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DOI 10.1007/s10953-016-0452-3 Complex Formation Study of Binary and Ternary Complexes Including 2,3-Dihydroxybenzoic Acid,

N-acetylcysteine and Divalent Metal Ions Shella Permatasari

Santoso1 • Artik Elisa Angkawijaya1,2 • Suryadi Ismadji3 • Aning Ayucitra3 • Felycia Edi Soetaredjo3 • Tran Nguyen Phuong Lan4 • Yi-Hsu Ju1

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Abstract

The binary and ternary complex stability constants between 2,3-dihydroxybenzoic acid (DA) and N-acetylcysteine (Nac) with the divalent metal ions (M) Mn2?, Co2?, Ni2?, Cu2? and Zn2? were studied in aqueous solution at 310.15 K and an ionic medium of 0.15 mol?dm-3 NaCl. The complexes' stability constants (log10 b), refined from the potentiometric data using the Hyperquad2008 program,

indicate that the ternary complexes are more stable than the binary complexes.

The stability constants were supported by additional computation, refined from the spectrophotometric data using the Hypspec program. The values of the ternary complex stability relative to their binary complex (Dlog10 K) and the disproportionation constant (log10 X) indicate that formation of ternary complex species [M(DA)(Nac)]3- is more favorable than that of species formed by two identical ligands, [M(DA)2]4- or [M(Nac)2]2-. For the investigated M, the stability of complexes follows the trend Cu2? [ Zn2? [ Ni2? [ Co2? [ Mn2?.

Keywords Stability constant • Potentiometry • N-acetylcysteine • 2,3-dihydroxybenzoic acid • Divalent metal

1 Introduction

2,3-Dihydroxybenzoic acid (DA) is a powerful iron chelator with a Fe3?-DA complex stability constant (log10 K1) value of 20.5 [1]. The chelating ability of DA makes this compound useful in the excretion of excess iron [2]. DA naturally exists in plants such as &

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Vietnam Salvinia molesta, lobi–lobi fruit (Flacourtia inermis) and gooseberries (Phyllanthus acidus) [3, 4] and also in blood plasma and urine of human, as the product of aspirin metabolism [5, 6]. Biologically, DA provides health benefits due to its antioxidant, anti-inflammatory and antimicrobial actions. DA may act as a salicylate (COO–, ortho–O–) type ligand or catecholate (ortho–O–, meta–O–) type ligand [7–10]. Recently, researchers demonstrated that DA also can bind metal ions such as Al3+, VO2+, Mn2+, Cu2+ and Cd2+ as summarized in IUPAC equilibration data report [11]. To the best of our knowledge, there are only a few reports on the stability constant of DA with divalent transition metal ions; excesses of these metal ions in human body may lead to metal toxicity. DA is often designated as a di-protic, H2L, ligand (with 2 protonation constants, for the COO– and meta–O– groups) instead of tri-protic, H3L, ligand [9–11]. Thus, in this work we attempted to treat DA as a tri-protic ligand by determining the protonation constant of the ortho–O– by means of spectrophotometry; this was then used for the stability constant determinations. Ternary complex study is interesting, because it is expected that the combination of two different ligands will give synergistic effect to strengthen stability of the complex, thus dissociation of the metal complex is less likely [12]. In this study, N-acetylcysteine (Nac), an antioxidant that is known as glutathione precursor, mucolytic agent and neuroprotective agent, was chosen to assist the complex formation of DA [13–17]. Nac is known as a drug for treating angina pectoris, acute respiratory distress syndrome, paracetamol overdoses, ischemia–reperfusion cardiac injury, schizophrenia and bipolar disorder [18–22]. Our previous study on Nac with some

2 divalent metal ions (Cu2+, Zn2+, Ni2+, Co2+ and Mn2+)

indicates that the chelate complexes have stability constants in the range of 3.67 to 6.57 for log10 K1 and 3.69 to 6.06 for log10 K2, which is sufficient for the chelate complex to disassociate [23]. Thus the combination of DA and Nac was expected to give a higher stability for the complexes formed. All the complexes formed were observed in conditions comparable to human blood (i.e. 310.15 K and

2 ionic strength of 0.15 mol?dm-3 NaCl). The equilibrium constants were refined using the

Hyperquad2008 and Hypspec computer programs. 2 Chemicals and Solutions Chemicals used in this study and their suppliers are as follows: analytical grade metal salts of

1 nickel chloride hexahydrate (NiCl2?6H2O, 98 %) was supplied by Alfa Aesar (Lan-cashire, UK);

copper chloride dehydrate (CuCl2?2H2O, 99 %), cobalt nitrate hexahydrate Fig. 1 Structural formulae of a 2,3-dihydroxybenzoic acid and b N-acetylcysteine (Co(NO3)2?6H2O, 98 %), and zinc
2-nitrate hexahydrate (Zn(NO₃)₂?6H₂O, 98 %) were purchased from Sigma Aldrich (St. Louis, USA); and manganese chloride tetrahydrate (MnCl₂?4H₂O, 98.8 %) was supplied from Fisher Scientific (New Jersey, USA). The 2,3-dihydroxybenzoic acid (DA, C₇H₆O₄, 99 %) was supplied by Alfa Aesar (Lancashire, UK) and N-acetylcysteine (Nac, C₅H₉NO₃S, 99 %) was purchased from Sigma Aldrich (St. Louis, USA); their structures are shown in Fig. 1. Sodium hydroxide (NaOH, 96 %) was provided by Yakuri Pure Chemical (Kyoto, Japan); potassium hydrogen phthalate (KHP, 99.95 %), and ethylenediaminetetraacetic acid (EDTA, C₁₀H₁₆N₂O₈, 98.5 %) were purchased from Sigma Aldrich (St. Louis, USA); sodium chloride (NaCl, 99.5 %) was obtained from Showa (Tokyo, Japan). Metal salt solutions were standardized by complexometry against EDTA. Carbonate free NaOH 17(0.1 mol?dm⁻³) used as titrant was standardized against KHP. HCl (0.03 mol?dm⁻³) was prepared and used after standardization. All solutions were prepared freshly before use, using ultra pure water obtained from an ultrapure water system with a resistance of 18.3 MΩ cm⁻¹.

3 Experimental and Computational
3.1 Potentiometric Method

Potentiometric titrations were performed in a 150 cm³ commercial double walled glass vessel under N₂ atmosphere. Reaction temperature was maintained at 310.15 ± 0.2 K and the ionic strength of 0.15 mol?dm⁻³ NaCl (pKw = -13.384). A Metrohm 888 Titrando potentiometer, with an 805 Dosimat, Ecotrode Plus pH glass electrode and 802 rod stirrer with 804 Ti stand, was used for the measurements. The electrode used for the measurements has a precision of ±0.001 pH unit. The potentiometer, equipped with the titration software Tiamo2.3 and coupled to a personal computer, was used to control the titration and record the data. Calibration of the electrode was by means of strong acid–strong base titration, towards solution (a) defined right below, using the GLEE program [24]. For the equilibrium constant determination of binary and ternary systems, the following solutions each with a total volume of 50 cm³ were prepared and titrated against equal increments of added 0.1 mol?dm⁻³ carbonate-free NaOH:

<table>
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<tr>
<th>Table 1 Experimental condition of the investigated systems</th>
<th>System Ratio</th>
<th>Concentration (mol?dm⁻³)</th>
<th>Metal salt</th>
<th>DA</th>
<th>Nac</th>
<th>Potentiometric method</th>
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</tr>
<tr>
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<td>2</td>
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<td>1.25</td>
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<tr>
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<td>5.9</td>
<td>10⁻⁴</td>
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<td>10⁻₄</td>
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<td>10⁻₃</td>
<td>10⁻₃</td>
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<td></td>
</tr>
</tbody>
</table>

9 mol?dm⁻³ HCl ? 0.15 mol?dm⁻³ NaCl (b) Solution (a) ? 0.001 mol?dm⁻³

ligand DA (c) Solution (a) ? ligand DA ? metal salt (d) Solution (a) ? ligand DA ? ligand Nac ? metal salt The equilibrium constants include: the acid dissociation constant of ligand DA, which was determined by titrating solution (b); the metal complex stability constant, which was determined by titrating solution (c) at four different metal to DA molar ratios of 1:1, 1:2, 1:2.5 and 1:3; while ternary metal complex solution (d) was
determined at a metal to DA to Nac molar ratio of 1:1:1. The total concentration of each compound used in the experiment is shown in Table 1. Each solution was thermostatted at 310.15 K and

11 left to stand for 15 min before titration. The titration was carried out up to pH = 11.0.

Each titration was repeated at least three times under controlled conditions, with a reproducibility of ±0.04 pH unit. Computations of complex equilibrium constants were performed

2 by processing the potentiometric data using Hyperquad2008 program [25]. The objective function was given as \( U = R (W_i r^2_i) \), where \( W_i \) is the weight at the \( i \)th data point and \( r_i \) is the square of the difference between the observed and the calculated pH values. The Gauss–Newton–Marquardt method was adopted to minimize the objective function. All constants are presented as overall formation constant in logarithm value (log10 bpqrs)

\[
\begin{align*}
\text{and expressed by the following equation: } & pM \quad qNac \quad rDA \quad sH \quad ? \\
& MpNacqDArHs \quad ?MpNacqDArHs? \quad \text{bpqrs} \\
& \frac{1}{2}M^{?p} \frac{1}{2}Nac \quad ?q\frac{1}{2} \quad DA \quad ?r\frac{1}{2}H{s}
\end{align*}
\]

The selected model was the one that gave the best statistical fit, was chemically sensible and consistent with the titration data. The species distribution of each metal complex at the observed pH was produced by the HySS2009 simulation program, based on the refined stability constants [26].

Spectrophotometric Method
Spectrophotometric measurements were conducted using a JASCO V-550 spectrophotometer in a standard 1 cm path length quartz cell. The measurement was done by scanning the spectra of the solutions of binary and ternary systems (Table 1) from 200 to 400 nm. The spectra of each solution were measured at pHs between 2.5 and 11.0, where the pH was adjusted by using 0.1 mol/dm-3 NaOH. The spectral data at various pHs were used to refine the formation constants using the Hypspec program [25, 27]. Spectral analyses were also carried out for the solution containing DA:Nac:metal (1:1:1) with a molar concentration of 2 \times 10^{-4} \text{ mol/dm}^{-3} prior to the confirmation of the ternary species formation.

4 Results and Discussion
4.1 Ligand Acid–Base Behavior
In aqueous solution, a ligand tends to deprotonate by releasing its hydrogen ion at certain pH; this deprotonation reaction property is expressed as pKa. A higher pKa value indicates that a more basic pH is needed to release a hydrogen ion. As a tri-protic ligand, DA possesses three functional groups, namely a carboxylic (COO–) group and two hydroxyl (O–) groups at ortho (ortho-O–) and meta (meta-O–) positions. As obtained from the potentiometry data, the deprotonation of COO– group has a pKa1 value of 2.63 and the second deprotonation occurs at the meta-O– group with a pKa2 value of 9.98. The second deprotonation is more likely to occur at meta-O– since this site is more reactive than the ortho-O–. This behavior is influenced by the electronic effect of the substituent groups and also the COO– functional group which makes the ortho-O– less nucleophilic than meta-O–. Since the ortho-
O– is less nucleophilic, a higher basic condition was needed for its deprotonation (third deprotonation). Thus, spectrophotometry was used to determine the deprotonation of the ortho-O– group instead of potentiometry; the pKα3 obtained for ortho-O– was 13.00. These pKα values and the deprotonation order of DA are in accord with the studies of Turkel et al. [10] and Kiss et al. [28]. In the case of Nac, the first deprotonation occurs at its COO– group with a pKα1 value of 3.18, followed by the thiol S– group with a pKα2 value of 9.48 [23]. The pKα values of the ligands are given in Table 2 and used for the calculation of the metal complex formation. Besides the pKαs of the ligands, the hydrolysis constants of the metal ions shown in Table 2 were also introduced into the calculation. Table 2 Dissociation constant of DA and Nac at

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<th>pKα2</th>
<th>pKα3</th>
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<td>2.68</td>
<td>9.98</td>
<td>13.00</td>
</tr>
<tr>
<td>Nac</td>
<td>2.68 (4)</td>
<td>9.98</td>
<td>13.00</td>
<td></td>
</tr>
</tbody>
</table>

pKα) are represented by standard deviations SD in the parentheses for last place of decimal a

Spectrophotometry, I = 0.15 mol?dm-3 NaCl,

4T = 310.15 K b Potentiometry, I = 0.20 mol?dm-3

KCl, T = 298.15 K c Potentiometry, I = 0.15 mol?dm-3 NaCl, T = 310.15 K

d Hydrolysis constant of metal ions presented as log10 b(SD) value, Ref. [29] 4.2 Complexation Study of Binary Systems The

were studied with DA and Nac. In our previous study on Nac–M chelate complexes, there were three species ([M(Nac)], [M(HNac)], and [M(Nac)2]2-) formed in the investigated pH range (2.5–11.0). The monoprotonated [M(HNac)] species, which is formed by the attachment of M2+ to the deprotonated COO– group, was observed in the Cu2+, Ni2+, Co2+ and Mn2+ systems. In this case, the proton is contributed by the H atom of the S– group. The formation of [M(Nac)] species occurs by the attachment of M2+ to two deprotonated groups COO– and S–. The other species was [M(Nac)2]2- which is formed by the attachment of fully deprotonated Nac to the [M(Nac)] species [23]. In DA binary systems, the refinement results from Hyperquad showed that M(HDA), [M(DA)]-, [M(HDA)2]2-, [M(HDA2)]3- and [M(DA)4]4- were the species that
gave the best fit to the potentiometric data. As observed in the potentiometry titration curve in Fig. 2, the occurrence of inflection points along with pH jumps in M2?–DA systems indicate the formation of metal complex species. In the case of the systems which contain ligand only, the inflection point in the titration curve indicates the deprotonation of an H atom of the ligand’s donor group. An inflection point occurs when sufficient base is added to deprotonate a group (higher value of m indicates more base was added). In the case of Fig. 2 Titration curve for the M2?–DA system

Yes at a metal to ligand ratio of 1:

2.5 DA, the inflection points occur at m = 4.0 and 5.0 indicating the deprotonation of COO– and meta-O– groups, respectively. In the case of M2?–DA, at the m * 5.0 range the M(HDA) species was formed. The inflection points concomitantly with pH jump suggest that two functional groups are involved in the formed species, namely the COO– and ortho-O– groups (salicylate type coordination), while the meta-O– group was still protonated. The deprotonation of ortho-O– group was promoted by the presence of metal ions that were firstly bond to the COO– group. A significant pH jump, observed from the inflection point at m = 6.0, suggests a stronger coordination of the metal complex compared to the salicylate type, specifically catecholate (ortho-O–, meta-O–) type, where the corresponding species in this point is [M(DA)]-. In the studies of Kiss et al. on Cu2?–DA complexes [28], Turkel et al. on Al3?-DA complexes [10], and Sahoo et al. on La3?-DA complexes [30], they also proposed that salicylate type complex species of DA tend to form at lower pH and catecholate type at higher pH. At m = 5.0–6.0 the presence of [M(HDA)]2- and [M(HDA2)]3-around this point suggests the involvement of protonated functional groups in the species. In this case, the most thermodynamically sensible forms are: two salicylate (COO–, ortho-O–) coordination in the formation of [M(HDA)]2-, and the combination of salicylate (COO–, ortho-O–) and catecholate (ortho-O–, meta-O–) coordination in the formation of [M(HDA2)]3-, while the [M(DA)]4- species, which are formed at higher pH, suggest the coordination of two catecholates. These proposed forms with specifically mixed combination of salicylate– catecholate type and two catecholate type (at higher pH) are also in good agreement with the literature [10, 28, 30]. In addition, as observed in the titration curve, Cu2?-DA exhibits the strongest pH jump indicating that Cu2? possesses the strongest coordination with DA. The overall stability constants (log10 b) of M2?-DA complexes are given in Table 3. There is good agreement between log10 b values from potentiometry and spectrophotometry. As summarized in Table 3,

13the stability of the complexes shows a decrease in the order of Cu2? [ Zn2? [ Ni2? [ Co2? [ Mn2? which

12is in accordance with the Irving–Williams order

[31]. This Irving–Williams order is linear with the decrement of metal ions atomic number, where Zn2? (30 pm) [ Cu2? (29 pm) [ Ni2? (28 pm) [ Co2? (27 pm) [ Mn2? (25 pm). The increase of the metal ion’s electronegativity is proportional to the increase of its atomic number. In the case of Cu2?, the atomic number of Cu2? is smaller than Zn2? but it has a more stable complex. This phenomenon is due to the smaller electronegativity of Zn (Zn (1.65) \ Cu (1.99)). The high log10 b of Cu2? is also due to Jahn–Teller distortion of an octahedral complex, which results in stabilization of the complex [32, 33]. The species distribution
diagrams of these species were calculated from the log10 b values and graphically presented by HySS as given in Fig. 3, representatively, by Cu2? and Co2?. As shown in Fig. 3a for Cu2? and 3b for Co2?, the [M(DA)]- is formed at higher pH than that of M(HDA), suggesting that further deprotonation is necessary to form [M(DA)]-, indicating the coordination of two hydroxyl group to form this species. The formation of [M(HDA)2]2- and [M(HDA2)]3- at lower pH compared to [M(DA)]2- species also support the assumption that the [M(DA)]2- species, which form at higher pH, are coordinated with the O– group and the other species are formed from the combination of salicylate–catecholate binding types. In addition to metal complexes with fully deprotonated ligand [M(DA)]- and [M(DA)]2-, the stability of adding a second ligand of the same species was calculated as the stepwise stability constant (log10 K) value in Table 3; with log10 K1 = log10 bMDA and Table 3 Stability constants of M2?–DA at

4310.15 K and l = 0. 15 mol?dm-3 NaCl Species p q r s log10 b ± SDa log10 KDA1 b log10 KDA2 b Hyperquadc Hypspec M = Cu2? M(HDA) [M(DA)]- [M(HDA2)

12]3- [M( DA )2]4- M = Zn2? M (HDA) [M(DA)]- [M(HDA2)

12]3- [M( DA )2]4- M = Ni2? M (HDA) [M(DA)]- [M(HDA2)

pKa) are represented by standard deviations SD in the parentheses for the last place of the decimal a p, q, r and s represent the number of metal ion, Nac, DA, and hydrogen ion, respectively b log10 K value based on Hyperquad refinement c Stability constants were refined by “Hyperquad” and “Hypspec” using potentiometric and spectrophotometric methods, respectively log10 K2 = log10 bMDA2 - log10 bMDA. It can be seen that log10 K2 \ log10 K1 due to repulsion between similar ligands in one complex, which causes a decrease in stability; this is also, due to there being fewer coordination sites on the metal ion, since it has already been occupied by the first coming ligand to form the [M(DA)]- complex [34]. This suggests that the attachment of the second ligand is weaker than that of the first ligand and the formation of [M(DA)]2- species is more difficult. Fig. 3 Speciation diagram of binary a Cu2?–DA and b Co2?–DA at metal to ligand
Complexation Study of Ternary Systems: Formation of the ternary species \([\text{M}(\text{HDA})(\text{HNac})]^-\), \([\text{M}(\text{HDA})(\text{Nac})]^{2-}\) and \([\text{M}(\text{DA})(\text{Nac})]^{3-}\) is justified from the analysis of potentiometry data. In Fig. 4, the observed ternary titration curve exhibits greater pH jump than that of the corresponding binary system. At \(m = 5.0–6.0\), a pH jump is observed suggesting a stronger coordination compared to that of the salicylate type (\(\text{COO}^–\), ortho-\(\text{O}^–\)) coordination in binary system. Thus it can be considered that Nac coordinates through the contribution of its \(\text{COO}^–\) group. Fig. 4 Titration curve on \(\text{M}2^+–\text{DA}–\text{Nac}\) system at a metal to ligand ratio of 1:1:

1 A significant pH jump at \(m = 7.0\) suggests deprotonation, which is more likely to occur on the S– group of Nac, participated in complex formation. Further deprotonation was observed from a big pH jump at \(m = 8.0\), which occurs on the meta-\(\text{O}^–\) group of DA, suggesting the catecholate type (ortho-\(\text{O}^–\), meta-\(\text{O}^–\)) coordination from DA and \(\text{COO}^–\), S– coordination from Nac. Stability constants (\(\log_{10} b\)) of ternary complexes are recorded in Table 4. The results from potentiometry and spectrophotometry measurements show good agreement. The species distribution of those ternary complex species are graphically represented by \(\text{Cu}^2+\) and \(\text{Co}^2+\) complexes. As shown in Fig. 5a, the first ternary species \([\text{Cu}(\text{HDA})(\text{HNac})]^-\) was formed in the pH region where \([\text{Cu}(\text{HNac})]^-\) was observed. As the \([\text{Cu}(\text{HNac})]^-\) concentration decreases the formation of \([\text{Cu}(\text{HDA})(\text{HNac})]^-\) increases, suggesting that one of the two protons in the ternary species was contributed by the protonated S– group of Nac. Thus, the other proton was contributed by DA through its meta-\(\text{O}^–\) group. Next, for \([\text{M}(\text{HDA})(\text{Nac})]^{2-}\) species, since the S– group of Nac is more likely to deprotonate earlier than the meta-\(\text{O}^–\) group of DA, this suggests that the proton in the complex is contributed by the meta-\(\text{O}^–\) group of DA. The final species \([\text{M}(\text{DA})(\text{Nac})]^{3-}\) was formed at highly basic pH suggesting deprotonation on the meta-\(\text{O}^–\) group and the species was formed from the binding through catecholate type coordination of ligand DA along with (\(\text{COO}^–\), S–) coordination of Nac. Table 4 Stability constant of ternary systems at

4310.15 K and \(l = 0.15\) mol?dm\(^{-3}\)

NaCl Species p q r s \(\log_{10} b\) \(\pm\) SDa Hyperquad Hyperquadc Hypspec Dlog10 Kb log10 Xb M = Cu2+ \([\text{M}(\text{HDA})(\text{HNac})]^-\) 1 1 1 1 29.77 (8) [\(\text{M}(\text{HDA})(\text{Nac})]^{2-}\) 2 1 1 1 28.24 (5) 29.81 (2) [\(\text{M}(\text{DA})(\text{Nac})]^{3-}\) 1 1 1 0 19.17 (8) 19.67 (5) -2.47 3.55 M = Zn2+ \([\text{M}(\text{HDA})(\text{Nac})]^{2-}\) 1 1 1 1 25.15 (9) 26.28 (2) [\(\text{M}(\text{DA})(\text{Nac})]^{3-}\) 1 1 1 0 16.38 (6) 16.66 (5) -0.33 4.27 M = Ni2+ \([\text{M}(\text{DA})(\text{HNac})]^-\) 1 1 1 1 31.79 (9) [\(\text{M}(\text{HDA})(\text{HNac})]^-\) 1 1 1 2 23.66 (7) 24.69 (3) [\(\text{M}(\text{DA})(\text{Nac})]^{3-}\) 1 1 1 0 14.40 (7) 14.79 (3) -0.13 -0.09 M = Co2+ \([\text{M}(\text{HDA})(\text{Nac})]^{2-}\) 2 1 1 1 23.05 (2) 23.39 (4) [\(\text{M}(\text{DA})(\text{Nac})]^{3-}\) 1 1 1 0 12.80 (5) 12.68 (7) -1.06 2.27 M = Mn2+ \([\text{M}(\text{HDA})(\text{HNac})]^-\) 2 1 1 1 21.59 (9) 22.15 (7) [\(\text{M}(\text{DA})(\text{Nac})]^{3-}\) 1 1 1 0 12.56 (4) 12.65 (3) 0.51 3.23

Standard uncertainties \(u\) are \(u(T) = 0.1\) K, \(u(\text{pKa})\)

\(\text{pKa}\) are represented by standard deviations SD in the parentheses for the last place of the decimal a p, q, r and s represent the number of metal ion, Nac, DA, and hydrogen ion, respectively b \(\log_{10} \text{value based on Hyperquad refinement } K\) c Stability constants were refined by “Hyperquad” and “Hypspec” using potentiometric and spectrophotometric methods, respectively The parameters Dlog10 K and log10 X were noted as useful.
complexes [35–39]. Dlog10 K expresses the stability of the ternary species [M(DA)(Nac)]3- relative to the stability of the binary species, [M(DA)]- and M(Nac); the value is calculated from equation: $D \log_{10} K = \frac{1}{4} \log_{10} b_{MAB} - \log_{10} b_{MA} - \log_{10} b_{MB} - \log_{10} b_{\delta_2}$. The parameter $\log_{10} X$ expresses the disproportionation tendency of binary species [M(Nac2)]2- and [M(DA2)]4- to form the ternary species [M(DA)(Nac)]3-, where $\log_{10} X$ is calculated from equation: $\log_{10} X = \frac{1}{2} \log_{10} b_{MAB} - \log_{10} b_{MA} - \log_{10} b_{MB} - \log_{10} b_{\delta_3}$. It was found that the complex with the highest $\log_{10} b$ value for its binary complex tends to have the most negative $D\log_{10} K$ value, suggesting that more energy is needed to form a stable ternary complex from a stable binary complex. However, after the ternary complex is formed, it possesses a greater stability than the binary complex suggesting that the ternary complex is unlikely to disassociate back to the binary. This is supported by the Fig. 5 Speciation diagram of ternary a Cu2?-DA–Nac and b Co2?–DA–Nac at metal to ligand ratio of 1:1:1 $\log_{10} X$ parameter of the ternary species, which generally have positive values, indicating that the formation of the ternary complex [M(DA)(Nac)]3- is more favorable than that of the binary species [M(DA2)]4- or [M(Nac2)]2- [40]. For instance, the [Cu(DA)(Nac)]3- species has the most negative Dlog10 K value (-2.47) since Cu2? possesses the most stable binary species $\log_{10} b$, indicating that less energy is gained in the formation of ternary species. However it has a positive $\log_{10} X$ value of 3.55 indicating greater stability of its ternary species. In the case of [Mn(DA)(Nac)]3-, the Dlog10 K value of 0.51 indicates that less energy is needed to form ternary species (compared to the Cu2? system) and a $\log_{10} X$ of 3.23 indicates that the ternary complex of Mn is more stable than its binary species. Fig. 6 Spectrum measurements of ternary a Cu2? and b Co2? system at M2?:Nac:DA = 1:1:1

4.4 Spectrophotometric Measurements

The addition of metal ion into the ligand system yields a metal–ligand complex, which causes an alteration in the spectral behavior [37, 40]. In this work, the spectral measurements were done on ternary systems as a function of pH; as shown in Fig. 6

wavelength range was 200–400 nm. The aromatic ring of DA gave strong absorbance at 220–250 nm for all systems. The bands observed at longer wavelength are related to the metal–ligand complex. The observed bands show similar shifts in all systems, so the Cu2? and Co2? systems were chosen as representative. For the Cu2? ternary system, as observed in Fig. 5a, at pH = 2.5 a band occurred at 312 nm which then exhibited a blue shift to 309 nm as the pH increased to 5.0, which was affected by the formation of [Cu(HDA)(Nac)]2- species. However with the pH increased to 11.0, the spectrum exhibited another red shift to 325 nm, which is more likely due to the formation of [Cu(DA)(Nac)]3- species. Similarly, for Co2? ternary system in Fig. 5b, at pH = 2.5 a band was firstly observed at 314 nm, which then exhibited a blue shift to 309 nm as the pH increased to 8.0 but, with increase of pH to 11.0, there was a red shift to 344 nm which was caused by the [Co(DA)(Nac)]3- species. 5 Conclusion Binary species of DA (M(HDA), [M(DA)]-, [M(HDA2)]2-, [M(HDA2)]3-, [M(DA)]4-) and ternary species of DA–Nac ([M(HDA)(HNac)]-, [M(HDA)(Nac)]2-, [M(DA)(Nac)]3-) were found in the potentiometry analysis, supported by spectrophotometry analysis. It was found that the binding of M2? to the COO– group of DA was initiated the deprotonation of the meta-O– group, and then formed salicylate type coor- dination. However, at higher pH the coordination changed to catecholate type with respect to the deprotonation of the ortho-O– group. While for Nac, the COO– group was also found to attach firstly to metal ions followed by the S– group as pH was increased.
The stability constants of the complexes in binary and ternary system showed the same order with that of log10 b values: i.e. Cu2? [Zn2?] Ni2? [Co2?] Mn2?. The analysis of Dlog10 K and log10 X indicated that formation of ternary species is favorable. Acknowledgments This work was supported by the Ministry of Science and Technology of Taiwan (NSC 102-2221-E-011-079) and National Taiwan University of Science and Technology (103M47006).

References