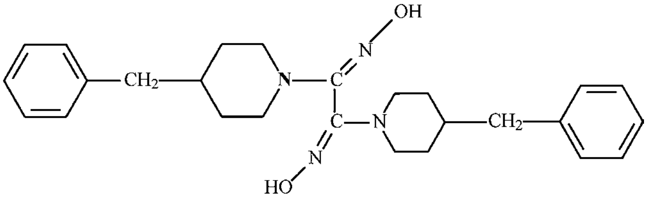
The coordination between *vic*-dioxime ligands and metal ions is essentially a *N*,*N*-coordinate square planar containing a conjugated NCCN system;[18,21−23] however, other structures are also feasible.[16] The square planar structure forms a five-membered ring and causes the dissociation of the hydroxyl group, leaving one or both of the oxime groups in the form of an oximate, ending up with a rigid structure. Interhydrogen bonding will certainly operate in the case where aqueous solutions are used in experimental work. This would enhance the whole structure of the metal complex as a result of electronic attraction.

The aim of the present research is to assess the coordination capability of the 1,2-bis(4-benzylpiperidine)glyoxime (BPG) ligand (Scheme 1) by evaluation of the dissociation constants of the ligand and the stability of its metal complexes.

Experimental Section

Chemicals. NaOH, KOH, NaCl, HCl, ethanol, 4-benzylpiperidine $CuCl_2\cdot 2H_2O$, $ZnCl_2\cdot 7H_2O$, and $NiCl_2\cdot 6H_2O$ were purchased from Merck and potassium hydrogen phthalate (KHP) from Fluka. All reagents were of analytical quality and were used without further purification. For the solutions, CO_2-free double-distilled deionized water was obtained with an aquaMAX-Ultra water purification system (Young Lin Inst.); the resistivity was 18.2 $M\Omega\cdot cm^{-1}$.

Scheme 1



1,2-bis(4-benzylpiperidine)glyoxime

Synthesis of BPG. BPG was synthesized as in the literature.[24] A solution of *anti*-dichloroglyoxime[25] (20 mmol: 3.14 g) in absolute ethanol (30 mL) at −10 °C was added to a solution of 4-benzylpiperidine (40 mmol: 7.01 g) in absolute ethanol (30 mL) dropwise over 1 h. The reaction mixture was stirred for 4 h at −10 °C. After adjusting the pH of the mixture to 6 to 7 with 1 % KOH solution at 0 °C, the mixture was stirred for an additional 4 h. The mixture was filtered, and the filtrate was dried in a vacuum. The crude product was recrystallized from absolute ethanol. Yield, 58 %. Elemental analysis. Calculated (%): C, 71.86; H, 7.87; N, 12.89; Found (%): C, 71.95; H, 8.12; N, 12.98. H NMR (DMSO-d_6): $\delta = 11.3$ (2H, s), 7.26−7.30 (10H, m), 2.90−3.00 (8H, m), 2.52−2.54 (4H, s), 1.86−1.90 (2H, m), 1.35−1.55 (8H, m) ppm. IR (KBr): [3240 (O−H), 1625 (C=N), 960 (N−O)] cm^{-1}.

Titration Procedure. Stock solutions ($2.00\cdot 10^{-3}$ $mol\cdot dm^{-3}$) of the metal ions were prepared for $CuCl_2\cdot 2H_2O$, $ZnCl_2\cdot 7H_2O$, and $NiCl_2\cdot 6H_2O$ at 25 °C and standardized with ethylenediaminetetraacetic acid (EDTA).[26] Other diluted solutions can be obtained simply by volumetric dilution. KHP was prepared as a buffer solution (0.05 *m*) and used for the calibration of the

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Table 1. Summary of the Experimental Parameters for the Potentiometric Stability Constants Measurements[a]

system	BPG, with H^+, Cu^{2+}, Ni^{2+}, and Zn^{2+} in water
solution composition	[L] range/mol·dm^{-3}: 0.001−0.002; [M] range/mol·dm^{-3}: 0.001; ionic strength/ mol·dm^{-3}: 0.1 electrolyte NaCl
experimental method	pH-metric titration in range of pH 3 to 11; log $\beta_{00\text{-}1}$ − 13.78
T/°C	25.0
n_{tot}[b]	250
n_{tit}[c]	3
method of calculation	SUPERQUAD
titration system	Molspin

[a] M: Metal ion, L: ligand, β: overall stability constant. [b] Number of titration points per titration. [c] Number of titrations per metal ligand system.

Table 2. pK_a Values for BPG together with pK_a Values for Other Similar *vic*-Oximes, 1,2-Bis(4-benzylpiperazine)glyoxime (BBPGH2), 1,2-Bis(4-methylpiperazine)glyoxime (BMPGH2), 1-Benzyl-4-piperazineglyoxime (BPGO), and 1-Methyl-4-piperazineglyoxime (MPGO), Which Have Been Taken from Literature[30,31] (I = 0.1 mol·dm^{-3} NaCl, at (25 ± 0.1) °C)

ligand	species	pK_a
BPG	LH_4	2.830 ± 0.034
	LH_3	6.066 ± 0.019
	LH_2	6.966 ± 0.020
	LH	9.510 ± 0.013
BBPGH2	LH_4	3.46
	LH_3	5.89
	LH_2	6.77
	LH	9.76
BMPGH2	LH_4	2.91
	LH_3	6.79
	LH_2	7.97
	LH	10.00
BPGO	LH_3	3.187
	LH_2	7.035
	LH	9.790
MPGO	LH_3	3.007
	LH_2	7.620
	LH	9.564

combination pH electrode according to the method of Molspin.[27] The NaOH concentration (0.025 mol·dm^{-3}) was standardized with primer standard KHP solution by a pH-metric titration. The HCl stock solutions used for obtaining pH 3.0 were prepared from concentrated HCl, and its concentration was determined with standard NaOH. All potentiometric titrations were carried out on solutions in 100 mL double-walled glass vessels using a Molspin automatic titration system, which interfaces to a PC, with a 10 cm^3 syringe and a SenTix 20 pH combination electrode (WTW, Weilheim), and the temperature was controlled at (25 ± 0.1) °C by circulating water from a constant-temperature bath. The cell was equipped with a magnetic stirrer and a tightly fitting cap which contained three holes for the combined electrode, nitrogen gas, and automatic buret. The pH was measured between pH 3.0 to 11.0 and under a nitrogen atmosphere. The ligand concentrations varied in the range ($1.00 \cdot 10^{-4}$ to $2.00 \cdot 10^{-4}$) mol·dm^{-3}. The summary of the titration conditions is given in Table 1. The pH-metric data were used to find the dissociation and stability constants using the SUPERQUAD computer program.[28] The standard deviations (σ values) computed by SUPERQUAD refer to random errors.

Results and Discussion

Dissociation Constants of BPG. The deprotonation equilibrium is as seen in the following equations (charges are omitted for simplicity).

$$LH_n \rightleftharpoons LH_{n-1} + H$$

and the deprotonation constants (K_n) are given as;

$$K_n = [LH_{n-1}][H]/[LH_n]$$

Table 2 contains dissociation constant (pK_a) values of the ligand under investigation. Four pK_a values are obtained for this ligand; two of them are associated with the oxime nitrogen atoms, and the other two are associated with hydroxyl groups. Comparing the pK_a values of the BPG ligand with that of 1,2-bis(dimethyl)glyoxime (DMG) shows to what extent the benzylpiperidine moiety in BPG affects the basicity. The pK_a of the oxime nitrogen atoms for BPG are 2.83 and 6.066, while that of dimethylglyoxime are 6.011 and 8.968.[29] Other values of pK_a of similar ligands are given in Table 2.[30,31] So, the benzylpiperidine moiety in the ligand gives significant electron withdrawing on the coordination center of the BGP. The sp^3 nitrogen of the piperidine might be the main cause of the decrease in basicity of the oxime nitrogen in BPG; as with its relatively high electronegativity, it tends to draw electron density away from the oxime group. This actually results in a reduction in the electron availability on the oxime nitrogen atoms and at the same time increases the dissociation of the hydroxyl group. In other words, the withdrawal property of benzylpiperidine has an impact on the hydrolysis of the hydroxyl group in the ligand, which would facilitate the release of protons. Protonation of the nitrogen atoms in *vic*-oximes, in acidic media, is expected to have very little influence on the acidity of the hydroxyl group, but coordination with metal ions will have an appreciable influence and ease the dissociation of the hydroxyl group.

pK_a values for other similar *vic*-dioximes from the literature rationalize and support data obtained in this work.[30] The above results are in good agreement with our expectations on the extent of basicity of this ligand. The basicity of the ligand does not necessarily reflect the right coordination power of the ligand; in other words, the highly basic ligand does not always form the most stable complexes. One of the major factors that affects stability is steric hindrance, which sometimes even precludes coordination.

The titration curves of the ligand demonstrated in Figure 1 illustrate the extent of the acidity of the ligand. All measurements in this study were achieved in mixed water and ethanol (see the Experimental Section). Dissociation constants would certainly vary with the percentage of constituents of mixed solvents, which finally depends on electrostatic and nonelectrostatic factors.[32−34] All ligand species of BPG, which are expected to be formed under our experimental conditions, are

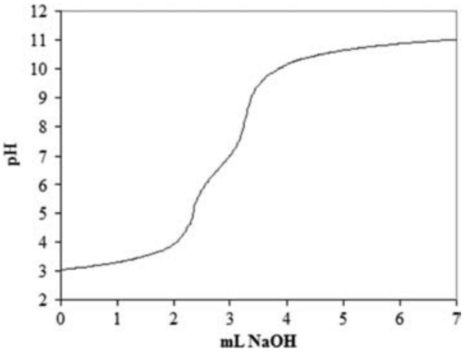

Figure 1. Titration curve of the BPG with 0.025 mol·dm^3 NaOH at 25 °C in aqueous NaCl (I = 0.100 mol·dm^{-3} NaCl).

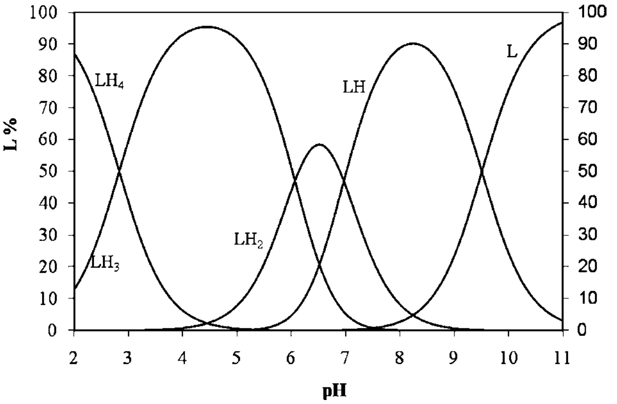

Figure 2. Species distribution diagram of BPG as a function of $-\log[H]^+$. L % = percentage concentration of species, $I = 0.1$ mol·dm^{-3} NaCl, at (25 ± 0.1) °C.

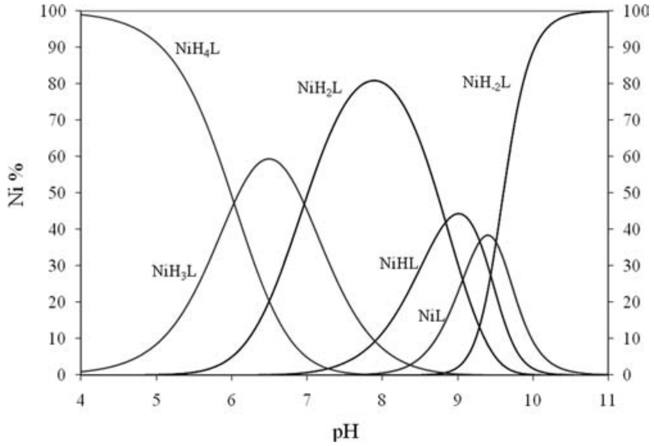

Figure 3. Species distribution diagrams for the Ni−BPG system, $I = 0.1$ M NaCl, (25 ± 0.1) °C.

presented in the distribution diagrams illustrated in Figure 2. The ligand species, which occurred in solution under our experimental conditions, are LH_4, LH_3, LH_2, LH, and L. The experimental parameters and conditions used here are the same as those used to determine the stability constants.

The distribution diagram of the ligand assists the determination of the experimental conditions where the coordination with metal ions would take place, especially in terms of pH.

The bidentate nature of the ligand imposes a *cis*-structure on the ligand upon coordination; this actually designates the coordination power of the ligands and indicates its affinity toward metal ions. As with the *trans*-form the ligand cannot act as a bidentate; however, this form exhibits less steric strain.

Stability Constants of Complexes. The overall stability constants (β_{pqr}) are defined as follows (charges are omitted for simplicity).

$$pM + qL + rH \rightleftharpoons M_pL_qH_r$$

$$\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$$

where M is the metal ion, L is the ligand, H is the proton, and p, q, and r are the respective stoichiometric coefficients.

The mode of coordination of *vic*-dioxime has been mentioned in the Introduction, where the *N*,*N*-donor atom is engaged to form a five-membered chelating ring. Several possible species would be formulated in the solution depending on pH. In other words, the pH function regulates the subsistence of plausible species in solution.

Figure 3 shows all of the possible species in the Ni−BPG system; there are six types of Ni−BPG species which are tracked through our computer program as they formed in substantial and measurable amounts. The complexes traced at pH ranges between 4 and 6.5 are NiH_4L and NiH_3L. The dominant species in the solution at a pH between 7.5 and 8.5 is NiH_2L, and it comprises at pH 8 about 80 % of all of the species. Other species such as NiHL and NiL start to exist in significant amounts at a pH above 8.5. The species $NiH_{-2}L$ starts to exist at pH values above 9.5.

There is a potential chance for the hydrolysis of the hydrated Ni(II) ion to take place in the pH range where the measurements were taken,[35] which gives rise to hydrolyzed species in solution. The formation of this type of partially hydrolyzed species not only depends on the pH but on the availability of water molecules on the solvated metal ion.[36]

Potentiometric measurements showed that the existence of monocomplexes only, under the experimental conditions used, despite the ligand-to-metal ratio and the extent of the pH range, should allow the possibility of the existence of bis-complexes. The main cause for the preclusion of the bis-BPG complexes is steric hindrance, which arises from the fact that the BPG ligand is quite a bulky molecule and there will not be enough room in the coordination sphere of the metal ion for a second ligand to be accommodated either in a square planar pattern or any other constitution. So the tendency of *vic*-dioxime toward bis-complex formation will be precluded by steric requirements. In fact, steric hindrance might be raised even among the coordinate ligand itself; as upon coordination of the ligand, the two bulky moieties of 4-benzylpiperidine would not really be far way from each other. However, according to our data, it showed that all types of mono complexes formed sustain good stability within certain experimental conditions. The coordinated ligand may withstand the impact of the steric effect through its high flexibility, as the two moieties of 4-benzylpiperidine, which cause the steric effect, could arrange themselves in a way so that they are away from each other. So as long as there is a single covalent bond connected between the attachments, there will be some bending via this type of bond. This distortion in structure is expected to influence the whole complex.

The mono binary Ni(II)−BPG system exists in several forms, as has been mentioned above, and each single species originates from the preceding one as a result of proton liberation. So, there is a deprotonation process persisting throughout the intact coordination course. The deprotonation, which includes the dissociation of hydroxyl groups, occurs as a result of the formation of the coordinate bond, which causes electron withdrawal toward the metal ion and therefore lessens the dissociation of the hydroxyl groups. In other words, the coordination of the ligand with the metal ion will intensify the dissociation of the hydroxyl group or in fact any other acidic hydrogen in the system due to an increase in the electron charge flow toward the metal ion, as a result of coordinate bond formation.

Our results show that the species NiH_4L, with the stability constant value of 47.481, is the most stable of all of the complexes formed. The species NiH_4L forms no intrahydrogen bonding, as the ligand kept all hydrogen atoms intact; this is because both hydroxyl groups are quite far away from each other and they are unlikely to be linked by intrahydrogen bonding, but interhydrogen bonding is significantly feasible as long as an aqueous solution is used. The two hydroxyl groups will

Table 3. Stability Constant Data for the Complexation of Cu^{2+}, Ni^{2+}, and Zn^{2+} with BPG at 25 °C in Aqueous NaCl ($I = 0.100$ $mol \cdot dm^{-3}$); $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$

	*pqr**	Ni(II)	Cu(II)	Zn(II)
M(II)-BPG complexes	101	16.345 ± 0.026	14.554 ± 0.051	15.40 ± 0.020
	111	25.640 ± 0.014	21.410 ± 0.047	
	121	34.484 ± 0.027	28.168 ± 0.024	30.913 ± 0.015
	131	41.448 ± 0.043	34.405 ± 0.023	38.301 ± 0.019
	141	47.481 ± 0.044	39.989 ± 0.027	42.539 ± 0.036
	1-11		6.904 ± 0.049	
	1-21	−2.679 ± 0.023	−2.766 ± 0.114	−0.404 ± 0.022
	1-31		−12.001 ± 0.083	−10.215 ± 0.043

engage in such bonding via either their hydrogen or oxygen atoms. This type of bonding would expect to have no or very little influence on the stability of the complex; it is expected that the interhydrogen bonding is reasonably strong due to an increase in the acidity of the hydroxyl group through the course of the coordination; this of course would increase the species solubility in the solution. Accordingly no precipitate has been noticed, even when neutral species were formed. This case was justified by the fact that the expected concentrations of the complexes were relatively small.

The high tendency of the Ni(II) ion toward *vic*-dioxime is actually the main cause of why the nickel(II) complexes are more stable than the corresponding copper(II) complexes (see Table 3).[37] This of course does not comply with the Irving−William series.[38] In this case, the highest stability constants of the Ni(II) complexes over the Cu(II) complexes might be due to the possible formation of metal−metal bonding, as this type of bonding is confirmed in solid *vic*-dioxime complexes.[39]

Figure 4 shows the similarity in the distribution of Cu(II)−BPG species, with that of the Ni(II)−BPG system, but with eight species being tracked by the computer program. The species CuH_4L formed almost in the same pH range as NiH_4L, but with different distribution percentages at any pH. The percentage composition of CuH_4L at pH 5.5 is about 50 % out of the total concentration of Cu(II) ion, while the percentage of NiH_4L at the same pH is about 80 %. This does not necessarily imply the extent of the stability of the Ni(II) complex. The other species is CuH_3L, which is formed in considerable amounts after exceeding pH 5 up to pH 6.5 and with a maximum percentage occurrence of 50 % at a pH of 5.75. This species is expected to persist within the low acidic area so it still can hold an extra proton. Increasing the basicity of the solution caused deprotonation with the existence of other species such as CuH_2L and CuHL within a pH range from just above 6 up to 7.5 followed by CuL which formed within the pH range 6.75 to just above 8, where more loss of protons occurred. Increasing the pH will result in the formation of other hydrolyzed species; $CuH_{-1}L$ starts to form at approximately a pH of 7.5, and the maximum percentage of its composition will be about 85 % at a pH of 8.5. The other hydrolyzed species $CuH_{-2}L$ formed in the pH range between 9 to 10 and was found in smaller quantities when compared with other species. Its maximum concentration was at pH 9.5 with a percentage of just less than 20 %. After the pH exceeds the value of 9.5, the species $CuH_{-3}L$ starts to form in significant amounts, and after going beyond pH 10, this last species will be dominant in the solution.

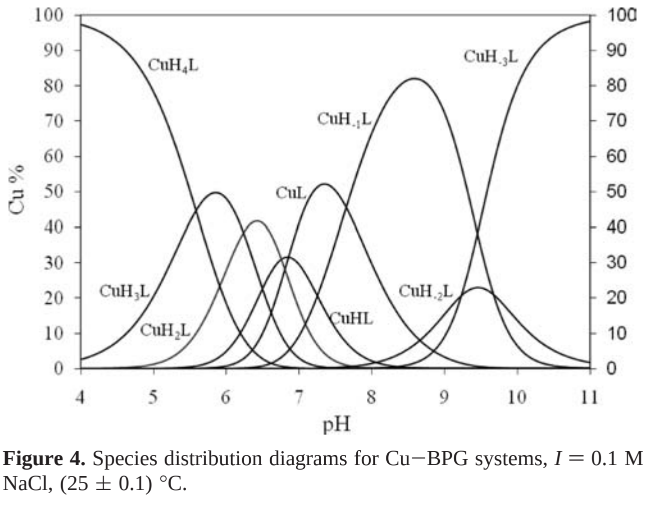

Figure 4. Species distribution diagrams for Cu−BPG systems, $I = 0.1$ M NaCl, (25 ± 0.1) °C.

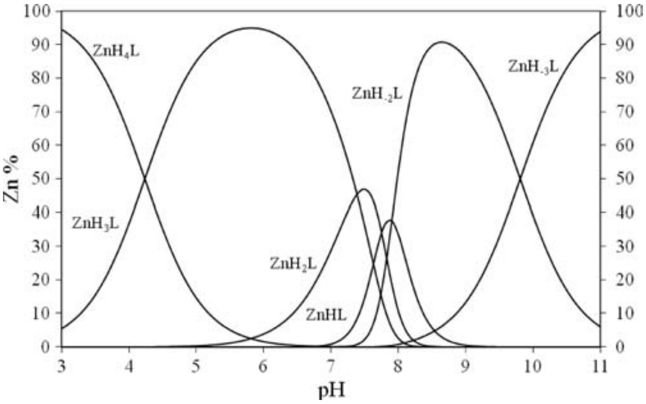

Figure 5. Species distribution diagrams for Zn−BPG systems, $I = 0.1$ M NaCl.

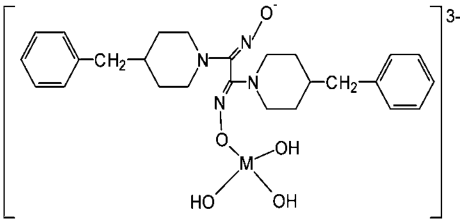

Figure 6. Structure of the $ZnH_{-3}L$ species.

In the M—BPH system, the moment the ligand was added to the metal ion, a certain species will come out as a result of reaction. So, the range of pH where the variety of species will start to form depends on the individual metal ion. The initial pH value of the diluted copper solution in general is less than the initial pH for the diluted nickel solution; therefore, we expected that copper complexes formed in pH will be less than that of nickel complexes. This probably may not hold for bis or tris-complexes and may depend on the structural shape of the bis or tris complexes.

Zinc(II)−BPG complexes seem to span over a wider range of pH values starting from pH 3.5 up to pH 11.5. Almost analogous species to that of the Ni(II) and Cu(II) systems are predicted to exist in solution. Stability constants of all Zn(II)−BPG species are higher than the corresponding Cu(II)−BPG species, which might suggest that the Zn(II) complexes have a tendency to adapt a tetrahedral structure. The extra stability is basically due to an increase in entropy as a result of alteration from an octahedral structure of $[Zn(H_2O)_6]^{2+}$ to a tetrahedral with a structure of $[Zn-(BPG)]^{2+}$. On the other hand, the stability of all Ni(II)−BPG complexes are higher than the corresponding Zn(II)−BPG complexes; this confirms the stability magnitude, caused by the assumed Ni−Ni bond in solution,[39] as mentioned previously. Also, the stability of Ni(II) complexes, in many cases, could be higher than the corresponding Zn(II) complexes without the establishment of metal−metal bonding.

The dominant species between pH 4.25 to pH 7.25 are ZnH_4L, ZnH_3L, and ZnH_2L, with a higher percentage (more than 90

%) of ZnH_4L at a pH of less than 3.5. The species ZnH_3L forms about 90 % of the total Zn ion concentration at pH 6.5, while the highest percentage of the ZnH_2L species would be at 7.25 at about 45 %. The increase in deprotonation is quite gradual and increases with the increase of pH. The ZnHL species formed in the neutral to low basic area with a maximum formation of 40 % at pH 8. All other deprotonated species $ZnH_{-2}L$ and $ZnH_{-3}L$ are formed in the pH range between 8.25 and 10.5. Figure 5 shows the distribution diagrams for these species. The existence of the deprotonated species $ZnH_{-3}L$ occurs at a high pH (see Figure 5) as a result of the dissociation of the two hydroxyls on the oxime groups. The aquated Zn(II) ion at such a high pH tends to be hydrolyzed and exists in a form of hydroxy species, which will attach to the deprotonated BPG ligand as demonstrated in Figure 6.

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