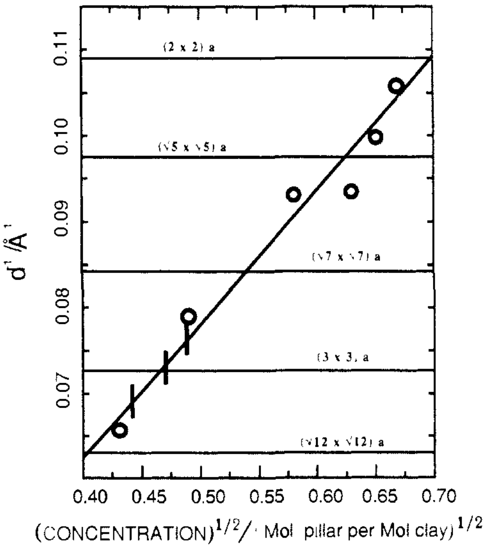

Figure 8. Dependence of $1/d$ on $(p)^{1/2}$, where p is pillar concentration given in Mol pillar per Mol clay and d is the experimental distance between pillars centers.

In the above no assumptions about pillar or clay charges have been made—only the X-ray and microanalysis results have been used. The slope of the line in Figure 8, however, does allow some further conclusion about relative charge on clay and pillar to be drawn following eq 3. Taking the determined values of the CEC's of the clays (which correspond with the usual values for these materials) we can say that the pillar charges are much higher than the ionic charges in solutions at the preparative pH. Thus acidity of the clay surface probably influence more protonation—as have been found elsewhere.[10]

In Figure 8 we show lines corresponding approximately to possible commensurate lattices on the clay surface. The fluorhectorites fall close to the $(5)^{1/2} \cdot (5)^{1/2}$ structure and the (Hg-diamsar)–fluorhectorite III close to the (2 × 2) structure. It may be that this correlates with the more perfect two-dimensional lattices (narrower Bragg peaks) in this case. The present work thus points to a general conclusion that the most rigid and stable pillared clay systems could be obtained when interpillar distances—determined primarily by charge balance—are equal very precisely to the clay basal plane lattice parameters. Conversely for regions of a clay particle surface where this obtains the most stable pillaring will result. Support for this statement comes from recent work of Pinnavaia et al.[13] For one out of the three Al-pillared clays described the interpillar distance calculated from Al concentration (Al_{13}^{7+} pillar) was equal to the clay lattice parameter. These pillared clays gave the biggest surface area and the best stacking order.

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Metal Ion Lability Constant Derived from a Linear Free Energy Relationship between Ligand-Substitution Rates of Tris(acetylacetonato) and Aqua Complexes of Various Tervalent Metal Ions

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Abstract: A linear relationship is found between the first-order rate constants of the ligand exchange of tris(acetylacetonato) complexes of tervalent metal ions [$M^{III}(acac)_3$] (M = Sc, V, Cr, Mo, Mn, Fe, Ru, Co, Rh, Al, Ga, and In) in acetylacetone and/or acetonitrile and those of substitution reactions of their aqua complexes in water. The slope is very close to unity over the range of 10^{14}. The former is shifted invariably by about $10^{-4.5}$ to the latter. The finding shows that the nature of central metal ions dominates the lability of complexes over the great differences in ligands and reactive environment around the ions. A metal ion lability constant σ is proposed and evaluated for each M^{III} as a measure of the lability of octahedral M^{III} complexes.

Taube[1] first classified metal complexes by the central metal ion into substitution labile and inert on the basis of the observations on the rate of their ligand-substitution processes. He pointed out that complexes of metal ions with d^3 and low-spin configurations of d electrons are inert. A large amount of kinetic results accumulated since then clarified that other natures of metal ions such as charge and ionic radii as well as the electronic and structural character of ligands also have a considerable effect on the rate.[2] Replacement of chelate ligands is understood to proceed considerably slower than that of unidentates in complexes of a given metal ion.[2b] For evaluation of the kinetic nature of metal ions separately, it is essential to compare more than one series of rates for complexes of various metal ions with common ligands of different character.

We have chosen the acetylacetonate ion (acac⁻) as the common chelating ligand, because it gives octahedral tris(bidentate)-type complexes [$M(acac)_3$] with a variety of tervalent metal ions.

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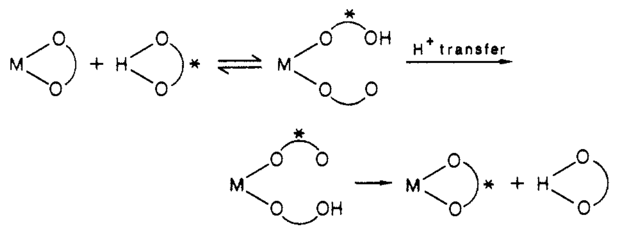
Table I. First-Order Rate Constants of Ligand-Exchange and -Substitution Reactions of $[M(acac)_3]$, $[M(H_2O)_6]^{3+}$, and $[M(NH_3)_5(H_2O)]^{3+}$ at 298 K

	$k_1(acac^-)/s^{-1}$		$k_1(H_2O)^a/s^{-1}$				reference^k					
			$[M(H_2O)_6]^{3+}$		$[M(NH_3)_5(H_2O)]^{3+}$							
M^{III}	in acetylacetone (A)	in acetonitrile (B)^b	H_2O exchange (C)	anation (D)^c	H_2O exchange (E)	anation (F)^c	A	B	C	D	E	F
Sc	$6 \times 10^{1\,d}$	4		$5 \times 10^{7\,e,i}$				13		28		
V	1.4×10^{-4}	2.0×10^{-5}	5.0×10^{2}	$1 \times 10^{1\,h}$			11	11	16	29		
Cr	4×10^{-10}	9×10^{-11}	2.5×10^{-6}	$1 \times 10^{-6\,h}$	5.2×10^{-5}	$1 \times 10^{-7\,g}$	9	7	17, 18	30	25	35
Mo	3.5×10^{-6}			$5 \times 10^{-4\,g}$			15			31		
				$3 \times 10^{-2\,h}$						31		
Mn		1		10^4–$10^{5\,j}$				14		32		
Fe	3.3×10^{-3}	$2 \times 10^{-4\,f}$	1.6×10^{2}	1^g			10	10	20	33		
				$1 \times 10^{1\,h}$						34		
Ru	3×10^{-11}		5×10^{-6}		2.3×10^{-4}	$1 \times 10^{-5\,g}$	9		20		27	36
Co	2×10^{-10}	1×10^{-10}			5.9×10^{-6}	$2 \times 10^{-8\,g}$	9	8			26	37
Rh	8×10^{-13}		3×10^{-8}		8.4×10^{-6}	$7 \times 10^{-7\,g}$	12		21		25	38
Al	9.1×10^{-5}	4.6×10^{-5}	1.3				12	12	22			
Ga	1.6×10^{-3}		4.0×10^{2}				15		23			
In	$(2)^d$	2×10^{-1}	4×10^{4}	$2 \times 10^{5\,i}$				15	24	28		
marks in Figure 1	open	closed	circle	hexagon	triangle	square						

^{a}In acidic aqueous solution. ^{b}Observed first-order rate constant under a common concentration region; [complex] = 0.001–0.01 M (0.05 M for Sc^{III}), [Hacac] = 0.1–2 M (0.02 M for Mn^{III}), and $[H_2O]$ = 0.01–0.1 M. ^{c}Reported second-order rate constant was divided by assumed outer-sphere association constant (see text). ^{d}Extrapolated value (see text). ^{e}At 285 K. ^{f}At 283 K. ^{g}Anation of Cl^-. ^{h}Anation of NCS^-. ^{i}Anation of murexide. ^{j}Estimated by Diebler for $[Mn(H_2O)_6]^{3+} + HF \rightarrow [Mn(H_2O)_5F]^{2+} + H^+$.[32] ^{k}Reference numbers in the text are indicated.

Ligand isotopic exchange kinetics of the complexes (M = Sc, V, Cr, Mo, Mn, Fe, Ru, Co, Rh, Al, Ga, and In) have been studied by the labeling method in neat acetylacetone and acetonitrile.[3-15] The rate laws, activation parameters, and deuterium isotope effect disclosed that the exchange is commonly expressed by eq 1 and



(1)

the first step is the common rate-determining step. (Arcs and asterisks denote the acetylacetonate chelate ring and ^{14}C labeling, respectively. Two chelate ligands are omitted for simplicity.) The first step corresponds to a substitution process of incoming Hacac for the leaving $acac^-$, which remains as a unidentate ligand in the intermediate state.

A reasonably clear linear relationship has been found between the first-order rate constants of the exchange reaction and those of ligand-substitution reactions of hexaaqua and pentaammineaqua complexes of the various tervalent transition-metal and main-group metal ions. Such a relationship indicates that the overall rate of substitution reactions is primarily an attribute of the metal ion. This paper introduces an empirical parameter, "metal ion lability constant", which can represent the lability of metal ions and is useful in estimating unknown rates of substitution reactions.

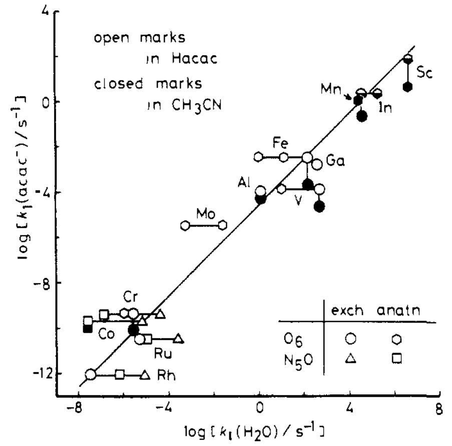


Figure 1. Linear free energy relationship between ligand-substitution rates of $M(acac)_3$ and aqua complexes of M^{III}. Ordinate: First-order exchange-rate constant of $M(acac)_3$ in Hacac (open marks; extrapolated value, half-closed) and in CH_3CN (closed marks) at 25 °C. Abscissa: First-order rate constants for water exchange (circles) and anation (hexagons) of $[M^{III}(H_2O)_6]^{3+}$ and water exchange (triangles) and anation (squares) of $[M^{III}(NH_3)_5(H_2O)]^{3+}$ in acidic aqueous solution at 25 °C. Details in the text. References in Table I.

Procedure

Kinetic data of our previous and unpublished work[7-15] and of the literatures[16-38] are collected and standardized (Table I). The first-order rate constants for the ligand exchange of $[M(acac)_3]$ in acetylacetone and that of $[M(H_2O)_6]^{3+}$ in acidic aqueous media are chosen in the first place

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because of simplicity of the reactions. There is clearly a linear relationship between the constants (the open circles in Figure 1, vide infra). However, the constants for the exchange reaction in acetonitrile, for the anation of a few sorts of anions to $[M(H_2O)_6]^{3+}$ and $[M(NH_3)_5(H_2O)]^{3+}$, and for the water exchange in the latter complex ion are also gathered, compensating for the limited availability of the data of the first group and connecting the scattered data for all the tervalent metal ions shown in Table I.

The observed exchange rates, R, of $[M(acac)_3]$ were proportional to the concentration of the complex for all the M^{III} in both the solvents; i.e., $R = k_o[\text{complex}]$. The observed first-order rate constants, k_o, were expressed commonly by $k_o = k_1 + k_2[H_2O]$ in acetylacetone under [complex] = 0.001–0.01 M and $[H_2O]$ = 0.01–0.1 M, the second term being absent in some complexes.[9-12,15] The observed k_1 values were collected and shown in Table I as k_1 (acac$^-$), except for Sc^{III}, Mn^{III}, and In^{III}. Extrapolation to 298 K was carried out for Cr^{III}, Mo^{III}, Fe^{III}, Ru^{III}, Co^{III}, and Rh^{III} with the observed $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The k_o in acetonitrile was expressed generally by $k_o = k_1' + k_2'[H_2O] + (k_3' + k_4'[H_2O])[\text{Hacac}]$, some terms being absent in some complexes.[7,8,10-15] The k_o values under a common condition, [complex] = 0.001–0.01 M (0.05 M for Sc^{III}), [Hacac] = 0.1–2 M, and $[H_2O]$ = 0.01–0.1 M, were adopted and shown as k_1(acac$^-$) in Table I. For Mn^{III}, k_o at [Hacac] = 0.02 M was employed as the lowest limit of k_1(acac$^-$). The k_1(acac$^-$) values in acetylacetone for Sc^{III} and In^{III} in parentheses in Table I were obtained by extrapolation of k_o in acetonitrile with respect to [Hacac] to 9.7 M, which is [Hacac] in acetylacetone. The extrapolation gives a k_o value very close to the k_o in acetylacetone for V^{III}, Cr^{III}, Fe^{III}, Co^{III}, and Al^{III}. For Mn^{III}, the extrapolation was not done because of the absence of k_3' and k_4' terms.

For water exchange of $[M(H_2O)_6]^{3+}$[16-24] and $[M(NH_3)_5(H_2O)]^{3+}$[25-27] in acidic aqueous solution, all the reported first-order rate constants were adopted and displayed in Table I as $k_1(H_2O)$. The $k_1(H_2O)$ values for the anation of mainly Cl$^-$ and NCS$^-$ and inevitably murexide to $[M(H_2O)_6]^{3+}$[28-34] and $[M(NH_3)_5(H_2O)]^{3+}$[35-38] were estimated from the reported second-order rate constants and assumed outer-sphere association constant, 10 M^{-1}, which is calculated by the Fuoss equation for Cl$^-$. The $k_1(H_2O)$ value of Mn^{III} has been the only datum available and estimated by Diebler[32] for

$$[Mn(H_2O)_6]^{3+} + HF \rightarrow [Mn(H_2O)F]^{2+} + H^+$$

Results and Discussion

Linear Free Energy Relationship. log k_1(acac$^-$) is plotted against log $k_1(H_2O)$ (Figure 1). The plot gave a straight line over a wide range of the magnitudes spanning 10^{14}. Scattering of the plots from the line is rather modest as compared with the range. The $k_1(H_2O)$ values of the four kinds (circle, hexagon, triangle, and square) for an M^{III} do not greatly deviate from one another as compared with the wide variation of k_1's for M^{III}'s. Moreover, the rather rough estimation of the $k_1(H_2O)$ values for the anations does not affect the general aspect of the widely varied rate constants. Therefore, averaged values of $k_1(H_2O)$ are used for an M^{III} in further analysis, when more than one $k_1(H_2O)$ is adopted in Table I. Since log k_1(acac$^-$) in acetylacetone is consistently greater by about 1 than log k_1(acac$^-$) in acetonitrile for several M^{III}'s, the observed values in acetylacetone are used together with the extrapolated ones for M^{III}'s other than Mn^{III}. The least-squares treatment for the k_1(acac$^-$) vs the averaged $k_1(H_2O)$ values gave

$$\log k_1(\text{acac}^-) = (0.98 \pm 0.08) \log k_1(H_2O) - (4.5 \pm 0.4)$$

at 70% confidence level with the correlation factor 0.95. That is, the line has a slope of unity, and the k_1(acac$^-$) values are invariably shifted by about $10^{-4.5}$ with respect to $k_1(H_2O)$.

Table II. Metal Ion Lability Constant σ for Tervalent Metal Ions

$M^{III\,a}$	log $k_1(\text{acac}^-)^b/\text{s}^{-1}$	log $k_1(\text{acac}^-)/\text{s}^{-1}$ + 4.5	log $k_1(H_2O)/\text{s}^{-1}$	σ^c
Sc	1.8^d	6.3	6.7	6.5
Mn (HS)	1^e	5.5	4.5	5
In	0.3^d	4.8	5.0	5
Ti			5^g	(5)^h
Ga	−2.8	1.7	2.6	2
Fe (HS)	−2.5	2.0	1.1	1.5
V	−3.9	0.6	1.9	1
Al	−4.0	0.5	0.1	0.5
Mo	−5.5	−1.0	−2.5	−1.5
Tc (LS)	−9.5^f	−5.0		(−5)^i
Cr	−9.4	−4.9	−5.7	−5.5
Ru (LS)	−10.5	−6.0	−4.7	−5.5
Co (LS)	−9.7	−5.2	−6.4	−6
Rh (LS)	−12.1	−7.6	−6.3	−7

[a] HS, high spin; LS, low spin. [b] In acetylacetone. [c] The average value of $k_1(H_2O)$'s in Table I for an M^{III}. [d] The extrapolated value. [e] In acetonitrile. [f] Reference 15. [g] Reference 46. [h] Estimated only from $k_1(H_2O)$. [i] Estimated only from k_1(acac$^-$).

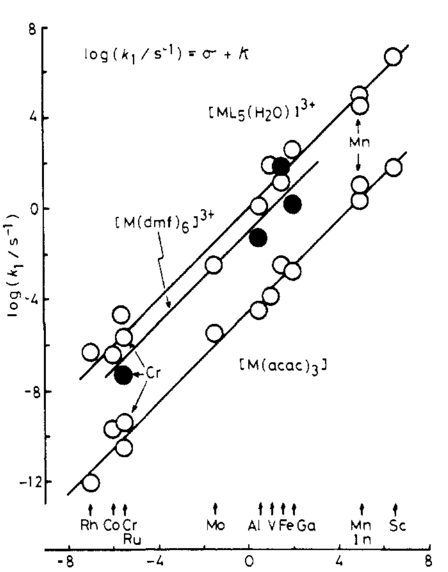

Figure 2. log k_1/s^{-1} vs σ plot. $\kappa = 0$ for water exchange and anation of $[ML_5(H_2O)]^{3+}$ (L = H_2O and NH_3), $\kappa = -4.5$ for ligand exchange of $[M(acac)_3]$, and $\kappa = -1$ for solvent exchange of $[M(dmf)_6]^{3+}$ (closed marks).

It is noteworthy that such a linear free energy relationship with unit slope was found for octahedral complexes of various tervalent metal ions, in spite of great differences in the natures of the reactions, i.e., a bidentate vs unidentates, in organic solvents vs in acidic aqueous solution, and a chargeless complex vs highly charged ones. It suggests lability as the kinetic nature of the metal ions is retained over such great changes. The difference in the free energies of activation ($\Delta G^{\ddagger}$) of the two reactions for an M^{III} is not greatly changed, independent of M^{III} (~25 kJ mol^{-1}). The changes of $\Delta G^{\ddagger}$ with the variation of M^{III} in the reactions are similar to each other. This means a common mechanism between the reactions for an M^{III} and similar mechanisms among M^{III}'s in each reaction (vide infra). In other words, the strength and the manner of the influence of M^{III} to the rates are similar within the reactions.

Metal Ion Lability Constant. The most probable line in Figure 1 is regarded to be equivalent to eq 2. Introduction of a set of

$$\log k_1(\text{acac}^-) = \log k_1(H_2O) - 4.5 \qquad (2)$$

the rate constants as a standard, log $k_1(H_2O)_{\text{std}}$ = 0 and log $k_1(\text{acac}^-)_{\text{std}}$ = −4.5, into eq 2 yields eq 3. Substraction of eq 3

$$\log k_1(\text{acac}^-)_{\text{std}} = \log k_1(H_2O)_{\text{std}} - 4.5 \qquad (3)$$

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from eq 2 affords the Hammett equation (eq 4), where σ is a

$$\log \frac{k_1(\text{acac}^-)}{k_1(\text{acac}^-)_{\text{std}}} = \log \frac{k_1(\text{H}_2\text{O})}{k_1(\text{H}_2\text{O})_{\text{std}}} = \sigma \qquad (4)$$

measure of the effect of metal ion on the lability and can be named the *metal ion lability constant*, which corresponds to substituent constant in the equation. σ values are evaluated as the mean of the first and second terms of eq 4 as shown in Table II (eq 5). They are rounded to the nearest whole or half number.

$$\sigma = \tfrac{1}{2}[\log k_1(\text{acac}^-)/\text{s}^{-1} + 4.5 + \log k_1(\text{H}_2\text{O})/\text{s}^{-1}] \qquad (5)$$

In order to check the evaluation, the observed values of k_1 are plotted against σ and shown in Figure 2. The lines for $[\text{ML}_5(\text{H}_2\text{O})]^{3+}$ (L = H_2O and NH_3) and $[\text{M(acac)}_3]$ are equivalent to eq 6, which is derived from eq 4, where $\kappa = 0$ for $k_1(\text{H}_2\text{O})$ and

$$\log k_1/\text{s}^{-1} = \sigma + \kappa \qquad (6)$$

$\kappa = -4.5$ for $k_1(\text{acac}^-)$, κ corresponding to $\log k_{1,\text{std}}$, $\log k_1$ at $\sigma = 0$. All the plots are satisfactorily close to the lines. Appropriateness of the present σ values can be demonstrated by the third series of the solvent exchange, for which k_1's are available for a wide range of σ, $[\text{M(DMF)}_6]^{3+}$ in dimethylformamide (DMF).[39-45] The plots (closed marks) are on the line with $\kappa = -1$, which also supports validity of the kinetic analysis.

General Considerations. Equation 6 is quite suggestive to the understanding of the nature of the ligand-substitution processes. This is also a modified form of the Hammett equation: $\log (k/k_0) = \rho\sigma$. Interestingly, the reaction constant ρ is unity. It means that the influence of the metal ions on the lability is strong and similar across the two extreme reactions of the aqua and the acetylacetonato complexes. In other words, the lability nature of the metal ions comes out dominantly and is unaffected by reactive conditions surrounding them, although the k_1 value is altered by the reactions and shifted by κ, which therefore should be understood as a reaction factor. The metal ion lability constant σ is considered to be dominated by the ease of M–O bond loosening associated with the bond making between an incoming nucleophile and the metal ion to form the activated complex of the I mechanism (vide infra), whereas the reaction factor κ is controlled by the nature of incoming, leaving, and nonsubstituting ligands, charge of complexes, properties of solvents, and so on. It is quite interesting that σ and κ contribute independently of each other to k_1 as shown in eq 6, at least for the reactions in question.

The rate-determining step of the exchange of M(acac)_3 was concluded to be the first step of eq 1, the first bond loosening of a chelate ring with the aid of incoming Hacac or H_2O, basically by the I mechanism.[7-15] To Sc^{III}, V^{III}, Mo^{III}, Fe^{III}, Ru^{III}, Rh^{III}, Ga^{III}, and In^{III} and to Co^{III} were assigned I_a[9-11,13-15] and I_d (or D)[8] mechanisms, respectively. For Cr^{III} and Al^{III}, an intermedaite I mechanism was concluded.[7,12] Similar assignments of the mechanisms to each M^{III} had been given to the exchange and anation reactions of $[\text{ML}_5(\text{H}_2\text{O})]^{3+}$ (L = H_2O, NH_3).[31,45] The LFER with unit slopes in the figures affords mechanistic conclusions: (1) common mechanisms for an M^{III} in the reactions; (2) common stoichiometric mechanism I (and the different intimate mechanisms) for the reactions of M^{III}'s; (3) mechanisms of exchange of M(acac)_3 containing no extremes (D and A) and varying from I_d to I_a continuously.

Equation 6 is also useful for rough estimation of unknown k_1 values. For example, $\log k_1$ of the water-exchange reactions of $[\text{M(H}_2\text{O)}_6]^{3+}$ for Sc^{III}, Mo^{III}, Mn^{III}, Tc^{III}, and Co^{III} are expected to be $\sim$6.5, $\sim$−1.5, $\sim$5, $\sim$−5, and $\sim$−6, respectively. $\log k_1$ of the ligand exchange of M(acac)_3 for Ti^{III} is foreseen to be $\sim$−0.5, on the basis of the observed k_1 for $[\text{M(H}_2\text{O)}_6]^{3+}$.[46]

The $k_1(\text{H}_2\text{O})$ values for solvent-exchange reactions of $[\text{M(H}_2\text{O)}_6]^{3+}$ have been regarded as the best measure of the lability of tervalent metal complexes. The σ value in Table II is standardized to be very close to $\log k_1(\text{H}_2\text{O})$; however, it is a more general measure derived from the rate constants of the two reactions with quite different characters and is an index of the lability of the metal ions rather than the rate constants of a specific complex.

The variation of σ on M^{III}'s is interpreted in terms of the electrostatic interaction between a metal ion and ligands (ionic radius) and the ligand-field activation energy (d-electron configuration).[47] The existence of the LFER despite the dissimilarity in the intimate mechanism is explained by the compensation effect between the enthalpy and the entropy of activation. These will be discussed elsewhere.

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