

DROP AMALGAM VOLTAMMETRIC STUDY OF LEAD COMPLEXATION BY NATURAL INORGANIC LIGANDS IN A SALT LAKE

Muhammad Ntale¹, Jude T. Nyangababo^{1*} and Knut Schroeder²

¹Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda

²Norwegian University of Science and Technology, Department of Chemistry, N-7055
Trondheim, Norway

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ABSTRACT. A study of inorganic complexation of lead using drop amalgam voltammetry is described. The study has been carried out in simulated salt lake water and at ionic strength of 7.35 M, the predetermined ionic strength of Lake Katwe. The complexation of lead with the simple ligands (Cl⁻, CO₃²⁻) created anodic waves and the shifts of the peak potentials of lead with the introduction of varying concentrations of each ligand measured. The analysis of these shifts furnished information about the stability constants of the lead complexes which was employed in the calculation of lead species distribution. These mathematical treatments revealed the existence of two lead chloride complexes with corresponding stability constants $\log \beta_1 = 0.88$, $\log \beta_2 = 2.95$; and two carbonate complexes with $\log \beta_1 = 8.50$ and $\log \beta_2 = 9.62$. The results obtained indicate that in Lake Katwe water (25 °C, carbonate alkalinity = 0.11 M, pH 11) approximately 0.00% of total inorganic lead exists as the free ion, and at chloride concentration of 1.8 M only 1.3% of lead exists as the free ion.

KEY WORDS: Drop amalgam, Lead speciation, Stability constants, Lake Katwe, Voltammetric complexation, Species distribution

INTRODUCTION

Lake, sea and river waters contain trace metals such as copper, zinc, cadmium and lead whose concentration may be raised by pollution emanating from industrial effluents [1], run off water [2] and air deposition [3]. In the aquatic system, these trace metals occur in a variety of dissolved, colloidal, complexed or particulate forms of different biogeochemical properties that can have a determining influence on their mobility, cycling and bioavailability. There is a general consensus that the biological effects and biogeochemical cycling of many trace metals are determined by the partitioning of the metals and total concentration among the enormous variety of chemical forms in a given aqueous environment. This has led to the recognition of the fact that speciation analyses resolve these different forms. This speciation operation involves identification and physico-chemical characterisation of various chemical species in which the elements exist in a particular environmental matrix. A comprehensive and systematic speciation scheme has been reported [4] which can provide data on all the physical and chemical forms of the element in the natural water system.

Several studies have been reported on the chemical speciation of metals and their bioavailability in aqueous systems [5, 6]. Filella *et al.* [7] have reported a method for the determination of the "best" values of stability constants. Other studies on the concepts and practice for trace analysis and speciation have also been reported [8]. Bilinski *et al.* [9] studied the stability constants of hydroxo and carbonate complexes of copper, cadmium, lead and zinc in synthetic sea water using anodic stripping voltammetry.

* Corresponding author. jtnyang@chemistry.mak.ac.ug

In Uganda, Lake Katwe is of particular interest for heavy metal monitoring studies because for over centuries it has been used as the main source of cooking salt, coupled with intense industrial and commercial activities. In our first investigation on Lake Katwe, we reported on the complexation of copper by hydroxide and bicarbonate ligands in simulated Lake Katwe water and on distribution of hydroxo and bicarbonato species [5]. In that report, three bicarbonato copper complexes were identified while two hydroxo copper reaction products were revealed by use of Inczedy [10] mathematical analysis. In the present study, further work was initiated to establish a thermodynamic based description of lead complexation by the natural inorganic ligands that exist in Lake Katwe by the use of drop amalgam voltammetry.

EXPERIMENTAL

Site description. The study site of Lake Katwe is indicated in Figure 1. Lake Katwe is situated in Kasese district in south-western Uganda, with an area of 2.5 km². It is the largest of the eight saline crater lakes in the volcanic field. It is neighbouring Lake Edward, a fresh water lake and its surface level is 30 m below that of Lake Edward. Most of the tuffs associated with Lake Katwe are of mililite and leucite composition and contain abundant rounded inclusions of the underlying metamorphic and sedimentary rocks, and rare blocks of lava. Typical exposures are seen around the Lake Katwe crater where tuffs contain inclusions of amphibolite and granite gneiss. Crystals of philogopite and olivine are predominant in places. Many of these tuffs show cross bedding suggesting reworking by water. Saline springs around the edge of the lake discharge water containing from about ½ to ¼% solutes and they add about 2000 tons of salts to the lake each year. They may have been the main source of the salts in the lake. Travertine is associated with many of the springs and conspicuous mounds of this material are seen at the north-eastern end of the lake. These mounds rise 18 metres above the present shoreline and were probably formed during an earlier period of higher lake level. The chief minerals present are: halite (NaCl) which are white cubes, trona (Na₂CO₃.NaHCO₃.2H₂O) which are glassy white acicular crystals that effloresce slightly when dry, burkeite (Na₂CO₃.2Na₂SO₄) and Hanksite (Na₂SO₄.(2Na₂CO₃.KCl)); both of which are usually fine grains and often occur in mixed crusts.

Sample collection. Lake water was sampled from Lake Katwe using twenty litre plastic containers. These containers were thoroughly cleaned and rinsed several times with the lake water. The lake water samples were then taken to the laboratory with minimum contamination. In the laboratory, the water samples were stored without any treatment at room temperature until subsequent analysis was done. The total ionic strength of the lake water was determined by analysing for all the major cations and anions present in the lake, using established standard methods [11, 12]. The equation

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (1)$$

was used to calculate the ionic strength (I) of the lake water. C_i is the concentration of the ion I while Z_i is its charge, the value obtained for the ionic strength was 7.35 M.

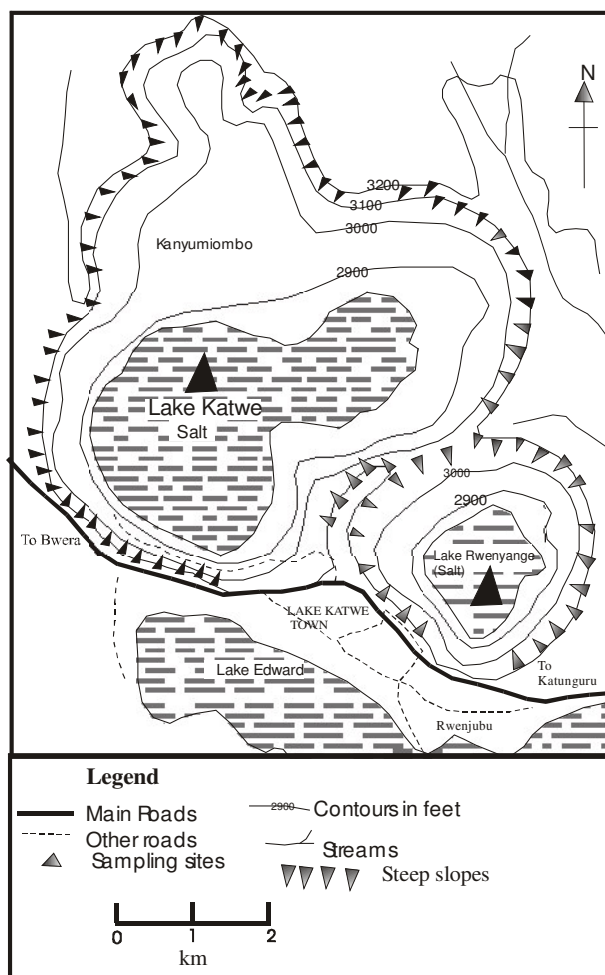


Figure 1. Map of Lake Katwe showing the sampling sites.

Instrumentation. A PAR 264A voltammetric analyser with a PAR 303A drop mercury electrode was used to obtain the voltammograms. A magnetic stirrer (EG & G Princeton applied research, Model 305) was used with accumulation step. All voltammetric measurements were obtained with a conventional 3-electrode system consisting of the dropping mercury working electrode (DME), an Ag/AgCl reference electrode and a platinum counter electrode. The differential pulse stripping mode used for all the study. All measurements were made at room temperature of 24 ± 2 °C.

Stripping procedure. A calculated portion of 0.01 M lead nitrate was pipetted into a volumetric flask so that after filling it to the mark, the concentration of the lead(II) would be 7.2×10^{-5} M. This was later to be used in the preparation of the amalgam. Also, a series of solutions with varying concentrations ($0.0 - 0.12$ M CO_3^{2-} , $0.0 - 0.18$ M Cl⁻) of the ligand to be studied was

prepared. Sodium perchlorate was used to maintain the ionic strength of 7.35 M. At the start of each run, about 6 mL of the ligand solution, the test solution, were placed into the voltammetric cell and purged with pure nitrogen for 30 seconds. The cell was then removed and covered with air-tight lids for the next stage. Another cell containing 6 mL of the 7.2×10^{-5} M of lead solution was connected, purged with nitrogen for 30 seconds, and deposition of lead onto the mercury drop was allowed to proceed for 50 seconds. After the deposition, the process was held for some time and this cell removed with care, making sure that the drop was not dislodged. The cell with the test solution was then connected and the lead stripped into the test solution. The same operation was repeated with varying concentrations of Cl^- and CO_3^{2-} separately in the solutions. The voltammograms obtained for the background, (free lead), chloro complexes, and carbonato complexes were printed out. Typical voltammograms are shown in Figures 2 and 3. The shifts in peak potentials (ΔE_p) provoked by the presence of different concentrations of the ligand were determined from these voltammograms. The method of DeFord and Hume [13] and the complementary method of Lingane [14] were used to analyse the data.

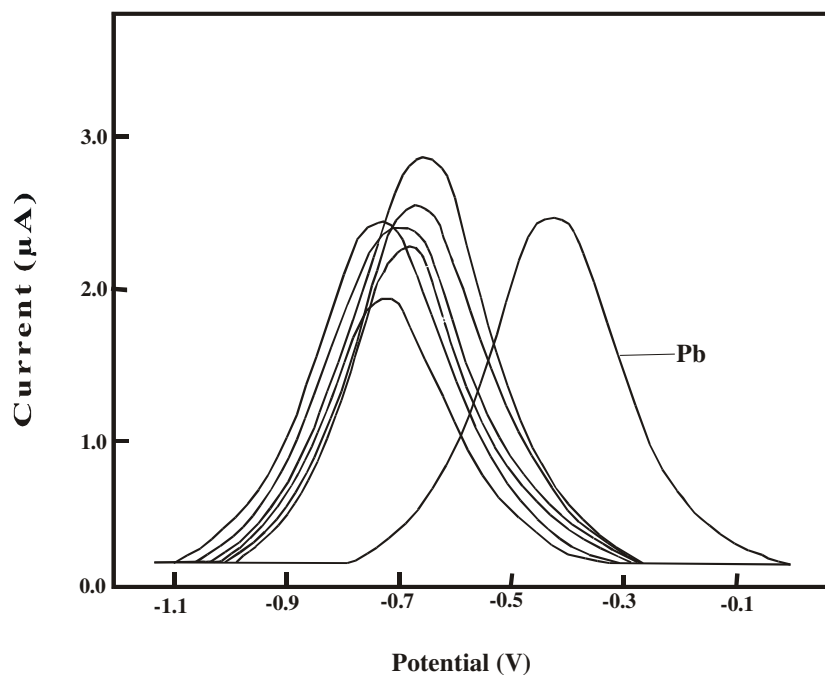


Figure 2. Differential pulse anodic stripping voltammograms of chloro complexes of lead in NaClO_4 medium.

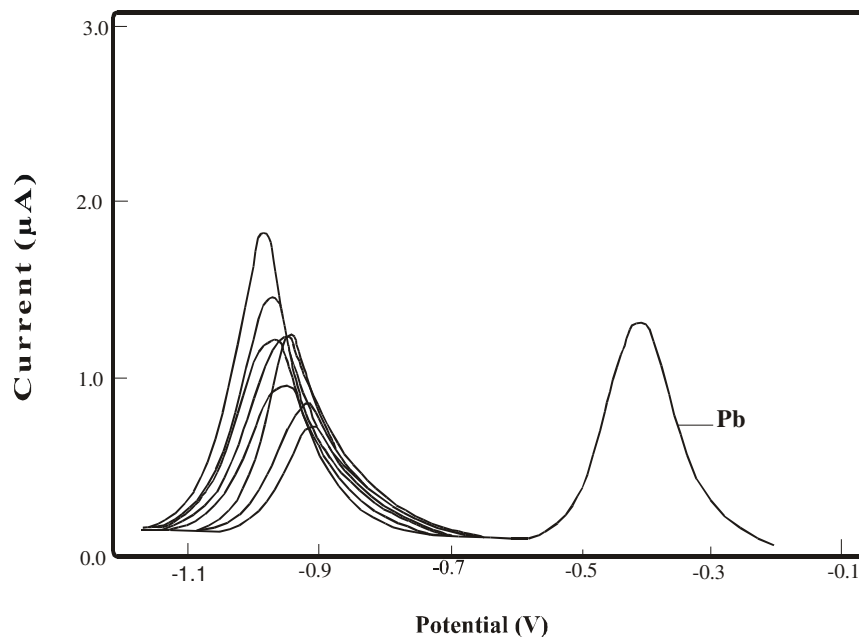


Figure 3. Differential pulse anodic stripping voltammograms of carbonato complexes of lead in NaClO_4 medium.

Calculation of F-functions. The evaluation of stability constants considers shifts in the voltammetric peak potential ($E_{p_s} - E_{p_0}$) of metal ions in the presence of complexing agent in order to provide information about the thermodynamic stability of complexes in solution [15]. For a series of metal mononuclear complexes formed in step equilibrium, a form of an equation derived by DeFord and Hume [13] is required:

$$\Delta E = \frac{RT}{nF} \ln \frac{I_c}{I_s} \sum \beta_i C_x \quad (2)$$

which by rearrangement becomes,

$$\frac{nF}{RT} \Delta E = \ln \frac{I_c}{I_s} \ln \sum \beta_i C_x \quad (3)$$

For measurements executed in solutions of the same viscosity and if the ligands are small, then I_c/I_s ratio is taken as unity, and the equation simplifies to:

$$\frac{nF}{RT} \Delta E = \ln \sum \beta_i C_x \quad (4)$$

and $\frac{nF}{RT} \Delta E_p = \log_e \sum \beta_i C_x$

$$\begin{aligned} \text{Exp} \left(\frac{nF}{RT} \Delta E_p \right) &= \exp(\log_e \Sigma \beta_i C_x) \\ \text{Exp} \left(\frac{nF}{RT} \Delta E \right) &= \exp(\ln \Sigma \beta_i C_x) \\ \therefore \text{Exp} \left(\frac{nF}{RT} \Delta E_p \right) &= \Sigma \beta_i C_x \end{aligned} \quad (5)$$

By defining exponential function in terms of an infinite series, the expression on the right hand side of the equation becomes

$$\begin{aligned} \Sigma \beta_i C_x &= \beta_0 + \beta_1 C_x + \beta_2 C_x^2 + \beta_3 C_x^3 + \dots \\ \therefore \text{Exp} \left(\frac{nF}{RT} \Delta E_p \right) &= \beta_0 + \beta_1 C_x + \beta_2 C_x^2 + \beta_3 C_x^3 + \dots \end{aligned} \quad (6)$$

The quantity on the left hand side of the equation (7) is the one that is experimentally measurable, and DeFord and Hume [13] conveniently gave it a symbol $F_0(x)$ so that

$$F_0(x) = \left(\frac{nF}{RT} \Delta E_p \right) = \beta_0 + \beta_1 C_x + \beta_2 C_x^2 + \beta_3 C_x^3 + \dots \quad (7)$$

$$F_0(x) = \beta_0 + \beta_1 C_x + \beta_2 C_x^2 + \beta_3 C_x^3 + \dots \quad (8)$$

To calculate the $F_0(x)$ values for lead, $n = 2$, $T = 295$ K, $R = 8.314$ JK⁻¹ mol⁻¹ and $F = 96486$ C mol⁻¹. This gives the ratio, nF/RT , value of 78.68. The ΔE_p values are obtained from the voltammograms of Figures 2 and 3, and the F-functions for the chloro and carbonato lead complexes evaluated.

Successive differentiation with respect to C_x reduces the equation to a constant equivalent to β , the value of the last complex. This operation gives the following expressions.

$$F_1(x) = \beta_1 + \beta_2 C_x + \beta_3 C_x^2 \quad (9)$$

$$F_2(x) = \beta_2 + \beta_3 C_x \quad (10)$$

$$F_3(x) = \beta_3 \quad (11)$$

The desired stability constant β_1 of a given species can be obtained by plotting $F_1(x)$ against C_x and extrapolating to $C_x = 0$. The value of $F_1(x)$ at the intercept is equal to β_1 . Such plots are made for each function until all the complex species are accounted for.

The penultimate graph is linear with a positive slope and for the highest complex, a straight line parallel to the concentration axis is obtained.

Calculation of species distribution. The equilibrium concentration of each species of lead was calculated using the method of Inczedy [10]. In this method the determined stability constants and the concentration of the complexing ligand are employed in the evaluation of mole fraction, ϕ . This parameter was calculated for all the species by using the following equation:

$$\phi_i = \frac{\beta_i [x]^i}{1 + \beta_1 [x] + \beta_2 [x]^2 + \beta_3 [x]^3 + \dots + \beta_n [x]^n} \quad (12)$$

where ϕ represents the mole fraction of the i^{th} complex in solution, β , the stability constant of the complex and x represents the particular concentration.

RESULTS AND DISCUSSION

The F-functions for chloro complexes obtained using DeFord and Hume relationship are shown in Table 1. The concentration range of the complexing ligand was chosen to be consistent with its solubility and extent of coordination with lead. In studying the plots of F-functions against ligand concentrations, curves were obtained for $F_0(x)$ while $F_1(x)$ gave a straight line. $F_2(x)$ gave a straight line parallel to the concentration axis. These results show that only two complexes should exist in the simulated salt lake water according to DeFord and Hume [13] relationship. The equations of the F-functions are therefore

$$F_0(x) = \beta_0 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 \quad (13)$$

$$F_1(x) = \beta_1 + \beta_2 [Cl^-] \quad (14)$$

$$F_2(x) = \beta_2 \quad (15)$$

where β_0 is the stability constant for the zero complex which is defined as one, β_1 = the stability constant for $PbCl^+$ and β_2 = the stability constant for $PbCl_2^0$.

In the investigation of carbonato lead complexes two complexes were found to exist in the simulated salt lake water as indicated by stability constants in Table 2.

Table 1. F-functions of lead chloride complexes in $NaClO_4$ medium by DPASV.

[Cl ⁻] (M)	I _p (μ A)	E _p (-) V	ΔE_p	F ₀ (x)	F ₁ (x)	F ₂ (x)
0.00	8.941	0.5373	0.0000	1.00	-	-
0.02	3.572	0.5421	0.0048	1.45	22.67	758.3
0.04	2.575	0.5505	0.0132	2.80	44.67	934.8
0.06	2.555	0.5571	0.0198	4.67	61.24	895.7
0.08	2.323	0.5631	0.0258	7.46	80.74	915.4
0.10	3.506	0.5557	0.0284	4.19	31.92	244.2
0.12	2.389	0.5596	0.0316	5.68	38.99	262.4
0.14	2.555	0.5689	0.0413	11.72	76.56	575.5
0.16	2.262	0.5786	0.0465	24.94	149.64	888.4
0.18	1.912	0.5838		37.40	202.21	1081.7
Stability constants			$\beta_0 = 1.00$	$\beta_1 = 7.50$	$\beta_2 = 9.00$	

Table 2. F-function of lead carbonate complexes in NaClO₄ medium by DPASV.

[CO ₃ ²⁻] M	I _p (μA)	E _p (-) V	ΔE _p	F ₀ (x)	F ₁ (x)
0.000	3.711	0.6505	0.0000	1.00	9.41 x 10 ⁸
0.015	1.709	0.8619	0.2114	1.41x10 ⁷	8.49 x 10 ⁸
0.030	2.262	0.8694	0.2189	1.55 x 10 ⁷	5.05 x 10 ⁸
0.045	1.753	0.8680	0.2175	2.27 x 10 ⁷	6.21 x 10 ⁸
0.060	1.899	0.8743	0.2238	3.73 x 10 ⁷	7.99 x 10 ⁸
0.075	2.995	0.8804	0.2299	5.99 x 10 ⁷	6.92 x 10 ⁸
0.090	2.919	0.8809	0.2204	6.23 x 10 ⁷	7.60 x 10 ⁸
0.105	3.086	0.8841	0.2336	7.98 x 10 ⁷	8.04 x 10 ⁸
0.120	2.577	0.8866	0.2361	9.65 x 10 ⁷	8.04x10 ⁸
Stability constants		β ₀ = 1.00	β ₁ = 3.15 x 10 ⁸	β ₂ = 4.20 x 10 ⁹	

The plot of F₀(x) against the concentration of carbonate gave a curve whereas for F₁(x) was a straight line. For the plot of F₁(x) gave a straight line parallel to the concentration axis. The results shown indicate that two lead carbonate species exist in the simulated salt lake water. The equations of the F-functions are as follows:

$$F_0(x) = \beta_0 + \beta_1 [\text{CO}_3^{2-}] + \beta_2 [\text{CO}_3^{2-}]^2 \quad (16)$$

$$F_1(x) = \beta_1 + \beta_2 [\text{CO}_3^{2-}] \quad (17)$$

$$F_2(x) = \beta_2 \quad (18)$$

where β₀ = the stability constant for the zero complex and is given the value one, β₁ = the stability constant for PbCO₃⁰ and β₂ = the stability constant for Pb(CO₃)₂²⁻.

Table 3 and 4 give the summary of species distribution of lead as a function of ligand concentration of chloride and carbonate, respectively. In the tables, it is clear that at zero ligand concentration, all the lead exists as simple lead aquo species. As the concentration of the ligand increases, the Pb²⁺ concentration diminishes towards zero. At low ligand concentration, low order complexes will dominate except for PbCl⁺ while higher order complexes become more significant at higher ligand concentration.

Table 3. The equilibrium distribution of lead species in the lead-chloride system as a function of ligand concentration in NaClO₄ medium.

[Cl ⁻]	% Pb ²⁺	% PbCl ⁺	% PbCl ₂ ⁻
0.00	100.00	0.00	0.00
0.01	48.07	7.81	44.11
0.04	20.02	6.51	73.48
0.06	10.26	5.00	84.74
0.08	6.12	3.98	89.90
0.10	4.04	3.28	92.68
0.12	2.86	2.79	94.36
0.14	2.12	2.42	95.46
0.16	1.64	2.13	96.23
0.18	1.30	1.90	96.79

Table 4. The equilibrium distribution of lead species in the lead-carbonate system as a function of ligand concentration in NaClO₄ medium.

[CO ₃ ²⁻]	% Pb ²⁺	% PbCO ₃ ⁰	% Pb(CO ₃) ₂ ²⁻
0.00	100.00	0.00	0.00
0.015	0.00	58.00	42.00
0.030	0.00	40.84	59.16
0.045	0.00	31.52	68.48
0.060	0.00	25.66	74.34
0.075	0.00	21.64	78.36
0.090	0.00	18.71	81.29
0.105	0.00	16.48	83.52

There has been little agreement between different workers that have dealt with the lead(II) chloride systems. Some have suggested that only two chloro complexes can exist in aqueous medium while others have insisted on the formation of three chloro complexes [8]. In this study, only two chloro complexes were identified. For the case of carbonato complexes, there is a general agreement that only two complexes do exist in the aqueous medium. Our study has also confirmed this. It is possible that the discrepancy with the number of chloro complexes formed may be due to the difference in ionic strength of the medium. This is supported by the work of Nasasen [16] who studied the stability of the mixed copper complexes of 1,2-diaminopropane and 5-sulphosalicylic acid in aqueous sodium perchlorate solution at different ionic strength (from I = 0 to I = 2.0).

CONCLUSION

Metal speciation is now well established in many areas of chemistry. Although a lot has been achieved in terms of increasing our knowledge of the behaviour of some elements in aquatic environment, much still needs to be done. The chemistry of Lake Katwe can now be re-addressed to provide more insight into the mobility of metals that do exist in the lake and those that enter it through pollution processes, and how these pathways link up with the bioavailability of the metals, bioaccumulation and possible toxicity.

At the forefront of such developments is the analytical chemist who must find new methods and techniques of isolating the metal species from the complex Lake Katwe water and further develop analytical procedures to perform both qualitative and quantitative analysis at lower levels. Thus the whole area of speciation continues to provide an exciting and challenging arena for research in the future.

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