BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1857—1861 (1967)

Spectrophotometric Study of the Solution Equilibria between Eriochrom Black T and Zinc(II)-Nitrilotriacetate or Copper(II)-Cyclohexanediaminetetraacetate

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(Received February 6, 1967)

The solution equilibria between Eriochrom Black T (BT) and the zinc(II)-NTA or copper(II)-CyDTA chelate were studied spectrophotometrically, and the stability constants and the compositions of 1-to-1 chelates of BT with these metal ions were determined. Under the experimental conditions employed, irrespective of pH, copper(II) forms only a normal chelate, CuD^-, with BT, the stability constant of which is $10^{21.98}(\mu=0.10)$. Zinc(II), however, forms a normal chelate, ZnD^-, at pH values lower than 9.00 and a mixed chelate, $ZnDX^{4-}$, with BT and NTA at pH values higher than 9.00. The stability constant for ZnD^- was determined to be $10^{12.76}$ ($\mu=0.10$) at pH 8.50, in good agreement with the value reported by Schwarzenbach, and that for $ZnDX^{4-}$, $10^{15.38}$ ($\mu=0.10$).

o, *o*'-Dihydroxyazo dye Eriochrom Black T (BT) has the property of forming metal chelates with colors different from those of the dye itself in the pH range from 8.00 to 10.50. Because of this sharp color transition, it is useful as an indicator in the chelatometric titrations of metal ions, such as magnesium(II)[1] and zinc(II)[2], with ethylenediaminetetraacetic acid (EDTA).

Systematic and quantitative treatments of the chelate formation reaction of BT with magnesium(II),[3,4] calcium(II),[3,4] barium(II),[5] and zinc(II)[6] ions have been made. However, no report on the chelate formation reaction of other metals has been published.

Therefore, it seemed that it would be worthwhile to study the complexation reaction of BT with metal ions other than magnesium(II), calcium(II), barium(II) and zinc(II) ions from the viewpoints of both analytical and coordination chemistry. The present report will be concerned with a spectrophotometric study of the solution equilibria between BT and zinc(II)-NTA or copper(II)-CyDTA chelates and with the determination of the compositions and the stability constants of 1-to-1 chelates of BT with zinc(II) and copper(II).

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Experimental

Apparatus. All the absorption spectra were measured with a Hitachi EPS-3 recording spectrophotometer, using a pair of 1 cm quartz cells at room temperature (20°C). Certain individual absorption measurements were made by mannual operations. All the pH measurements were conducted using a Hitachi-Horiba M-4 pH meter, equipped with a 1026-05 type glass electrode. The pH of the sample solution was adjusted to the desired value just prior to all the measurements by adding perchloric acid or a sodium hydroxide solution.

Reagents. Commercial Eriochrom Black T (1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid sodium salt) was purified by employing the procedure described by Diehl and Lindstrom.[4]

The molar extinction coefficient of the purified dye, which was obtained as crystalline dimethylammonium salt, was found to be 32200 at 615 mμ, the maximum, in the solution of pH 10.0, indicating no contamination.

The standard solution of zinc(II) and copper(II) were prepared by the following procedure. A suitable amount of sodium hydroxide was added to metal sulfate solutions to precipitate metal ions as hydroxides. The precipitates were then filtered off and washed thoroughly with redistilled water. The resulting metal hydroxide was dissolved in a diluted perchloric acid solution to prepare a standard metal perchlorate solution of an appropriate concentration. The concentrations of metal ions were then determined by titration with a standard EDTA solution.[1,2]

Nitrilotriacetic acid (NTA) and cyclohexanediaminetetraacetic acid (CyDTA) recrystallized from a hydrochloric acid solution were used. The concentration of the NTA solution was checked by titration with a standard nickel(II) solution, using murexide as an indicator.[7] The solution of CyDTA was standardized against pure metallic zinc(Kahlbaum).

All the other chemicals used were of analytical reagent grade. Redistilled water was used to dilute the stock solutions and to prepare the sample solution.

All the absorption and pH measurements were conducted on solutions of a constant ionic strength (μ= 0.30) by adding an appropriate quantity of a sodium perchlorate solution. All the dye solutions were prepared using crystalline dimethylammonium salt; they were measured within 2 hr of their preparation. In all cases, measurements were made against a solution containing the same amount of metal clelate of NTA or CyDTA as the blank solution. In the present study, no other buffer reagent was used, because a solution containing free NTA or CyDTA may be expected to have sufficient buffer capacity to maintain the pH value of the solution constant in the pH region from 8.50 to 10.0.

Results and Discussion

The dye is red in solutions with pH values lower than 8.0, and orange in solutions with pH values higher than 10.5. In the pH range from 8.0 to 10.5, it is blue, and the maximum of its absorption spectrum in the visible region is located at 615 mμ. These findings are in agreement with those of Ringbom[5] and Diehl.[4]

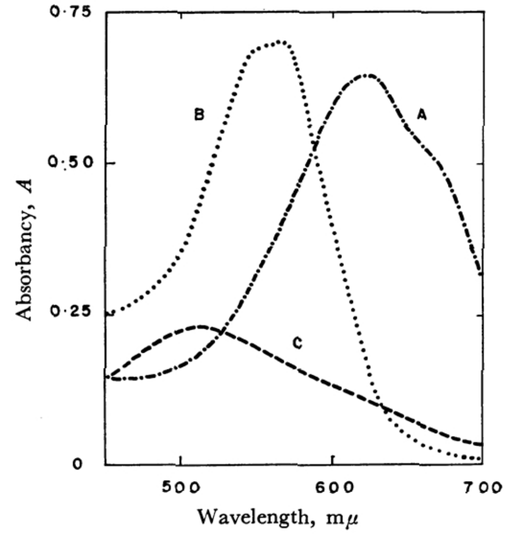

Fig. 1. Absorption curves.
A 2.00×10^{-5} M BT, 1.00×10^{-2} M EDTA, μ=0.30, pH=9.50
B 2.00×10^{-5} M BT, 2.50×10^{-2} M NTA, pH=8.50; 2.00×10^{-2} M Zn(II), μ=0.30
C 2.00×10^{-5} M BT, 2.50×10^{-2} M CyDTA, pH=10.0; 2.05×10^{-2} M Cu(II), μ=0.30

The color change of the dye from red to blue is considered to be connected with the ionization of one of the two phenolic OH groups, while that from blue to orange at pH values higher than 10.5 corresponds to the ionization of the second group. BT has been reported to form stable chelates with zinc(II)[3] and copper(II).[8] The absorption spectra of zinc(II) and copper(II) chelates of BT are shown in Fig. 1. As may be seen from the curves in Fig. 1, the shape of the absorption spectrum of the zinc(II)-BT chelate is similar to that of the magnesium(II)-BT chelate,[9] but the absorption srecturm of the copper(II)-BT chelate has a quite different shape.

In a solution containing another chelating agent, such as NTA or CyDTA, a complexation reaction of BT with those metal ions can not proceed completely. The fraction of the BT chelate formed depends on the concentrations of uncomplexed and complexed chelating agents and on the pH value of the solution. The absorption spectra in Fig. 2 clearly indicate that the fraction of the zinc(II)-BT chelate increases with an increase in the concentration ratio of the zinc(II)-NTA chelate to free NTA. A similar finding has been found for

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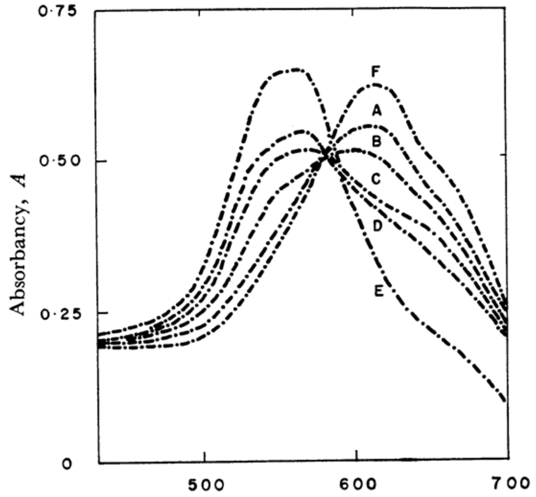

Fig. 2. The effect of the concentration of zinc(II) on the absorption curve of BT.
1.95×10^{-5} M BT, 2.50×10^{-2} M NTA, $\mu=0.30$
pH=8.50

A	2.50×10^{-3} M Zn(II)
B	5.00×10^{-3} M Zn(II)
C	7.50×10^{-3} M Zn(II)
D	1.00×10^{-2} M Zn(II)
E	1.50×10^{-2} M Zn(II)
F	no Zn(II)

the copper(II)-BT-CyDTA system (graphs of which are not shown).

In general, for the following exchange reaction of BT and a zinc(II)-NTA or copper(II)-CyDTA chelate:

$$D + \underset{\displaystyle MX_2}{\overset{}{\underset{\parallel}{MX}}} = MD + X \tag{1}$$

where D and X refer to BT and NTA or CyDTA species respectively, and where the changes are neglected for the sake of simplicity, one can assume the following apparent equilibrium constant:

$$K_e = \frac{[MD]\cdot[X]_f}{[D]_f\cdot[MX]_t} \tag{2-a}$$

$$= \frac{K_{MD}\cdot(\alpha_H)_c}{K_{MX}\cdot(\alpha_H)_{BT}}\cdot\frac{1}{1+K_{MX_2}\cdot[X]_f/(\alpha_H)_c} \tag{2-b}$$

where $[D]_f$ and $[X]_f$ refer to the concentrations of uncomplexed BT and the chelating agent; [MD], to the concentration of the metal-BT complex, and $[MX]_t$, to the total concentration of zinc(II)-NTA or copper(II)-CyDTA chelates.

K_{MD}, K_{MX}, and K_{MX_2} in Eq. (2) are the formation constants corresponding to the following reactions:

$$M + D = MD,\quad K_{MD} = [MD]/[M]\cdot[D]$$

$$M + X = MX,\quad K_{MX} = [MX]/[M]\cdot[X]$$

$$MX + X = MX_2,\quad K_{MX_2} = [MX_2]/[MX]\cdot[X]$$

and (α_H)'s have their usual meanings. Here, $(\alpha_H)_{BT}$ corresponds to the (α_H) value of BT, and $(\alpha_H)_c$, to that of NTA or CyDTA.

By rearranging Eq. (2) and by casting the resulting relation into a logarithmic form, relation (3) can be obtained:

$$\log\frac{[MD]}{[D]_f} = \log\frac{K_{MD}\cdot(\alpha_H)_c}{K_{MX}\cdot(\alpha_H)_{BT}} + \log\frac{[MX]_t}{[X]_f\cdot(1+K_{MX_2}\cdot[X]_f/(\alpha_H)_c)} \tag{3}$$

Relation (3) indicates that the plot of $\log [MD]/[D]_f$ against $\log[MX]_t/[X]_f\cdot(1+K_{MX_2}\cdot[X]_f/(\alpha_H)_c)$ should give a straight line with a slope of unity, and that the $\log [MD]/[D]_f$ value obtained when $\log [MX]_t/[X]_f(1+K_{MX_2}\cdot[X]_f/(\alpha_H)_c)$ is equal to zero must be $\log K_{MD}\cdot(\alpha_H)_c/K_{MX}\cdot(\alpha_H)_{BT}$.

The $[MD]/[D]_f$ ratio in Eq. (3) can be obtained from the absorption data using the relationship described below. When $[X]_f$ and $[MX]_t$ are much greater than the total concentration of BT added, by the law of additive absorbancies the absorbancy of each of the solutions, A, is expressed as:

$$A = \varepsilon_{BT}\cdot[D]_f + \varepsilon_{MD}\cdot[MD] \tag{4}$$

Since, under the present experimental conditions (pH 8.50 to 10.50), the total concentration of uncomplexed BT is considered to be equal to $[HD^{2-}]+[D^{3-}]$, ε_{BT} in Eq. (4) must be given by $\varepsilon_{HD}+(\varepsilon_{HD}-\varepsilon_D)/(\alpha_H)_{BT}$ and must be constant at a constant pH. Here, the ε's represent the molar extinction coefficients of the corresponding species.

When the total concentration of BT added is kept constant, the absorbancy, A_D, of the solution containing no metal ion is given by:

$$A_D = \varepsilon_{BT}\cdot[D]_t = \varepsilon_{BT}\cdot([D]_f + [MD]) \tag{5}$$

For the solution with a large excess of metal ions, where all the BT dye added is considered to exist in the form of MD^-, the absorbancy, A_{MD}, is expressed as:

$$A_{MD} = \varepsilon_{MD}\cdot[D]_t = \varepsilon_{MD}\cdot([D]_f + [MD]) \tag{6}$$

where $[D]_t$ represents the total concentration of BT added.

From the three relations, (4), (5) and (6), the concentrations of the metal-BT chelate and of uncomplexed BT can be derived as:

$$[MD] = (A_D - A)/(\varepsilon_{BT} - \varepsilon_{MD}) \tag{7}$$

$$[D]_f = (A - A_{MD})/(\varepsilon_{BT} - \varepsilon_{MD}) \tag{8}$$

Therefore, the $[MD]/[D]_f$ ratio must be $(A_D-A)/(A-A_{MD})$.

If the BT chelate in solution exists in the form of MDX, *i. e.*, if the mixed complex, MDX, is formed among metal, BT and NTA or CyDTA, the following equilibrium must become most important:

$$\mathrm{D} + \underset{\underset{\mathrm{MX_2}}{\|}}{\mathrm{MX}} = \mathrm{MDX} \qquad (9)$$

and Eq. (3) should be replaced by Eq. (10), with only the plot of log$[\mathrm{MDX}]/[\mathrm{D}]_f$ *vs.* log $[\mathrm{MX}]_t/(1+K_{\mathrm{MX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c)$ giving a straight line, one with a slope of *1.00.*

$$\log\frac{[\mathrm{MDX}]}{[\mathrm{D}]_f} = \log\frac{[\mathrm{MX}]_t}{1+K_{\mathrm{MX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c} + \log\frac{K^{\mathrm{MX}}_{\mathrm{MDX}}}{(\alpha_\mathrm{H})_{\mathrm{BT}}} \qquad (10)$$

where $K^{\mathrm{MX}}_{\mathrm{MDX}}$ is equal to $[\mathrm{MDX}]/[\mathrm{MX}]\cdot[\mathrm{D}]$ and the $[\mathrm{MDX}]/[\mathrm{D}]_f$ ratio is also given by $(A_\mathrm{D}-A)/(A-A'_{\mathrm{MD}})$. Here, A'_{MD} is the absorbancy for the solution containing only MDX.

For the system where only MX is formed between metal ions and the chelating agent, the $1+K_{\mathrm{MX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c$ term in Eqs. (3) and (10) can be simplified to 1.

The relations (3) and (10) were examined by using some of the typical experimental data obtained for the copper(II)-CyDTA and zinc(II)-NTA systems.

In the case of a copper(II) system, irrespective of the pH, a linear relation with a slope of unity could be found between log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$and log $[\mathrm{MX}]_t/[\mathrm{X}]_f$, but not between log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ and log $[\mathrm{MX}]_t$ (Fig. 3). $[\mathrm{MX}]_t$, here, is practically equal to the total concentration of copper(II) added.

In the case of zinc(II) system, at pH values lower than 9.00, the plot of log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ against log $[\mathrm{MX}]_t/(1+K_{\mathrm{MX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c)\cdot[\mathrm{X}]_f$ yielded a stright line with a slope pf unity, but at pH values higher than 9.00, only the plot of log$(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ *vs.* log $[\mathrm{MX}]_t/(1+K_{\mathrm{MX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c)$ gave a straight line, one with a slope of 1.00 (Figs. 4 and 5).

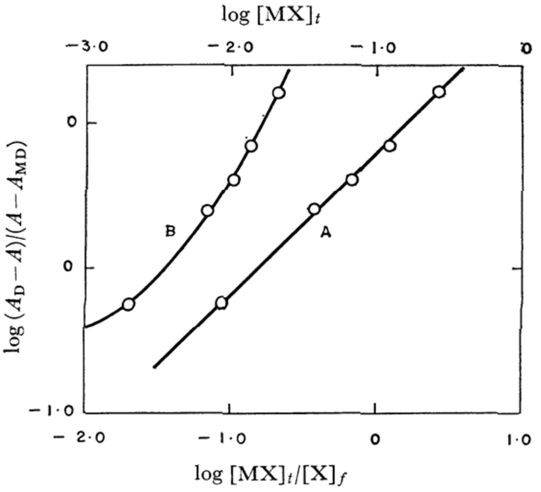

Fig. 3. Log-ratio plot for determining the equilibrium constant 1.25×10^{-5} M BT, 2.50×10^{-2} M CyDTA, $\mu=0.30$ pH$=10.0$, $\lambda=620$ mμ
Concentration of copper(II): 2.0 mM to 20.0 mM
A the plot of log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ *vs.* log $[\mathrm{CuZ}]/[\mathrm{Z}]_f$.
B the plot of log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ *vs.* log [CuZ].

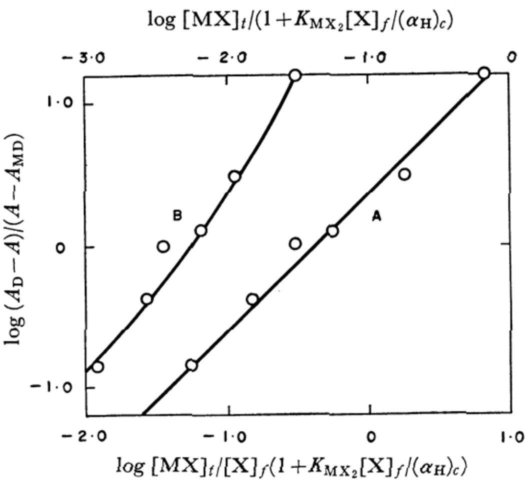

Fig. 4. Log-ratio plot for determining the equilibrium constant.
1.95×10^{5} M BT, 2.50×10^{-2} M NTA, $\mu=0.30$
pH$=8.50$, $\lambda=620$ mμ
Concentration of zinc(II): 2.50 mM to 15.0 mM
A the plot of log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ *vs.* log $[\mathrm{ZnX}]_t/[\mathrm{X}]_f\cdot(1+K_{\mathrm{ZnX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c)$
B the plot of log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ *vs.* log $[\mathrm{ZnX}]_t/[\mathrm{X}]_f\cdot(1+K_{\mathrm{ZnX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c)$

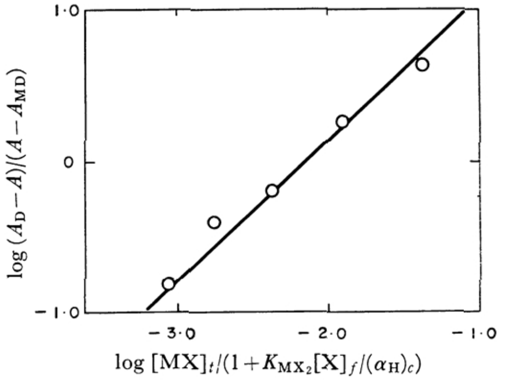

Fig. 5. The plot of log $(A_\mathrm{D}-A)/(A-A_{\mathrm{MD}})$ *vs.* log $[\mathrm{ZnX}]_t/(1+K_{\mathrm{ZnX_2}}\cdot[\mathrm{X}]_f/(\alpha_\mathrm{H})_c)$ for determining the equilibrium constant.
1.82×10^{-5} M BT, 2.50×10^{-2} M NTA
$\mu=0.30$, pH$=10.30$, $\lambda=630$ mμ
Concentration of zinc(II): 0.25 mM to 10.0 mM

Consequently, it can be concluded that, in the presence of a large excess of uncomplexed and complexed CyDTA, the copper(II) ion forms the $\mathrm{CuD^-}$ chelate, irrespective of the pH, while the zinc(II) ion, in the presence of the zinc(II)-NTA chelate and free NTA, forms the normal chelate, $\mathrm{ZnD^-}$, at pH values lower than 9.00, and the mixed chelate,

$ZnDX^{4-}$, at pH values higehr than 9.00. This could also be confirmed by the fact that the maximum of the absorption curve of the zinc(II)-BT chelate, occurring at $\lambda=570$ mμ, shifted to a longer wavelength (580 mμ) at pH values higher than 9.00.

In view of the fact that zinc(II) can form the ZnX_2^{4-} chelate with the quadridentate ligand NTA, the conclusion that zinc(II) forms the mixed chelate, $ZnDX^{4-}$, with NTA and BT, which can function as the tridentate ligand, is reasonable.

With the aid of Eqs. (3) and (10), the stability constants for zinc(II)- and copper(II)-BT chelates were calculated from the value of $\log(A_D-A)/(A-A_{MD})$, obtained when $\log[MX_t]/[X]_f\cdot(1+K_{MX_2}\cdot[X]_f/(\alpha_H)_c)$ or $\log[MX]_t/(1+K_{MX_2}\cdot[X]_f/(\alpha_H)_c)$ is equal to zero. The numerical values for NTA, CyDTA and their chelates used in the calculations are listed in Tables 1, along with the results reported by Schwarzenbach6) and Diehl.4) These numerical values were calculated from the related dissociation constants10,11) and formation constants10,12,13) in the solution with an ionic strength of 0.10 at 20°C, while the activity coefficients of the ions were calculated by means of the Davies equation,14) assuming the temperature coefficients of these equilibrium constants to be equal to zero.

Table 1

i) Dissociation constants of NTA and CyDTA (mixed constants,5) $\mu=0.30$)

a) NTA10) $pK_1=1.86$, $pK_2=2.38$, $pK_3=9.54$

b) CyDTA11) $pK_1=2.39$, $pK_3=3.41$, $pK_3=5.93$

ii) Formation constants of chelates ($\mu=0.30$)

K_{ZnX}10) $=10^{10.22}$, K_{ZnX_2}12) $=10^{2.77}$

K_{CuY}13) $=10^{20.70}$

K_{ZnD}6) $=10^{12.45}$, $K^{ZnX}_{ZnDX}{}^*=10^{2.83}$

$K_{ZnD}{}^*=10^{12.31}$ $K_{ZnDX}{}^*=10^{15.15}$

$K_{CuD}{}^*=10^{21.38}$

X: NTA, Y: CyDTA

* Obtained by the present authors

K_{ZnDX} in Table 1 corresponds to the equilibrium constant of the following reaction:

$$Zn + D + X = ZnDX$$

and was calculated with the aid of the $K_{ZnDX}=K^{ZnX}_{ZnDX}\cdot K_{ZnX}$ relation.

The stability constant found for the zinc(II)-BT chelate ZnD^- agrees well with the value given by Schwarzenbach.6) The results obtained for the copper(II)-BT chelate may explain the well-known observation that the presence of the copper(II) ion interferes with the color change of BT in EDTA-Mg(II) or EDTA-Zn(II) titrations.8) Considering that, at pH 10.0, $\log K_{CuD}\cdot(\alpha_H)_{EDTA}/K_{CuY}\cdot(\alpha_H)_{BT}$ is calculated to be 2.0, the color change of BT can be expected to occur only when the ratio of the concentration of free EDTA to that of the copper(II)-EDTA chelate exceeds 100.

The authors wish to thank the Ministry of Education for the financial support given to this reseach.

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