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Extraction Studies of Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II) using *N,N',N,N'*-bis[(2-hydroxy-3,5-di-*tert*-butylbenzyl)(2-pyridylmethyl)]-ethylenediamine as a novel ligand

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Abstract

In the present study, the use of *N,N',N,N'*-bis[(2-hydroxy-3,5-di-*tert*-butylbenzyl)(2-pyridylmethyl)]-ethylenediamine (H_2L) as ligand was evaluated in the liquid-liquid (water-chloroform) extraction of Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II). Experiments were carried out to determine the pH for maximum extraction for each metal ion by ligand, maximum extraction capacity, extraction kinetics and extraction selectivity. The results revealed that the extraction of metal ions is dependent on the pH: maximum extraction maximum was obtained in the pH range of 4.5 - 6.0 for Cu(II) and 8.0 - 9.0 for Zn(II). Cd(II) and Mn(II) were best extracted at pH 9.0 and Ni(II) at 10.0. The ligand H_2L was effective for the extraction of Cd(II), Cu(II) and Zn(II) (extraction efficient, %E ~100%), whereas %E of 76% and 23.5% were observed for Mn(II) and Ni(II), respectively. The ligand presented high selectivity for the extraction of Cu(II) at pH 4.0.

Keywords: liquid-liquid extraction, metal ions, selectivity, FAAS.

Introduction

Liquid-liquid extraction is an efficient analytical method which is extensively utilized in the separation, preconcentration and selective determination of analytes in solution [1-6]. Via this technique, the analyte is distributed between two immiscible phases. In most cases, one of these phases is an aqueous solution or a buffered solution and the second phase is an organic solvent [7-10].

The easiest procedure to transfer an analyte, initially dissolved in an aqueous solution, to an organic phase is by neutralizing its charge. This can be accomplished either by forming a neutral complex or an ionic couple [9, 10].

The concentration of the metallic complex (an ionic couple) in the organic phase can then be directly determined by ultraviolet, visible or atomic absorption spectrophotometric methods [10].

The use of organic solvents in flame atomic absorption spectrometry (FAAS) increases the efficiency of the atomization, as the viscosity and surface tension of most organic solvents are lower than those of water, resulting in smaller drops and larger volumes of sample entering the flame [11, 12]. However, the use of organic solvents containing chlorine should be avoided in FAAS, since they can generate toxic products and/or extinguish the air-acetylene flame [9, 13].

The *N,N',N,N'*-bis[(2-hydroxy-3,5-di-*tert*-butylbenzyl)(2-pyridylmethyl)]-ethylenediamine (H_2L) complex agent (Fig. 1) is an hexadentate ligand, with six electron donor groups (i.e, two phenolic oxygen atoms, two pyridine nitrogen atoms and two tertiary amine nitrogen atoms). The phenolic groups are adequately protected by large substituents (*tert*-butyl) in the -*ortho* and -*para* positions. Hence, the ligand can form stable complexes [14, 15].

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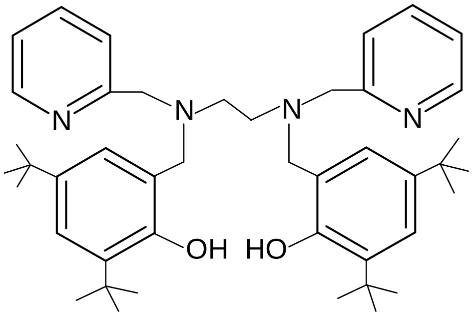

Figure 1. **Chemical structure of H_2L ligand**

The synthesis and characterization of several mononuclear Cu(II), Zn(II), Mn(III), Ga(III), In(III) and Fe(III) complexes using H_2L as the ligand have been reported [15-17]. All complexes were synthesized at slightly elevated temperatures from the reaction between H_2L and appropriate transition metal salts (acetates, nitrates or perchlorates) in a 1:1 stoichiometry, using methanol as the solvent. In some cases, the counter-ion is exchanged using sodium perchlorate [17].

The objective of the present study was to evaluate the potential use of H_2L as ligand in the liquid-liquid extraction of Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II), as well as to study the extraction process.

Experimental

Reagents

All reagents were of analytical grade. H_2L was prepared by the reaction between ethylenediamine and 2-pyridinecarboxaldehyde followed by reduction with sodium borohydride and subsequent addition of 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride [15,16]. The following buffer solutions were used to adjust the pH: chloroacetic/sodium chloroacetate for $2.5 < pH < 3.5$, acetic acid/sodium acetate for $4.0 < pH < 6.0$, tris(hydroxymethyl) aminomethane adjusted with sodium hydroxide for $7.0 < pH < 9.0$ and ammonia/ammonia chloride for $10.0 < pH < 11.0$. Standard Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II) solutions were prepared daily by the dilution of 1000mg L^{-1} stock solutions of the corresponding analytes (atomic absorption grade, Titrisol® - Merck, Darmstadt, Germany). The solutions were prepared using distilled water.

Apparatus

A Marconi MA 832 mini-shaker thermostatic bath was used in all liquid-liquid extraction experiments. The pH of the solutions was measured using a Corning pH/ion analyzer 350 system, equipped with a combinated glass electrode. The concentration of metal ions in aqueous solution was determined by FAAS using a Varian SpectrAA 50 spectrometer equipped with an air-acetylene flame atomizer and Hitachi hollow cathode lamps specific for each metal ion. Operating parameters of the AAS instrument are summarized in Table 1.

All glassware used in the preparation of the solutions were washed with neutral detergent, kept overnight in a 10% (v/v) nitric acid solution and then rinsed with distilled water.

Table 1. **Operational parameters for FAAS system**

Instrumental conditions	**Cd**	**Cu**	**Mn**	**Ni**	**Zn**
Wavelength (nm)	228.8	324.7	279.5	232.0	213.9
Lamp intensity (mA)	4	4	5	4	5
Slit width (nm)	0.5	0.5	0.2	0.2	1.0

Effect of pH on the extraction of metal ions

In order to establish the effect of the pH on the extraction of metal ions, a 10 mL aliquot of an aqueous phase containing M^{2+} (M = Cd, Cu, Mn, Ni or Zn) in the concentration range between of $4.45x10^{-5}$ to $9.10x10^{-5}$ mol L^{-1}, 5.0 x 10^{-2} mol L^{-1} of potassium nitrate and 4.5 x 10^{-2} mol L^{-1} of the buffer solutions in the pH range of 2.5 to 11.0 were used. The same volume of ligand (H_2L) dissolved in chloroform with a concentration varying from 4.45 x 10^{-4} to 9.10 x 10^{-4} mol L^{-1} was added to the solution. The solutions were placed in 50 mL Erlenmeyer flasks the flasks were placed out in thermostatized bath at 25 ºC and constant stirring at 250 rpm, for time periods of 24 to 72 h. After pre-established periods, aliquots of the aqueous phase were removed and then diluted in volumetric flasks and the remaining concentrations of the metal ions were determined by FAAS.

The extraction efficiency (%E) of each metal ion was calculated as:

$$\%E = \left(\frac{C_i - C_f}{C_i} \right) \times 100$$

where C_i and C_f represent the initial and final concentration of the metal ion in aqueous solution, respectively.

Determination of maximum extraction efficiency

The maximum extraction efficiency for the metal ions using H_2L as the ligand was determined using a series of 50mL Erlenmeyer flasks placed in a thermostatized bath at 25 ºC with constant stirring at 250 rpm, for time periods of 24 to 72 h. Exactly 10 mL aliquots of the aqueous phase containing 5 mg L^{-1} of M^{2+} (M = Cd, Cu, Mn, Ni or Zn), 5.0 x 10^{-2} mol L^{-1} of potassium nitrate and 4.5x10^{-2}mol L^{-1} of the appropriate buffer solution were used. The pH was adjusted in order to achieve the maximum extraction of each metal ion. To each of those solutions, 10mL of the ligand (varying the concentration from 1.0x10^{-5} to 5.0x10^{-3}mol L^{-1}) were added. After equilibrium, aliquots of the aqueous phase were removed and then diluted in volumetric flasks and the remaining concentrations of the metal ions were determined by FAAS.

Extraction kinetics of metal ions

The procedure described in the previous section was also used in the kinetic extraction experiments using the optimum pH for extraction of each metal ion and the optimized concentration of the ligand. The time reached to reach equilibrium and the corresponding kinetic constants were determined.

Extraction selectivity

Selectivity experiments were carried out in triplicate using aqueous solutions containing a mixture of Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II) buffered at three different pH values (4.0, 7.0 and 9.0). The experiments were carried out in 50mL Erlenmeyer flasks, using a thermostatized bath at 25ºC with constant stirring at 250 rpm. 10mL of the aqueous phase containing 5 mg L^{-1} of each metal ion, 5.0 x 10^{-2}mol L^{-1} of potassium nitrate and 3.5 x 10^{-2} mol L^{-1} of the buffer solution at pH 4.0, 7.0 or 9.0 were placed in contact with 10mL of 1.0x10^{-3}mol L^{-1} ligand. The contact time between the aqueous and organic phases was 20 h. Aliquots were then removed and diluted to an adequate volume in order to determine the concentration of the metal ions by FAAS.

Results and Discussion

Effect of pH on the extraction of metal ions

The effect of the pH on the extraction of Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II) by H_2L, is illustrated in Fig. 2. Whereas the percent of Cu(II) extracted remained nearly constant, the pH significantly affected the extraction of the other metals. Higher pH values increased the amounts of metal ions extracted.

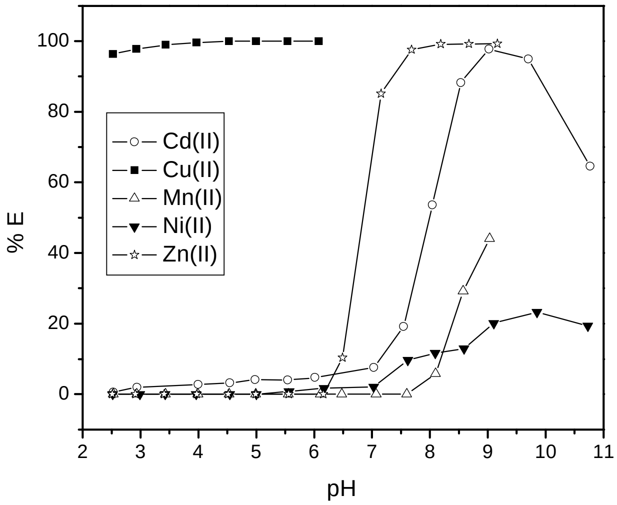

Figure 2. **Effect of pH on the extraction of metal ions.**

Although the percent of Cu(II) extracted remained approximately constant in the pH range of 2.5 to 6.0. The maximum extraction (100%) occurred in the pH range 4.5 to 6.0. For the Cu(II) extraction, the aqueous and organic phases remained in contact for shoter periods of time when compared to the other ions. It was observed that the color of the solution changed to violet at the beginning of the stirring process and became more intense with time, suggesting the formation of a complex in the early stages of contact.

The extraction of Cd(II) from the aqueous phase was rather limited in the pH range of 2.5 and 7.0. However, starting at pH 7.5, the amount of Cd(II) extracted increased significantly, reaching a maximum (~ 98%) at pH 9.0. After which, further increases in pH decreased the %E. The observed decrease at higher pH is possibly due to the formation of a charged complex that is soluble in the aqueous phase. Complexes must be neutral to be extracted into and remain in an organic phase.

No extraction of Mn(II) occurred in the pH range of 2.5 to 7.5. The maximum extraction of Mn(II) was 44% at pH 9.0. Further increases in the pH resulted in formation a of precipitate.

Ni(II) was not extracted in the pH range of 2.5 and 5.0. However, at pH values greater than 7.0, the % Ni(II) extracted started to increase reaching a maximum of 23.3% at pH 10.0. The extraction efficiency decreased with a further increases in pH.

No extraction of Zn(II) occurred in the pH ranged of 2.5 to 6.0. In the pH region of 6.5 and 7.5, the amount of Zn(II) extracted abruptly increased from 10.4% to 97.6%. However, at pH ≥ 8.0, the extraction of Zn(II) was of 99%.

Hirayama *et al*. carried out studies on the extraction behavior of divalent first row transition metals ions with *N*,*N'*-bis(2-hydroxyphenylmethyl)-*N*, *N'*-bis(2-pyridylm-ethyl)-1,2-ethanediamine (H_2bbpen) and its derivatives [6]. The extractions were closed to 100% for almost all metals except Cu(II) for which the extraction yield was 50%. Although the H_2L ligand was not able to extract 100% of Mn(II) and Ni(II), it allowed extraction of 100% of Cu(II). Therefore, this H_2L ligand containing the hydrophobic groups (*tert*-butyl) has potential use as a complexing agent for copper ions.

The results showed that the H_2L ligand exhibited low extraction capacity for Mn(II) and Ni(II). However, it was able to extract nearly 100% of Cd(II), Cu(II) and Zn(II) at the optimum pH for each metal ion. The extraction of Cu(II) was greater for pH values lower than 6.0, suggesting a good selectivity for this ion, as confirmed through selectivity studies.

Extraction mechanism of metal ions

The chemical equilibria involved in the extraction of metal ions by H_2L are depicted in Figure 3 and were based on a previous study [6].

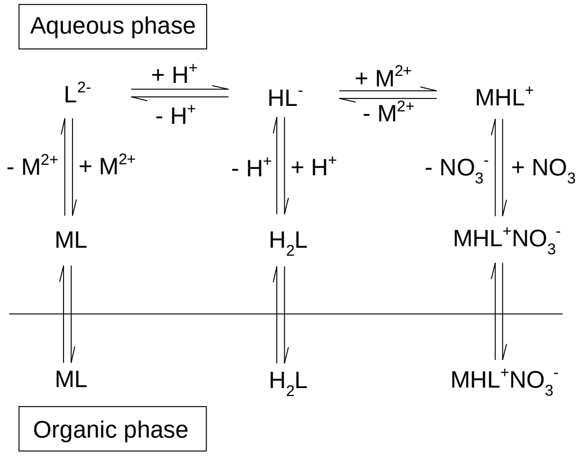

***Figure 3*. Chemical equilibria of the M^{2+}-H_2L-KNO_3 extraction systems**

The H_2L ligand is hydrophobic due to the presence of *tert*-butyl substituents in the *-orto* and *-para* positions of the two phenolic groups. The ligand may be in equilibrium with the aqueous phase in which it can undergo deprotonation of its phenolic group, thus becoming a monoanionic ligand (HL^-). In this form, the ligand can complex M^{2+} (M = Cd, Cu, Mn, Ni or Zn) to form a charged complex, MHL^+. In the presence of nitrate ions, an ion pair $MHL^+NO_3^-$ forms. This hydrophobic ion pair can be preferentially extracted into an organic phase. In addition, depending on the reaction medium, the HL^- ligand can undergo the deprotonation of a second phenolic proton, forming a divalent ligand, L^{2-}, which can react with M^{2+} (M = Cd, Cu, Mn, Ni or Zn) forming the neutral ML complex, which exhibits a good solubility in the organic phase.

Anjos [17] synthesized and characterized the $[Cu(HL)](ClO_4).0.5H_2O$ complex from H_2L in the presence of a solution of $Cu(ClO_4)_2.6H_2O$. Chemical equilibrium studies of this complex carried out in water/ethanol solution (30:70% v/v) by potentiometric titration revealed protonation/deprotonation constants (pK_a) of 3.34 and 11.28 for the phenolic groups coordinated by Cu(II) ions [17].

The $[Zn(HL)](ClO_4)$ complex was synthesized and characterized using H_2L as the ligand in the presence of zinc acetate dihydrate. The potentiometric equilibrium curves of the zinc complex revealed the presence of three protons with pK_a values of 4.04, 7.81 and 11.34. The pK_a values of 4.04 and 11.34 were attributed to the deprotonation of two phenolic oxygen atoms and the value of 7.81 was consistent with the dissociation of a water molecule coordinated to the metal center [15].

Therefore, based on the pH extraction profiles for the metals examined and the range evaluated in the scope of this study as well as on the potentiometric titration results reported by Anjos, it can be postulated that the M^{2+} (M = Cd, Cu, Mn, Ni or Zn) can coordinates to the two pyridine nitrogen atoms, two tertiary amine nitrogen atoms and one phenolic oxygen atoms from the H_2L ligand [17]. The other phenol oxygen atom remains protonated and does not coordinate with M^{2+}.

Determination of the maximum extraction capacity

The effects of ligand concentration on the amount of Cd(II), Cu(II), Mn(II), Ni(II) and Zn(II) extracted are shown in Fig. 4. Experiments were carried out for each metal ion at its optimum pH for extraction. 100% Cu(II) was extracted using 8.0 x 10^{-5} mol L^{-1} of ligand. Higher concentrations did not affect the Cu(II) extraction. By contrast, 6.0 x 10^{-4} mol L^{-1}, 3.0 x 10^{-3} mol L^{-1}, 8.5 x 10^{-4} mol L^{-1} and 1.0 x 10^{-4} mol L^{-1} of ligand were required to extract 98% Cd(II), 76% Mn(II), 23.5% Ni(II) and 99% Zn(II), respectively. Hence, the results indicated that the extraction was highly effective for Cd(II), Cu(II) and Zn(II), which required lower concentrations of the ligand to quantitatively extract essentially all (≥98%) of these metal ions.

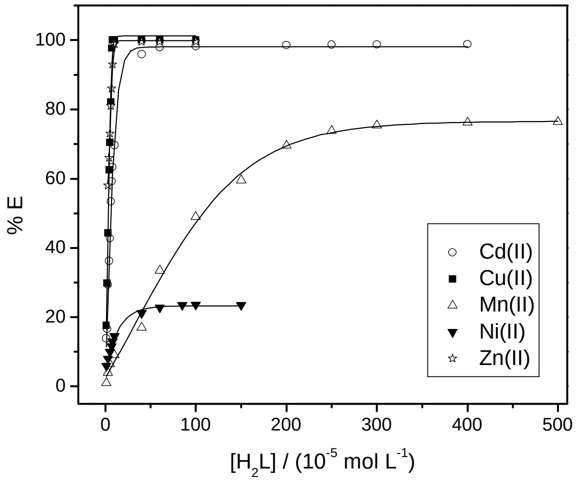

Figure 4. **Maximum extraction capacity of metal ions**

Extraction kinetics of metal ions

Fig. 5 shows the extraction kinetics of the metal ions using the H_2L ligand. The results showed that the extraction of Cu(II) is rapid in the first minutes and reached equilibrium after approximately 60 min and then remained constant (%E 100%). For the extraction of Zn(II) and Cd(II) the results showed a similar behavior, with equilibrium being reached after 17 h (%E 99%) and 18 h (%E ~98%), respectively. Conversely, the extraction profiles of Mn(II) and Ni(II) were rather sluggish. For the extraction of Mn(II), the equilibrium was reached after 50 h (%E 76%) and for the extraction of Ni(II), the equilibrium was reached after around 70 h (%E 20%).

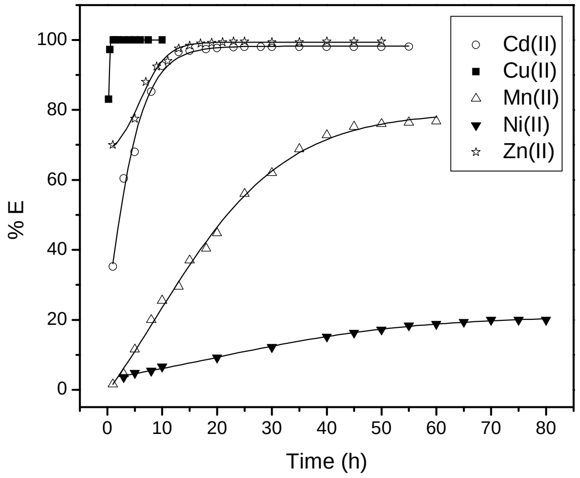

Figure 5. **Extraction kinetics of metal ions**

Determination of rate constants for the extraction of metal ions

The rate constants for the extraction of metal ions were determined using equation:

$$\ln[M^{2+}]_t = -kt + \ln[M^{2+}]_0$$

where $[M^{2+}]_0$ and $[M^{2+}]_t$ represent the initial concentration and the concentration at time t of the metal ion in aqueous solution, respectively. k is the extraction rate constant.

For pseudo-first-order reactions the plot of $\ln[M^{2+}]_t$ *vs* time, results in a straight line with the slope corresponding to –k [18]. The extraction rate constants for the metal ions were calculated from the slope of the linear plots illustrated in Figure 6. The values obtained were 6.39 h^{-1} for Cu(II), 0.232 h^{-1} for Cd(II), 0.227 h^{-1} for Zn(II), 0.033 h^{-1} for Mn(II) and 2.88 x 10^{-3} h^{-1} for Ni(II), i.e., the extraction rate constant is much higher for Cu(II) in comparison with the other metal ions.

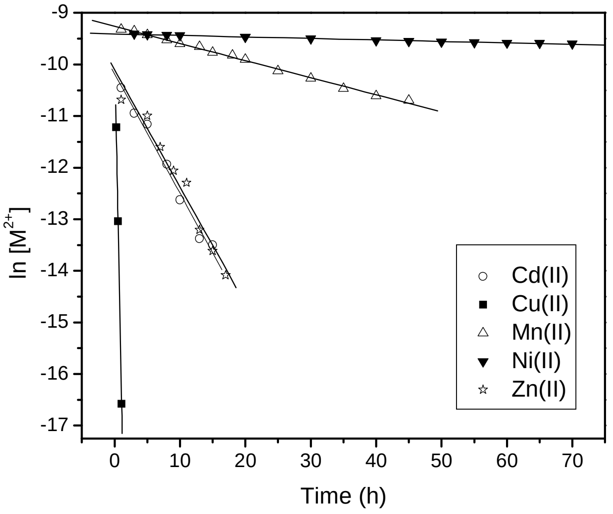

Figure 6. **Pseudo-first-order kinetic model for the extraction of metal ions**

The correlation coefficients (R) of the pseudo-first-order kinetic plots were higher than 0.992, revealing that the experimental data was adequately fitted by this such model.

Extraction selectivity

Compilation of the %E *vs* pH data (Fig. 7) indicates that the H_2L ligand displayed high selectivity for the extraction of Cu(II) at pH 4.0. At pH 7.0, the ligand also exhibited improved extraction capacity for Cu(II) and Zn(II). At pH 9.0, the amount of Cd(II) and

Zn(II) extracted increased whereas that of Cu(II) abruptly decrease relative to the data obtained at pH 7.0. In the pH range of between 4.0 and 9.0, Mn(II) and Ni(II) could not be extracted with the H_2L ligand.

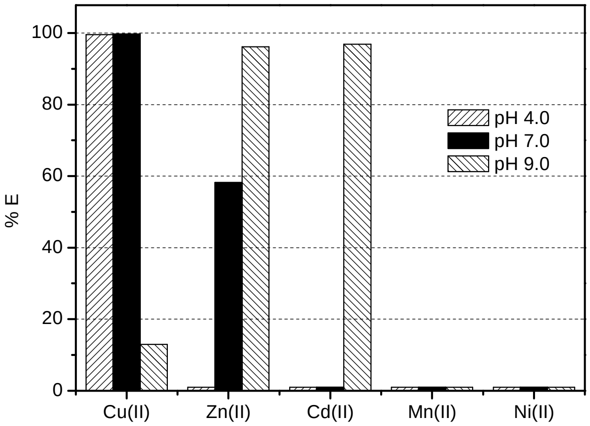

Figure 7. **Extent of extraction as a function of pH**

Conclusions

As expected, the results of this study show that the extraction process of the studied metal ions was dependent on the pH. The amount extracted of each ion extracted generally increased as the pH increased. The extraction mechanism of the metal ions suggests that they coordinate to the ligand via one phenolic oxygen atom, two nitrogen atoms of the tertiary amine and two pyridinic nitrogen atoms. Results on the maximum extraction capacity revealed that lower concentrations of the ligand were needed to extract Cd(II), Cu(II) and Zn(II) compared to Mn(II) and Ni(II). Finally, the ligand was selective for Cu(II) at pH 4.0, since no extraction of the remaining ions was observed.

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