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1**Equilibrium Studies of Complexes between N-Acetylcysteine and Divalent Metal Ions in Aqueous Solutions Shella Permatasari Santoso,† Ivon Kusmijo Chandra,† Felycia Edi Soetaredjo,‡ Artik Elisa Angkawijaya,† and Yi-Hsu Ju*,† †Chemical Engineering**

Department, National Taiwan University of Science and Technology, Taipei City 106-07, Taiwan ‡Chemical Engineering Department, Widya Mandala Catholic University, Surabaya 60114, Indonesia

1**ABSTRACT: The complex formations of N-acetylcysteine with divalent transition metals Cu2+, Zn2+, Ni2+, Co2+, Mn2+ have been investigated in aqueous solution of 0.15 mol·dm−3 NaCl at 310.15 K by the potentiometric method. The protonation and stability constant of**

the complexes were obtained based on nonlinear least-squares curve fitting performed by the HYPER-QUAD2008 program along with an estimation using Bjerrum− Calvin half integral method. Distribution diagrams of complex species at certain pH range were generated by the HySS2009 simulation program. From optimization and thermochemical analysis by using the Gaussian09W program, it showed that the ligand formed a six-membered chelate ring with the investigated metal ions via its sulfur and oxygen donor atoms. ■ INTRODUCTION As is widely known, some heavy metals such as Fe2+, Co2+, Cu2+, Mn2+, Ni2+, and Zn2+ are essential trace elements that act as micronutrients. These play critical roles in human metabolism, bone structure, brain and nervous system, muscle contraction, nerve transmission, blood clotting, immune function, enzymes activities, and oxygen transport.1−6 Excessive uptake of these metals can be dangerous for one's health because the human body is not equipped with the mechanism to regulate most of these elements.3,5 These heavy metals are not easily excreted and will be kept in the body for a relatively long time. Accumulation of these metals may lead to the generation of reactive oxygen species (ROS) and depletion of antioxidants such as glutathione. Toxic species such as ROS are well-known to cause oxidative damage to cells. Long-term exposure of these species may result in serious illness of the nervous system and cells.7−10 N-acetylcysteine (Nac) is

9**a biologically important organic substance that is known to have metal-chelating properties and can be used for metal poisoning therapy.**

7,11−13 Nac is a cysteine derivative with an acetyl group attached to the N- terminus. This converts zwitterionic cysteine to a monovalent organic anion. The acetyl group of Nac provides a beneficial effect for the generation of glutathione and also may increase the solubility of Nac in water. Nac is a potential antioxidant chelator agent with its thiol and carboxyl groups as the functional groups. This compound is also capable of inactivating ROS as well as metal ions. It can prevent the toxic effect caused by metals.7,14−16 Nac can attenuate the oxidative damage that is induced by a copper overload and has the cytotoxic effect in cancer cells. Although the interaction between Nac and copper, a strong oxidative metal, may trigger © 2014 American Chemical Society the formation of hydrogen peroxide. Hydrogen peroxide may have a negative effect on the human body. However the Nac− copper interaction may be beneficial to prevent the growth of cancer cell because the formed H_2O_2 may have a cytotoxic effect on cancer cells.14,17,18 Nac also has been used

1**as a mucolytic agent,** a neuroprotective agent, **for** the **treatment of** paracetamol overdoses **and**

brain disorders. The occurrence of thiol group in Nac structure also provides many antioxidant properties such as anti inflammation, free radical scavenger, and prevents sulfur depletion in the body.19−21 Many

studies have been conducted to prove the effectiveness of Nac in reducing the effect of heavy metal poisoning in the human body and preventing the oxidative damage of the cells. Neal et al. reported that Nac has beneficial role in treating lead poisoning.13,19,22 A thorough literature review showed that only a few studies have been done on the complexation between divalent metal ions, especially transition metals and Nac in aqueous solutions. Recent reports on the equilibrium constant of Nac were studied using Ni2+, Co2+, Zn2+, Cd2+, and Hg2+.11,23 In our study, the interaction between divalent metals and Nac were observed in biologic conditions (310.15

3**K and ionic strength 0.** 15 **mol·dm−3**

NaCl) and presented as the value of protonation and metal complex stability constants. Determinations of these constants were done by using a potentiometric titration method and data analysis was done by Bjerrum−Calvin half integral method and the HYPER- QUAD2008 program. The structure of complexes species were proposed by using Gaussian09W program.

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■ EXPERIMENTAL SECTION Materials and Solutions. All the chemicals were analytical grade and were used without further purification. N- acetylcysteine (Nac, C5H9NO3S, 99% purity), copper chloride dehydrate (CuCl2·2H2O, 99% purity), cobalt nitrate hexahy- drate (Co(NO3)2·6H2O,

14**98% purity), and zinc nitrate hexahydrate (Zn(NO3)2·6H2O, 98% purity) were purchased from Sigma-Aldrich**

(U.S.A.).

12**Sodium chloride (NaCl, 99.5% purity) was obtained from Showa (Japan).**

12**Sodium hydroxide (NaOH,** 99% **purity) was** purchased from **Yakuri**

(Japan). Hydrochloric acid (37.6% purity) and manganese chloride tetrahydrate (MnCl2·4H2O, 99.8% purity) were supplied by Fisher Scientific (U.S.A.).

7**Nickel chloride hexahydrate (NiCl2· 6H2O, 98% purity) was** obtained **from Alfa Aesar (UK).**

Free- carbonate NaOH and HCl were prepared and standardized before used. All solutions were prepared freshly before experiments using ultra pure water obtained from NANO Pure Ultrapure water 18.3 MΩ·cm−1. Potentiometric Titration. pH−potentiometric titrations were performed using a Metrohm 888 Titrando with a 805 Dosimat equipped with a 802 rod stirrer, a 804 Ti stand, and an Ecotrode Plus pH glass electrode. The electrode response can be read to the third decimal place for pH with a precision of ± 0.001. The device was coupled to a personal computer and the titration software Tiamo version 2.3 was used to control the titration process and record the data.

3**Before and after each** series **of the** measurements, the **glass electrode was calibrated**

at 310.15 K by immersing the electrode in buffer standard solution at pH 4.00, 7.00, and 10.00. The titrations were carried out in a 150 cm3 commercial double walled glass vessel equipped with a refrigerated circulating bath to maintain the temperature at 310.15 K. For

10**determination of the protonation** constant **of the ligand and the stability** constant **of**

binary complex between metal and ligand,

4**the following solutions were prepared** each with a **total volume 50 cm3:**

4**(a) 0.003 mol·dm−3** HCl + **0.** 15 **mol·dm−3** NaCl **(b) Solution a + 0.** 01 **mol·dm−3**

Nac (c) Solution a + 0.01 to 0.03

15**mol·dm−3 Nac + 0.** 01 **mol·dm−3 metal ion**

The protonation constant of ligand was determined by titrating a solution b potentiometrically against carbonate-free NaOH, whereas

15**the stability constants of metal−** ligand **complexes**

were determined by titrating the mixture c. In addition to maintaining experimental temperature at 310.15 K, the ionic strength of each solution was controlled at 0.15 mol· dm−3 by using NaCl as the supporting electrolyte. The potentiometric titration of the binary complexes were carried in the pH range of ∼2.5 to 11, with more than 80 points of pH reading collected for each set of titration, and at four different molar ratio of

metal to ligand (1:1, 1:2, 1:2.5, and 1:3). This fulfilled all possible coordination numbers of the metal ions. Each set of titration was repeated at least three times under controlled experimental conditions with a reproducibility of ± 0.04 in pH units. Data Analysis. To determine the protonation and stability constants of Nac and its metal complexes, HYPERQUAD2008 was used to make nonlinear least-squares curve fitting based on experimental pH-potentiometric titration data.24−28 Various models with possible compositions of complex species were proposed in the program to refine the protonation and stability constants. This program adopted Gauss−Newton−Marquardt algorithm

10**to minimize the objective function (U) which is** described **as**

$$U = \sum_i W_i r_i,$$

16**where W is the weight and r is the residual** that **is** equal to **the difference between** the calculated **and** the experimental **data**

of the titration curves. Initial estimations of these constants were needed to prevent errors during HYPERQUAD2008 refinement. For this estimation purpose, the stability constants of these complexes were calculated by using Bjerrum−Calvin half integral method.29−31 These values were compared to the ones obtained from the HYPERQUAD2008 refinement results. During all refinements, the ionization constant of water at chosen experimental condition was kept constant (pKw = 13.384 at 310.15

3**K and ionic strength 0.** 15 **mol·dm−3** NaCl). To measure **the** goodness of fit **in**

a system, sigma (σ) can be obtained from σ= U (m − n) where m is the number of data points that were used during refinement and n is the number of parameters refined.24 In this program, both protonation and stability constants were presented as log values of the overall formation constant (log βpqr) with stoichiometric coefficients p, q, and r that represent divalent metal ions, N-acetylcysteine, and hydrogen atoms respectively. The formation constant is a function of complex species concentration [MpNacqHr] and the free reactant concentrations [M], [Nac] and [H] and is expressed by the following equation: pM + qNac + rH ⇌ MpNacqHr β pqr = [MpNacqHr] [M]p [Nac]q [H]r The refined formation constant values of each complex species then were introduced to HySS2009 program to provide a speciation diagram that can be used to depict the distributions of various complex species that were formed in certain pH ranges.32 Molecular Modeling. Optimization of the complexes structures were carried out using the Gausian09W program with the density functional theory (DFT) calculation and B3LYP hybrid functional and the 6-311++G(d) was used as the basis set.19,33−36 Geometry optimization and frequency analysis was done to obtain the thermochemical properties of the complexes. The modeling was performed by employing some simplifications, such as only considering the complex formation of one metal ion and one ligand (MNac species) and the usage of fully deprotonated ligands and not considering the usage of salt or not considering the addition of an acid/base during pH− potentiometric titration. ■ RESULTS AND DISCUSSION Protonation Constant of N-Acetylcysteine. The proto- nation constant is one of several fundamental properties in pharmacological studies. This constant may indicate at which pH the ligand is ionized. These constants were

13**used to estimate the absorption, distribution, metabolism, and excretion of compounds in biological systems and** in **the environment.**

37 In this study, the protonation

7**constants of** Nac **were presented as** the **minus logarithm of** a **stepwise hydrogen dissociation** constant **(pKa)**

which is expressed by the following equations: H2Nac ⇌ H+ + HNac−[H+][HNac−] Ka1[H2Nac] = HNac− ⇌ H+ + Nac2−[H+][Nac2−] Ka2[HNac−] = From the refinement of potentiometric result by HYPER- QUAD2008 program, the protonation constants were obtained as overall formation constants (log β) H+ + Nac2− ⇌ HNac−[HNac−] = β1[H+][Nac2−] 2H+ Nac2− ⇌ H2Nac[H2Nac] β2[H+]2[Nac2−] + = Based on the above equations, the relation between log β and pKa can be described as log β1 = pKa2 and log β2 = pKa2 + pKa1.

2**strength of 0.15 mol·dm−3 NaCl was** initially estimated by **The** protonation constant **of**

Nac at 310.15 K and an ionic Bjerrum−Calvin half integral method and the actual value was determined by HYPERQUAD2008 program. These values were presented in Table 1 along with values reported in Table 1. Protonation Constant (pKa) of N-Acetylcysteine (T =

2**310.15 K and** I = **0.15 mol·dm−3 NaCl)**

a pKa ± SD reference functional Bjerrum− group Calvin HYPERQUAD σb carboxyl 3.13 ± 0.01 3.18 ± 0.02 1.02 3.08c 3.31d thiol 9.47 ± 0.01 9.48 ± 0.05 9.62c 9.85d aStandard

5**uncertainties u are u(T) = 0.1 K, u(**

pKa) are represented by standard deviations SD. bSigma (σ) is the goodness of fit in a system with expectation value of 1.00. cRef 11,

11**I = 0.12 mol·dm−3 NaClO4, T** = 310.15 **K.**

dRef 20, H NMR spectra using 10% D2O and 90% H2O. Scheme 1. Stepwise Hydrogen Dissociation of N-Acetylcysteine (Nac) literature.11,20 As depicted in Scheme 1, the stepwise acid dissociation of [H2Nac] was started with the dissociation of hydrogen ion in carboxyl group at pKa1 3.18 and formed a negative charge ligand [NacH]−, followed by the deprotonation in thiol group at pKa2 9.48 and formed free ligand

[Nac]2−. Stability Constant of MNac Complexes. The stability constant of the complex of Nac and metal ions (Cu2+, Ni2+, Co2+, Zn2+, and Mn2+) was determined by titrating solution (c) at a constant ionic strength (0.15 mol·dm−3 NaCl) and temperature (310.15 K) against free-carbonate NaOH. According to typical titration curves (Figure 1) for a metal to ligand ratio of 1:2.5, it can be seen that at a fixed titrant volume there is a shift in pH for MNac curves to lower pH compared to Nac ligand titration curve. The shifts occur due to the formation of complexes between metal ions and Nac. In addition, a close observation at pH 4 to 9 shows that Cu2+ and Zn2+ titration curves overlap and have larger shifts than those of Ni2+, Co2+, and Mn2+. There is a larger shift of the MNac curve than the Nac curve. This indicates a higher stability of the Figure 1. Potentiometric titration curves of N-acetylcysteine (Nac) with divalent metal ions

4**at T** = 310 **.15 K and I = 0.** 15 **mol·dm−3,**

pH versus the amount of NaOH added (x). □, Nac; red ◆, Cu2+-Nac; blue ■, Zn2+-Nac; green ●, Ni2+-Nac; yellow ▼, Co2+-Nac; × , Mn2+- Nac. complex, and the overlapping of curves indicates that they have close stability constant values. The unknown stability constants of MNac species were determined by calculating the stability constants using the Bjerrum−Calvin half integral method, and this value then were introduced as the estimated stability constants into the HYPERQUAD2008. These values then were refined to obtain the best model that yielded a reasonably good curve fit compared to the potentiometry experimental result. The stability constants of these complexes were expressed in log β value and were presented in Table 2. The goodness of fit, sigma (σ), indicates a good fit of the proposed model in a system, with an expectation of a value of 1.00. The σ value range (1.02 to 1.41) obtained for all systems (Tables 1 and 2) is acceptable because there are many species included in the system.38 From the HYPERQUAD2008 program, the model with the best fit of titration data indicates that three species, [MNac], [MNac2]2−, and [MNacH]+, existed in the solutions during titration. As shown in Table 2, the stability constant of Nac with the metal ions

8**decreases in the following order Cu2+ > Zn2+ > Ni2+ > Co2+ > Mn2+**

for [MNac] and [MNac2]2− species. The order of the stability constant for the divalent metal ions is appropriate with the order of stability constant suggested by Irving− Williams, where Mn2+ < Co2+ < Ni2+ < Cu2+ > Zn2+.39 There is a difference between the obtained pKa and log β values (Tables 1 and 2) and the values reported in the literature.11,20 The differences in these constants might be due to variance in experimental conditions or the calculation procedure used. In addition to the overall formation constants of complexes used to indicate how tightly ligand is bound to metal ions; the stepwise stability constant (log K) of these complexes were calculated according to (log K1 = log βMNac) and (log K2 = log βMNac2 − log βMNac) and were presented in Table 3. From this table, log K2 is lower than log K1, which indicates that the first Nac binds more tightly to the metal ions than the second Nac. This phenomenon happened due the attachment of second Nac to [MNac] species thus forming a bulkier complex [MNac2]2−. The second Nac ligand's attachment was weaker than the attachment of the first Nac ligand. There is a decreased positive charge on the complex due to the negatively charged ligands. This lowered positive charge along with the steric Table 2. Overall Stability Constant (log β) of MNac Complexes (T =

2**310.15 K and** I = **0.15 mol·dm−3)**

a log βpqr ± SD complex species p q r Bjerrum−Calvin HYPERQUAD σb ref M = Cu2+ [MNac] 1 1 0 6.57 ± 0.02 6.64 ± 0.09 1.30 [MNac2]2− 1 2 0 12.66 ± 0.02 12.70 ± 0.06 [MNacH]+ 1 1 1 13.35 ± 0.09 M = Zn2+ [MNac] 1 1 0 6.34 ± 0.05 6.23 ± 0.08 1.41 4.90c [MNac2]2− 1 2 0 12.05 ± 0.05 11.97 ± 0.08 11.48c M = Ni2+ [MNac] 1 1 0 4.84 ± 0.01 4.86 ± 0.04 1.21 4.84d [MNac2]2− 1 2 0 9.04 ± 0.01 9.22 ± 0.04 9.22d [MNacH]+ 1 1 1 13.15 ± 0.09 M = Co2+ [MNac] 1 1 0 4.12 ± 0.02 4.28 ± 0.08 1.31 4.22d [MNac2]2− 1 2 0 7.87 ± 0.02 7.97 ± 0.09 7.94d [MNacH]+ 1 1 1 12.63 ± 0.07 M = Mn2+ [MNac] 1 1 0 3.67 ± 0.01 3.64 ± 0.05 1.27 [MNac2]2− 1 2 0 7.44 ± 0.02 7.47 ± 0.08 [MNacH]+ 1 1 1 12.66 ± 0.09 aStandard

5**uncertainties u are u(T) = 0.1 K, u(**

log β) represented by standard deviations SD. bSigma (σ) are the goodness of fit in a system with expectation value of 1.00. cReference 23,

3**I = 0.10 mol·dm−3** NaClO4, **T = 298.** 15 **K.**

dReference 11,

11**I = 0.12 mol·dm−3 NaClO4, T** = 310.15 **K.**

Table 3. Stepwise Stability (log K) Constant of MNac Complexes (T =

2**310.15 K and** I = **0.15 mol·dm−3)**

a metal ion log K1 Cu2+ 6.64 Zn2+ 6.23 Ni2+ 4.86 Co2+ 4.28 Mn2+ 3.64 aStandard

5**uncertainties u are u(T) = 0.1 K.**

log K2 6.06 5.74 4.36 3.69 3.83 interactions between ligands can also influence the stability constant. The speciation diagrams for MNac complexes are shown in Figure 2 as the percentage of the species relative to M. As shown in the figures, the presence of free metal ions decreased with increasing pH, indicating that metal ions were consumed by a ligand-forming ligand−metal complex. The [MNacH]+ species started to form at an acidic pH, indicating that the formation of the [MNacH]+ species involved the oxygen donor atom of the carboxylic group since the thiol group is deprotonated at higher pH. However, [MNac] and [MNac2]2− species started to form at a less acidic pH, indicating that sulfur donor atom also took part in the formation of the complexes. Molecular Modeling. The structures of the [MNac] complexes were fully optimized at the B3LYP/6-311G level of the DFT. The frequency analyses were obtained by Gaussian 09W program. The Gibbs free energy of formation (G) obtained from the output of frequency analysis then was used to verify the contributing binding site of the ligands and to predict the structure of the complexes. The Gibbs free energy of reaction (ΔrG), which is proportional to metal complex formation constant (log β), were calculated by using the following equation. M2+ + Nac2− ⇌ MNac ΔrG = ΣGproduct − ΣGreactant According to

correlation between log β and ΔrG, the more negative the ΔrG is, the larger the formation constant value will be and the complex formed will be more stable. For each metal−ligand combination, Gaussian modeling was done by considering the possible binding site that may contribute in complex formation. The ΔrG for metal ligand formation with their possible binding site of ligands were calculated. The one that gave the most negative value of the ΔrG was chosen as a possible contributing binding site, and the structure of this complex then will be used as the predicted structure of the formed complex. Representative [MNac] models for the Ni2+ and the Nac complex are presented in Figure 3. As depicted in the models A, B, and C, Nac may form a complex with the metal ion through its carboxyl group, the thiol group or form chelate through its carboxyl and thiol groups. It turned out that model C is the most stable complex with the most negative value of ΔrG (−0.0904 hartree/particle) compared to model A (ΔrG = −0.0744 hartree/particle) and model B (ΔrG = −0.0865 hartree/particle). All other metal ions studied (Cu2+, Zn2+, Co2+, and Mn2+) showed the same behavior as Ni2+ in forming [MNac] species. The most negative ΔrG values were found in the interaction of thiol and carboxyl donor atoms with metal ions. Complexes with six-membered chelate ring were formed. In agreement with HYPERQUAD refined result, the negativity of ΔrG (Table 4)

8decreases in the order of Cu2+ > Zn2+ > Ni2+ > Co2+ > Mn2+. ■ CONCLUSION The interactions of Nac and

metal ions under the biological condition of I =

10.15 mol·dm−3 NaCl and T = 310.15 K have been studied by the pH −potentiometric

technique. Proto- nation constants and complex stability constants as overall formation constants (log βpqr) were obtained by the HYPER- QUAD2008 along with the estimation of unknown stability Figure 2. The species distribution of (a) Cu2+-Nac, (b) Zn2+-Nac, (c) Ni2+-Nac, (f) Co2+-Nac, and (e) Mn2+-Nac at 1:2.5 metal to ligand ratio. Percentages are calculated with respect to the concentration of metal ion. ■ AUTHOR INFORMATION Corresponding Author *Y.-H. Ju. Phone: +886 2 2737 6612. Fax: +886 2 2737 6644.

6E-mail: yhju @mail. ntust .edu.tw. Notes The authors declare no competing financial interest. ■ ACKNOWLEDGMENTS This work was supported by the National Science Council of Taiwan through the project NSC

102-2221-E-011-079. The authors thank Prof. Jiang Jyh-Chiang for his valuable discussion regarding the Gaussian program and Dr. Fred Quarnstrom for Figure 3. Optimized structure of nickel (Ni2+) and N-acetylcysteine help in English writing. (Nac), [NiNac] species, generated from Gaussian09 program. REFERENCES Table 4. Gibb's Free Energy of Reaction (ΔrG) of MNac ■ (1) Duffus, J. H. Pure Appl. Chem. 2002, 74, 793−807. Species Obtained by the Gaussian09 Program (2) Fang, Y. Z.; Yang, S.; Wu, G. J. Nutr. 2002, 18, 872−879. (3) Nordberg, G. F.; Fowler, B. A.; Nordberg, M.; Friberg, L. T. In metal ion ΔrG (hartree/particle)a Handbook on the Toxicology of Metals, 3rd ed.; Elsevier: Amsterdam, Cu2+ −0.2687 2007; p 267−273. Zn2+ −0.1038 (4) Puchta, R. Nat. Chem. 2011, 3, 416. Ni2+ −0.0904 (5) Shobana, S.; Dharmaraja, J.; Selvaraj, S. Spectrochim. Acta, Part A Co2+ −0.0865 2013, 107, 117−132. Mn2+ −0.0670

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