net change of concentration occurring during the relaxation process in the system of (3A). By use of the conservation and equilibrium equations, the rate law (4A) can be derived:

$$-\frac{d\delta}{dt} = \left[k_1\left(-\frac{\delta_{M,L}}{\delta_{ML}} \right) + k_{-1} \right]\delta \qquad (4A)$$

where

$$-\delta_{M,L}/\delta_{ML} = [K_{os}(|M| + |L|) + K_{os}K_2|M|^2|L|]/[1 + K_{os}(|M| + |L|) + K_2|M|^2 + 2K_2|M||L| + K_{os}K_2|M|^2|L|] \qquad (5A)$$

Being under the conditions of this work, $K_{os}K_2|M|^2|L| << K_{os}(|M| + |L|)$ and $2K_2|M||L| + K_{os}K_2|M|^2|L| << 1 + K_{os}(|M| + |L|) + K_2|M|^2$, eq 5A is reduced to (6A). Introduction of (6A) into (4A) and subsequent integration yield the relationship (8).

$$-\frac{\delta_{M,L}}{\delta_{ML}} = \frac{K_{os}(|M|+ |L|)}{1 + K_{os}(|M| + |L|) + K_2|M|^2} \qquad (6A)$$

Registry No. Fe, 7439-89-6; $Fe(CN)_6^{3-}$, 13408-62-3; $Co(CN)_6^{3-}$, 14897-04-2; $Mo(CN)_8^{4-}$, 17923-49-8.

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Complexation Kinetics of Copper(II) with the Cryptand (2,2,1) in Dimethyl Sulfoxide

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The complexation kinetics of the cryptand (2,2,1), a macrobicyclic diaza polyether, with Cu^{2+} have been measured in dimethyl sulfoxide (Me_2SO) with stopped-flow methods. This system is one of a few cryptate systems where not only the rate constant of dissociation but also the rate constant of complex formation can be determined independently. The ratio of the rate constants for $Cu(2,2,1)^{2+}$ is found to be in agreement with the stability constant measured by calorimetric titration. As a result of the strong solvation of Cu^{2+} by Me_2SO, the formation rate constant is strikingly small, its value being unparalleled by those of other cryptand complexes. The thermodynamic quantities of the copper complex suggest that (2,2,1) forms with Cu^{2+} an inclusion complex. The changes of the dissociation rate and of the stability constant with temperature have also been studied, and activation parameters have been derived from the experimental data.

Introduction

The selective complexation of alkali- and alkaline-earth metal ions by polyether crown and cryptand molecules has been studied extensively,[2-5] and kinetic aspects of such complexation processes have also received increasing interest.[6-9] This is partly attributable to the fact that the complexes are considered as model systems for metal ion transportation in biological systems.[10,11] However, transition-metal ion complexation has been studied predominantly with open-chain and macrocyclic tetraaza and higher polyaza ligands.[12,13] These complexes are extraordinarily stable and can be regarded as simple models for naturally occurring structures found in proteins.[14] Replacement of the nitrogen-binding sites by oxygen sites decreases the stability of corresponding transition-metal ion complexes considerably.[15-17] Therefore, in only a few studies the complex formation of transition-metal ions with cryptands (2,1,1), (2,2,1), and (2,2,2) has been determined in water and in methanol. To our knowledge the present paper reports the first kinetic study on transition-metal ion complexation with a cryptand molecule in a nonaqueous solvent. Because of serious interference by hydrolysis of transition-metal ions in aqueous cryptand solutions, we have measured the rate constants for the formation and dissociation of $Cu(2,2,1)^{2+}$ in dimethyl sulfoxide (Me_2SO).

Table I. Stability Constant (log K_c) and Heat and Entropy of Complex Formation for $Cu(2,2,1)^{2+}$ in Me_2SO from Calorimetry and Activation Enthalpy and Entropy for the Cryptate Dissociation Reaction, Also at 25 °C

log K_c	ΔH_c, kJ mol^{-1}	ΔS_c, J K^{-1} mol^{-1}	$\Delta H_d^{\ddagger}$, kJ mol^{-1}	$\Delta S_d^{\ddagger}$, J K^{-1} mol^{-1}
2.7 ± 0.1	−17.9 ± 2.1	−8.4 ± 9.1	49.9 ± 4.2	−99 ± 17

Experimental Section and Results

(a) Materials. Cryptand (2,2,1) was purchased from Merck and used without further purification. Its purity of 98% given by Merck

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(1) (a) University of Stirling. (b) Max-Planck-Institut für Biophysikalische Chemie.

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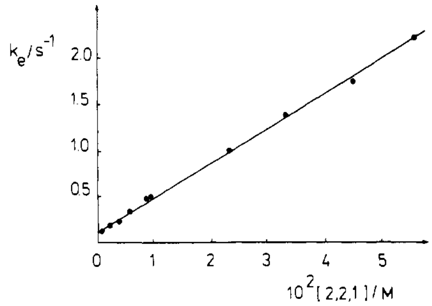

Figure 1. Dependence of the rates of reaction between Cu^{2+} and (2,2,1) upon the free cryptand concentration in Me_2SO at 25 °C.

has been checked by pH metric, conductometric, and NMR methods.

$Cu(Me_2SO)_4(ClO_4)_2$ was prepared from $Cu(ClO_4)_2 \cdot 6H_2O$ (Ventron) following the procedure from van Leeuwen and Groneveld.[18] After being dried under vacuum over P_4O_{10} at 50 °C for 48 h, the copper(II)–Me_2SO salt was dissolved in Me_2SO and kept as a stock solution. The concentration of Cu^{2+} was determined by complexometric titration with EDTA. Dimethyl sulfoxide (Merck, p.a.) was dried over molecular sieves (4 Å) for several days and then fractionally distilled under nitrogen at 3 torr. The water content was checked by Karl-Fischer titration and was found to be always less than 50 ppm.

Methanesulfonic acid (Fluka 99%) was used without further purification. $NaClO_4$ (anhydrous) was purchased from Alfa and was dried under vacuum for 48 h at 60 °C before used.

(b) Stability Constant Measurements. The stability constant for $Cu(2,2,1)^{2+}$ in Me_2SO (eq 1) was obtained by calorimetric titration

$$K_c = [Cu(2,2,1)^{2+}]/[Cu^{2+}][(2,2,1)] \qquad (1)$$

experiments, with a Tronac Model 450 calorimeter. In each experimental run, a cryptand solution (ca. 7.5 × 10^{-2} M) was added to a solution of copper(II) perchlorate (ca. 5 × 10^{-3} M), with an automatic burette (2.5-mL Tronac). The heat of dilution of the ligand was found to be negligible. The heats of complexation ΔH_c and also the stability constant K_c were calculated with a procedure of Eatough et al.[19] The data are listed in Table I.

(c) Kinetic Measurements. Those reactions which were followed by optical detection were measured in an all-glass stopped-flow unit manufactured by Tecquipment. The change in absorbance was monitored with photo diodes (Optronic OS-1). When changes in conductance were used to follow the progress of a reaction, a home-built stopped flow was employed, together with facilities for automatic data collection and processing.

Rate of Complex Formation. Since the $Cu(2,2,1)^{2+}$ complex has a relatively small stability constant in Me_2SO, the complex is only incompletely formed at ordinary concentrations of Cu^{2+} and (2,2,1). In the rate experiments the concentration of (2,2,1) ranged between 8 × 10^{-4} M and 5 × 10^{-2} M. When a more than 10-fold excess of (2,2,1) was mixed with the copper(II) solution, reaction 2 reduces

$$Cu^{2+} + (2,2,1) \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Cu(2,2,1)^{2+} \qquad (2)$$

to a pseudo-first-order type of reaction. The experimental rate constant is therefore a linear function of ligand concentration as shown in eq 3. The reaction was monitored at 800 nm, near the end of the

$$k_e = k_d + k_f[(2,2,1)] \qquad (3)$$

wavelength range of the monochromator (Bausch and Lomb, Type 338676) used. Since the uncomplexed ligand has no absorption at this wavelength and the absorption of the cryptate is much more intense than that of solvated Cu^{2+}, with a broad maximum around 840 nm, the change in optical density during the progress of reaction was attributed entirely to the formation of $Cu(2,2,1)^{2+}$.

The experimental rate constants k_e are plotted in Figure 1 vs. the actual concentration [(2,2,1)] of the free cryptand and follow eq 3.

Table II. Rate Constants of Dissociation and Formation of $Cu(2,2,1)^{2+}$ in Me_2SO at 25 °C and the Stability Constant (log K_c) Calculated from Eq 4

k_d/s^{-1}	$k_f/M^{-1}\ s^{-1}$	log K_s	type of reaction
0.11 ± 0.02	37.0 ± 0.6	2.5 ± 0.2	$Cu^{2+} + (2,2,1) \rightarrow$
0.08 ± 0.02	40.1[a]		$Cu(2,2,1)^{2+} + Na^+ \rightarrow$, (50 ppm H_2O)
0.07			$Cu(2,2,1)^{2+} + Na^+ \rightarrow$, (extrapolated to O ppm H_2O)
0.08 ± 0.02	40.1[a]		$Cu(2,2,1) + 2CH_3SO_3H \rightarrow$

[a] Calculated, $k_f = K_c k_d$, with log K_c = 2.7 (Table I).

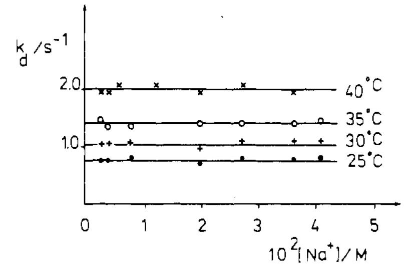

Figure 2. Dependence of the rates of dissociation of $Cu(2,2,1)^{2+}$ upon $NaClO_4$ concentration in Me_2SO.

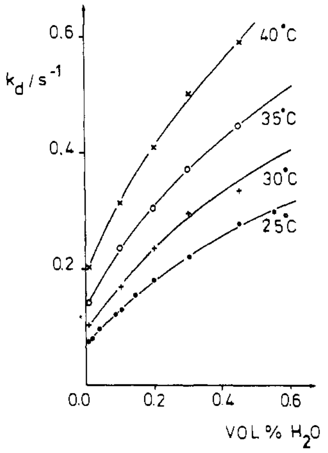

Figure 3. Water dependence of the rates of dissociation of $Cu(2,2,1)^{2+}$ in Me_2SO in the reaction $Cu(2,2,1)^{2+} + Na^+ \rightarrow Cu^{2+} + Na(2,2,1)^+$.

The rate constants of dissociation (intercept) and of formation (slope) are listed in Table II together with the stability constant K_s calculated from the rate constants (eq 4). Experimental uncertainties in k_e have

$$K_s = k_f/k_d \qquad (4)$$

a much larger effect in percentage terms on the dissociation rate constant, k_d, than the rate constant of formation, k_f, because of the small intercept in Figure 1. Therefore, only the k_f values obtained from these experiments have been accepted as reliable.

In a large number of preliminary experiments it was found that the results obtained from these measurements were very sensitive to the residual water content of the Me_2SO. Only in solutions with less than 50 ppm water were the effects on k_d and k_f negligibly small.

Rates of Complex Dissociation. So that a more accurate value for k_d could be obtained, the dissociation rate was measured as a pseudo-first-order type of reaction by mixing $Cu(2,2,1)^{2+}$ solutions with those containing an excess of either $NaClO_4$ or methanesulfonic acid. The observed rate constant k of reaction 5, was obtained from

$$Cu(2,2,1)^{2+} + Na^+ \xrightarrow{k} Na(2,2,1)^{2+} + Cu^{2+} \qquad (5)$$

spectrophotometric measurements at 800 nm. It was found to be independent of the Na^+ concentration at temperatures between 25 and 40 °C (Figure 2) and was therefore identified with the dissociation rate constant k_d for $Cu(2,2,1)^{2+}$. ln k_d is linearly dependent upon $1/T$, and the enthalpy and entropy of activation are listed in Table I. The value of k_d at 25 °C may be taken together with the stability constant determined by calorimetry to calculate the formation rate

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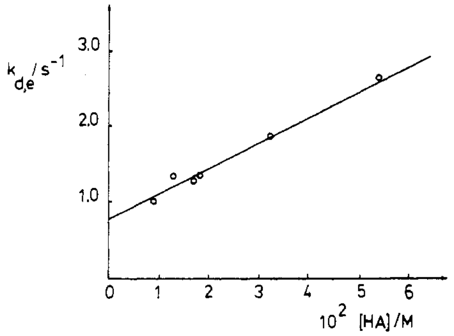

Figure 4. Dependence of the rates of dissociation of $Cu(2,2,1)^{2+}$ upon the actual concentration of undissociated methanesulfonic acid in Me_2SO at 25 °C.

constant. The data in Table II show a good agreement between calculated and experimental k_f values.

The system was also carefully studied to examine the effect of residual water in the solutions on the observed dissociation rates. It was found that the dissociation rate is strongly enhanced by increases in the amount of water up to 0.3 M. The variation of k_d with water concentration and temperature is shown in Figure 3.

The dissociation rate at 25 °C was also checked by using methanesulfonic acid as a general acid scavenger. In earlier studies[9,20,21] it was shown that the dissociation rate may be conveniently measured by following the conductance change when an excess of acid is added to an equilibrium cation–cryptand mixture. The observed rates for the reaction (eq 6) were found to be linearly dependent upon the free

$$Cu(2,2,1)^{2+} + 2HA \xrightarrow{k_{d,e}} (2,2,1)H_2^{2+} + 2A^- \qquad (6)$$

acid concentration (due allowance being made for the slight decrease in [HA] occurring during the reaction). Since methanesulfonic acid is only incompletely dissociated in Me_2SO, pK = 1.56 at 298 K,[22] the concentration of ions, and hence the conductance, increases when the cryptand is protonated. Metal ion concentrations used were ca. 5×10^{-3} M–10^{-2} M and those of [(2,2,1)] ca. 5×10^{-4} M–5×10^{-3} M. The excess of acid with respect to (2,2,1) was always more than 10-fold. Since the observed rates were found to be dependent upon the total acid concentration, the experimental $k_{d,e}$ values were plotted against the actual [H^+] as well as against the concentration of undissociated methanesulfonic acid (always corrected for the portion of doubly protonated cryptand). Only the plot of $k_{d,e}$ vs. concentration of undissociated acid (Figure 4, eq 7) shows a nice linear dependence

$$k_{d,e} = k_d + k_{HA}[CH_3SO_3H] \qquad (7)$$

with an acid catalysis constant k_{HA} of 34.2 M^{-1} s^{-1}. This behavior contrasts with that of the alkali-metal cryptates in Me_2SO, where dissociation rates show no catalysis by protons or general acids.[9]

Discussion

It is difficult to pressent a detailed discussion of the results for $Cu(2,2,1)^{2+}$ at this stage because of the lack of comparative results for other systems. Thus there are no other data reported for copper(II) cryptates in Me_2SO or other polar aprotic solvents. This paper gives for the first time a rate constant for copper(II) cryptate formation. Similarly, a comparison with stabilities and rate constants for other doubly charged metal ion cryptates is restricted because of the relatively few experimental studies published[2,4,6,8,9] and also because Mg^{2+}, which is almost the same size as Cu^{2+}, is the least studied of the alkaline-earth cations. Therefore, only preliminary conclusion may be drawn from our results. However, because the formation and dissociation rates have been measured independently, it is possible to compare their quotient with the experimental value of the stability constant.

Table III. Gibbs Energies of Transfer from Water to Me_2SO for Metal Ions and Their Complexes with (2,2,1)

M^{z+}	$\Delta G_{tr}(M^{z+})$, kJ mol^{-1}	$\Delta G_{tr}(M(2,2,1)^{z+})$, kJ mol^{-1}
Li^+	−14.6	−14.0
Na^+	−13.8	−20.3
Cu^{2+}	−41.0	−11.2

Arnaud-Neu et al.[23] and Spiess et al.[24] in thorough investigations have determined, among other systems, the stabilities of Cu^{2+} complexes with several cryptands, including (2,2,1), in water and methanol. The stability constants, K_s, vary only between 3.63×10^7 M^{-1} and 1.20×10^{10} M^{-1} for the various ligands. By contrast, the corresponding values for the alkaline-earth metal ion complexes in water and 95 wt % methanol/water vary over at least 10 orders of magnitude and show a pronounced maximum when the cavity diameter of the ligand and the ionic radii of the metal ions are nearly equal.[3] As the characteristic behavior associated with the optimal fit requirement, which has been suggested to follow mainly from electrostatic interactions between the cation and the binding sites of the ligand,[2] is absent for the copper(II) cryptates, the interactions involved between Cu^{2+} and the cryptand binding sites must be mainly nonelectrostatic in nature.

Some information on whether Cu^{2+} forms an exclusive complex[25] because of the special type of bonding or an inclusive complex can be gained from a comparison of the solvent dependence of the stabilities of $Cu(2,2,1)^{2+}$ with those of other cations. The Gibbs energy of transfer, ΔG_{tr}, for $Cu(2,2,1)^{2+}$ from water to Me_2SO has been calculated from eq 8 with use

$$\Delta G_{tr}(M(2,2,1)^{2+}) = \Delta G_{tr}(M^{2+}) + \Delta G_{tr}(2,2,1) - RT \ln \frac{K_s(Me_2SO)}{K_s(H_2O)} \qquad (8)$$

of the stability constants of the cryptate in water[23] and in Me_2SO and the Gibbs transfer energy for Cu^{2+}.[26] $\Delta G_{tr}(2,2,1)$ is known only for transfer between water and methanol, but this value, ΔG_{tr} = 2.1 kJ mol, has been previously used successfully to interpret the results for alkali-metal ion cryptates in aprotic solvents[4] and is also used in this work. The result for $\Delta G_{tr}(Cu(2,2,1)^{2+})$, together with those for $Li(2,2,1)^+$ and $Na(2,2,1)^+$,[9,27] are listed in Table III. Although it should be noted that the differences between Cu^{2+} and the M^+ values depend on an extrathermodynamic assumption,[26] they are obviously larger than the differences between ΔG_{tr} values for the cryptates, which indicates a similarity in the solvation of the cryptates. Therefore, one may propose that Cu^{2+} forms an inclusion complex with (2,2,1) since (2,2,1) forms inclusion complexes with Li^+ and Na^+, which has been proved most directly by Popov[28,29] from ^7Li and ^{23}Na NMR experiments. The low formation rate of $Cu(2,2,1)^{2+}$ is also strongly indicative of an inclusion complex.

The dissociation rate of $Cu(2,2,1)^{2+}$, with k_d = 0.08 s^{-1}, is not particularly unusual. Thus k_d for $Ca(2,2,1)^{2+}$ in dimethylformamide is a factor of 100 smaller, and k_d of Na-

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(2,2,1)$^+$ in Me$_2$SO is a factor of 10 larger than that of Cu(2,2,1)$^{2+}$.[9] However, the formation rate of Cu(2,2,1)$^{2+}$ is much lower than that of either of the two aforementioned cryptates: k_f of Cu(2,2,1)$^{2+}$ is 100 times smaller than k_f of the corresponding Ca^{2+} cryptate in DMF and 2×10^5 times below k_f of Na(2,2,1)$^+$ in Me$_2$SO. This is due to the very strong solvation of Cu^{2+} by Me$_2$SO.[26] The low value of the formation rate constant of Cu(2,2,1)$^{2+}$ is more similar to k_f values for the formation of Na^{2+} complexes with tetraaza ligands,[12] that also form extremely stable Cu^{2+} complexes, than to corresponding values for N$_2$O$_2$-type ligands, where no axial arrangement of nitrogen atoms is present. The rates of formation of Cu^{2+} complexes with these latter ligands have been studied by Adam et al.,[15] and k_f is always $>10^5$ M^{-1} s^{-1} in 95 wt % methanol/water. It is probably premature to explain the small formation rate constant for Cu(2,2,1)$^{2+}$ in Me$_2$SO as a result of Jahn–Teller distortions being effective in one or more of the several intermediate steps in cryptate formation, when solvent molecules in the ionic solvation shell have to be replaced continuously by binding groups in the cryptand.

The dissociation rate constant of Cu(2,2,1)$^{2+}$ is strongly dependent upon the water content of the solvent (Figure 3). The dependence upon water concentration is nonlinear, and it is difficult to propose a simple explanation for this behavior. It is possible that an interaction between the water protons and the donor atoms of the ligand is involved.

The activation enthalpies and entropies of dissociation and of formation of Cu(2,2,1)$^{2+}$ can only be compared with the corresponding quantities for alkaline-earth metal ion cryptates in water[6] because of lack of further data. From such a comparison it may be seen that only the activation entropy of formation of Cu(2,2,1)$^{2+}$ ($\Delta S_f^{\ddagger} = -107$ J K^{-1} mol^{-1}) is outside the range found for alkaline-earth cryptates. The most negative $\Delta S_f^{\ddagger}$ of these is that of Ca(2,2,2)$^{2+}$, which is only half as large as that for the copper(II) complex.

Registry No. (2,2,1), 31364-42-8; Cu, 7440-50-8; Cu(2,2,1)$^{2+}$, 80890-31-9.

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Reactions in Detergentless Microemulsions: Incorporation of Copper(II) into *meso*-Tetraphenylporphine ((TPP)H$_2$) in a Water/Oil Microemulsion

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The rate of incorporation of Cu(II) into tetraphenylporphine has been followed in ternary solvent systems consisting of water, toluene, and 2-propanol. Studies carried out in microemulsions at pH 3 show that when the surfactants hexadecyltrimethylammonium perchlorate and hexadecylpyridinium perchlorate are added, little or no change in rate from that observed in detergent-free systems occurs. When the surfactant anion is Cl$^-$ or Br$^-$, there is a marked increase in rate (ClO$_4^-$ $\ll$ Cl$^-$ $<$ Br$^-$). Addition of the anionic surfactant sodium hexadecyl sulfate and the nonionic Alfonic 1412-60 has little effect on the rate of reaction. A study of the rate of metalation as a function of solvent composition shows an increase in rate in the small-aggregate and normal ternary solution regions.

Introduction

Microemulsions are a unique class of quaternary solutions prepared from water, hydrocarbon, surfactant, and cosurfactant (usually a short-chain alcohol).[2] They are clear, thermodynamically stable solutions consisting of small droplets of one phase dispersed throughout a second phase. The diameter of these droplets may range from 50 to approximately 1000 Å. The core of the dispersed droplet, which possesses bulk-solvent character, is surrounded by an interphase, which consists of the surfactant and cosurfactant.[3] If the dispersed phase is water and the continuous phase is the hydrocarbon (i.e., a W/O microemulsion), a layer of water molecules at the interphase will be hydrogen bonded to the polar head groups of the surfactant and molecules of the continuous external phase will be found between the hydrophobic tails of the surfactant molecules.[4]

Because of their unique structure, microemulsions exhibit unusual solvation properties. They possess the ability to dissolve a wide variety of water-insoluble organic reagents and water-soluble inorganic salts.[2] As a consequence, they have great potential for utilization in chemical reactions that presently require expensive polar solvents (e.g. DMF, Me$_2$SO), phase-transfer catalysts, or formation of micelles.[5-8]

There is a group of ternary solutions that has also been labeled microemulsions. These systems are prepared from water, hydrocarbon, and 2-propanol but do not require the addition of a "classical" surfactant in order to bring about a stable dispersion.[9] Ultracentrifugation data, ^{1}H and ^{13}C NMR spectroscopy, and light-scattering measurements have tended to support the designation of these ternary solutions as microemulsions.[9-11] In addition, an investigation of the base hydrolysis of a variety of alkyl esters[12] has provided additional supportive data as have preliminary investigations on the rate of metalation of *meso*-tetraphenylporphine.[13]

Detergentless microemulsions possess tremendous potential importance as media for chemical reactions. As with the surfactant-containing systems they have the ability to dissolve both hydrophobic and hydrophilic reagents, possess enormous interphase area, can be prepared from inexpensive solvents, and in contrast to the surfactant-containing systems, require no long-chain amphiphile, which is difficult to remove in the

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