

The Formation of Zinc(II) Complexes with Ethoxyacetate and (Ethylthio)acetate Ions

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The formation in aqueous solution of ethoxyacetate and (ethylthio)-acetate complexes of Zn^{2+} has been studied by determination of the concentration of free ligand in the complex solutions. The measurements have been performed at 25°C in a perchlorate medium at an ionic strength of 1 M. In both systems at least two mononuclear complexes are formed. The ethoxyacetate complexes are stronger than the (ethylthio)acetate complexes, in contrast to earlier findings on bivalent Cu-, Cd-, and Ni-ions. This is ascribed to a certain degree of chelate formation in the zinc ethoxyacetate system.

From investigations by Tichane and Bennet¹ and by Yasuda *et al.*² it is known that the zinc ion forms a stronger 1:1 complex with the oxydiacetate ion than with the thiodiacetate ion, and that both ligands obviously act tridentately. Since oxydiacetic acid is stronger than thiodiacetic acid it seems reasonable to conclude³ that the zinc ion has a larger affinity towards an oxygen atom in an ether position than towards a sulphur atom in an equivalent position. The results from an investigation by Schwarzenbach *et al.*⁴ on the zinc complexes of $CH_3O \cdot CH_2 \cdot CH_2 \cdot N(CH_2 \cdot COO^-)_2$ and $CH_3S \cdot CH_2 \cdot CH_2 \cdot N(CH_2 \cdot COO^-)_2$ also indicate this effect.

In the case of the 1:1 zinc complexes of phenoxyacetate and phenylthioacetate, Suzuki and Yamasaki⁵ report a larger stability constant for the latter. The complexity being weak and phenoxyacetic acid being stronger than phenylthioacetic acid, the authors conclude, however, that the ligands act monodentately.

It should be valuable, however, to obtain experimental evidence regarding the coordination of O and S in this simple type of potentially bidentate ligand. The present investigation is an attempt to obtain such evidence by selecting a pair of ligands with almost equal and comparatively large basicity ($pK_a = 3.5$ for ethoxyacetic acid and 3.6 for (ethylthio)acetic acid). According to a report by Irving and Fernelius⁶ the stability constant for the 1:1 (ethylthio)-acetate complex in 50 % dioxane is somewhat larger for zinc than for nickel(II).

Preliminary experiments showed weak complexity in both the systems to be investigated. Thus a direct measurement of the concentration of free central ion the complex solutions should be the most favourable method of investigation from a theoretical point of view. Experimentally this could be done by means of zinc amalgam, unless oxidation of the amalgam caused interference.

An earlier investigation, however, of the nickel complexes of the ligands in question⁷ showed that it is possible to determine rather small stability constants with fairly good accuracy by measuring the concentration of free ligand, provided the measurements are performed with great care. To obtain the most favourable conditions for a comparison of the complex formation in the nickel and the zinc systems, the present investigation was performed by the same method as the investigation of the nickel systems, *viz.* by indirect determination of the concentration of free ligand by measuring the concentration of hydrogen ion in buffer solutions.

CALCULATIONS

The theory behind the investigation has been described in an earlier paper⁷ together with the method of calculation. Below are stated the notations and final expressions used in the calculations.

C_M	= total concentration of Zn^{2+} -ion
$[M]$	= concentration of free Zn^{2+} -ion
α	= proportionality factor. The excess of acid in the zinc perchlorate stock solution is $\alpha \cdot C_M$.
C_L'	= stoichiometric total concentration of ligand L
C_L	= corrected total concentration of ligand L
δ	= buffer quotient in the ligand buffer. The stoichiometric concentration of the acid HL is $\delta \cdot C_L'$
$[L]$	= concentration of free ligand
K_a	= $[H_3O^+] \cdot [L] / [HL]$
N	= maximum coordination number
β_n	= $[ML_n] / [M] [L]^n$ = gross stability constant
K_n	= $[ML_n] / [ML_{n-1}] [L]$ = stepwise stability constant
X	= $1 + \sum_{n=1}^N \beta_n [L]^n$
X'	= $dX/d[L]$
\bar{n}	= $(C_L - [L]) / C_M$ = the ligand number
$\bar{n}/[L]$	= X'/X
$\ln X([L]_j)$	= $\int_0^{[L]_j} (\bar{n}/[L]) \cdot d[L]$
X_i	= $(X_{i-1} - \beta_{i-1}) / [L]$; ($1 \leq i \leq N$; $X_0 = X$; $\beta_0 = 1$)
h_m and h_0	= $[H_3O^+]$ in solutions with the same C_L' -value, h_0 referring to a solution with $C_M = 0$
h_R	= $[H_3O^+]$ in a reference buffer
E_M	= $59.16 \log (h_m/h_R)$ mV

$$\begin{aligned}
 E_0 &= 59.16 \log (h_0/h_R) \text{ mV} \\
 E_L &= E_M - E_0 = 59.16 \log (h_m/h_0) \text{ mV} \\
 h_s &= \text{concentration of free acid in the sodium perchlorate stock} \\
 &\quad \text{solution}
 \end{aligned}$$

The concentration of free ligand is calculated according to the formula

$$[L] = \frac{h_0}{h_m} (C_L' - s_0 + h_0) \frac{\delta \cdot C_L' + \alpha \cdot C_M + s_m - h_m}{\delta \cdot C_L' + s_0 - h_0} \quad (1)$$

where s_0 and s_m are due to the excess of free acid in the stock solution of sodium perchlorate. In the present case they are calculated from

$$s_0 = h_s \cdot (1 - C_L') \quad \text{and} \quad s_m = h_s \cdot (1 - C_L' - 3C_M)$$

When $[L]$ has been calculated the ligand number \bar{n} is obtained from

$$\bar{n} = (C_L' - \alpha \cdot C_M - s_m + h_m - [L])/C_M \quad (2)$$

EXPERIMENTAL

Chemicals

Zinc perchlorate solution was obtained by dissolving zinc oxide *p.a.* in a slight excess of perchloric acid *p.a.* The concentration of zinc in the stock solution was found to be (0.334 ± 0.001) M by titration with EDTA.⁸ By potentiometric titrations as earlier described⁹ α was found to be $(1.014 \pm 0.005) \times 10^{-2}$. No impurities could be detected in the stock solution.

The same *ethoxyacetic acid* and *(ethylthio)acetic acid* preparations were used as in an earlier investigation.⁷

The *sodium perchlorate* was the same as used in an earlier investigation¹⁰ and h_s had the value -3.8×10^{-4} M.

All other chemicals were of analytical grade.

Method

The measurements were arranged as titrations at constant C_M . The method is described in Ref. 7. The concentration of hydrogen ion was determined by means of a Jena Type U (150 Mohms) glass electrode. The slope of this electrode was found to be the theoretical in the relevant pH-range. With the ethoxyacetate system the emf was read by means of a Radiometer PHM 4 potentiometer. In this case the reproducibility was in general within ± 0.2 mV. For the measurements on the very weak (ethylthio)-acetate system a Fluke DC Differential Voltmeter Model 885 AB was available, rebuilt at this institute to measure with an accuracy of 0.01 mV the emf of a cell with 150 Mohms internal resistance. In practice it was not possible to reproduce the emf readings with this precision. In general, however, the reproducibility was within ± 0.1 mV.

The temperature of the cells was kept at $(25.00 \pm 0.05)^\circ\text{C}$ by means of a water thermostat.

MEASUREMENTS

The zinc ethoxyacetate system. The experimental results from the main investigation, which was performed with a buffer with $\delta = 0.214$, are collected in Table 1.

Table 1. Corresponding values of [L] and $\bar{n}/[L]$ in the zinc ethoxyacetate system. The values of E_0 refer to $h_R = 5.81 \times 10^{-5}$ M.

C_L' mM	E_0 mV	$C_M = 80$ mM			$C_M = 60$ mM			$C_M = 40$ mM		
		E_L mV	[L] mM	$\bar{n}/[L]$ M ⁻¹	E_L mV	[L] mM	$\bar{n}/[L]$ M ⁻¹	E_L mV	[L] mM	$\bar{n}/[L]$ M ⁻¹
4.30	-0.3	37.0	1.84	13.0	29.8	2.20	13.0	21.2	2.71	12.4
6.06	0.8	32.8	2.67	13.2	25.9	3.21	12.7	18.6	3.85	12.8
8.14	1.4	29.9	3.65	13.4	23.6	4.34	13.0	16.9	5.19	13.0
11.23	1.9	27.3	5.11	13.5	21.6	6.02	13.2	15.4	7.19	13.1
15.04	2.2	25.3	6.95	13.4	20.1	8.12	13.3	14.2	9.73	13.0
19.73	2.5	23.7	9.27	13.3	18.8	10.80	13.1	13.3	12.87	12.8
29.24	2.7	21.9	14.00	13.0	17.3	16.31	12.8	12.2	19.35	12.4
38.5	2.7	20.9	18.7	12.9	16.6	21.6	12.7	11.5	25.8	12.0
51.9	2.6	20.0	25.5	12.6	15.9	29.5	12.5	10.9	35.2	11.7
69.1	2.3	19.1	34.6	12.2	15.2	39.8	12.1	10.4	47.4	11.3
89.4	2.0	18.4	45.5	11.9	14.4	52.6	11.5	9.9	62.1	10.9
126.7	1.4	17.0	67.3	10.9	13.2	77.5	10.5	8.9	91.0	9.7
166.3	0.9	15.5	93.0	9.8	12.1	105.6	9.5	8.0	123.2	8.7
222.3	0.0	14.0	131.1	8.6	10.6	149.0	8.1	6.9	171.4	7.4
304	-1.5	12.3	191	7.4	9.2	215	6.9	5.8	244	6.1
434	-3.9	9.8	299	5.6	7.3	329	5.3	4.8	362	5.0
553	-6.0	8.2	404	4.6	6.1	438	4.3	3.9	477	4.0
620	-7.3	7.6	464	4.2	5.6	501	3.9	3.6	540	3.7
691	-8.6	6.8	533	3.7	5.0	571	3.5	3.2	612	3.2
760	-9.9	6.1	602	3.3	—	—	—	—	—	—

Plotting $\bar{n}/[L]$ against [L] showed $\bar{n}/[L]$ to be independent of C_M . This is illustrated in Fig. 1 for smaller values of [L], and indicates that no polynuclear complexes are formed in the system.⁷

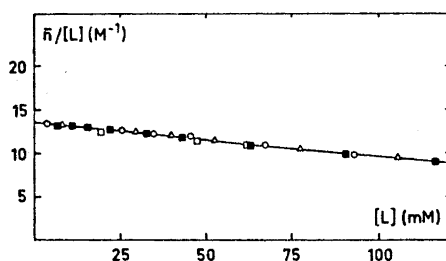


Fig. 1. Some of the $\bar{n}/[L]$ -values for smaller [L] in the zinc ethoxyacetate system. The main investigation: $C_M = 80$ mM (○), $C_M = 60$ mM (△), $C_M = 40$ mM (□). Buffer with $\delta = 0.421$, $C_M = 60$ mM (■). The full-drawn curve is calculated from the β_n -values obtained in this investigation.

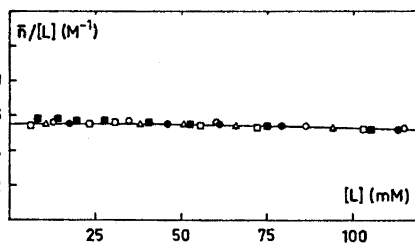


Fig. 2. Some of the $\bar{n}/[L]$ -values for [L] < 120 mM in the zinc (ethylthio)acetate system. The main investigation: $C_M = 80$ mM (○), $C_M = 60$ mM (△), $C_M = 40$ mM (□), $C_M = 20$ mM (●). Buffer with $\delta = 0.493$, $C_M = 60$ mM (■). The full-drawn curve is calculated by means of the β_n -values listed in Table 5.

Table 2. X-Values from the graphical integration of the $\bar{n}/[L]$ -function for the zinc ethoxyacetate system.

$\frac{[L]}{M}$	X([L])	X_1 M ⁻¹	X_2 M ⁻²	X_3 M ⁻³
0	1	13.5	74	58
0.005	1.070	14.0		
0.010	1.144	14.4		
0.015	1.220	14.7		
0.020	1.300	15.0		
0.025	1.385	15.4		
0.030	1.472	15.7		
0.040	1.660	16.5		
0.050	1.864	17.3		
0.060	2.087	18.1		
0.070	2.33	19.0		
0.100	3.16	21.6	81	
0.120	3.81	23.4	83	
0.140	4.52	25.2	84	
0.170	5.73	27.8	84	
0.200	7.14	30.7	86	60
0.250	9.92	35.7	89	60
0.300	13.26	40.9	91	57
0.380	20.11	50.3	97	61
0.460	28.7	60.2	102	61
0.540	39.2	70.8	106	59
0.620	51.5	81.4	110	58

Measurements were also made at $C_M = 60$ mM using a buffer with $\delta = 0.421$. As illustrated in Fig. 1 the $\bar{n}/[L]$ -values obtained in this case agree well with those obtained in the main investigation. Hence it seems likely that no complex formation occurs between the zinc ion and the free ethoxyacetic acid.

Since $\bar{n}/[L]$ was independent of both C_M and δ the protolysis of the hydrated central ion seemed to be negligible under the present experimental conditions.

The X-values obtained by graphical integration of the smoothed $\bar{n}/[L]$ -curve are collected in Table 2. The β_n -values were determined graphically by extrapolation to $[L] = 0$ of the successive X_n -functions.

An estimate of the error in the determination of the β_n -values was obtained by repeating the entire graphical procedure on the upper and lower limiting curves of the $\bar{n}/[L]$ -plot.

The following β_n -values were obtained:

$$\begin{aligned}\beta_1 &= (13.5 \pm 0.3) \text{ M}^{-1} \\ \beta_2 &= (74 \pm 4) \text{ M}^{-2} \\ \beta_3 &= (60 \pm 10) \text{ M}^{-3}\end{aligned}$$

The zinc (ethylthio)acetate system. In the main part of the present investigation a buffer with $\delta = 0.206$ was used. The experimental results are collected in Table 3. The E_r -values obtained at $C_M = 20$ mM were extremely small and were hardly expected to give valuable information. The $\bar{n}/[L]$ -values, how-

Table 3. Determination of corresponding values of [L] and $\bar{n}/[L]$ in the zinc (ethylthio)acetate system. The values of E_0 refer to $h_R = 6.27 \times 10^{-5}$ M.

C_L' mM	E_0 mV	$C_M=80$ mM			$C_M=60$ mM			$C_M=40$ mM			$C_M=20$ mM		
		E_L mV	[L] mM	$\bar{n}/[L]$ M^{-1}	E_L mV	[L] mM	$\bar{n}/[L]$ M^{-1}	E_L mV	[L] mM	$\bar{n}/[L]$ M^{-1}	E_L mV	[L] mM	$\bar{n}/[L]$ M^{-1}
8.01	-9.16	21.62	5.19	5.2	16.86	5.74	5.2	11.92	6.34	5.4	6.01	7.20	4.9
11.05	-8.85	18.90	7.21	5.5	14.68	7.95	5.5	10.37	8.75	5.7	5.28	9.87	5.4
14.80	-8.54	16.82	9.76	5.6	12.97	10.76	5.5	9.14	11.80	5.7	4.64	13.24	5.4
19.42	-8.38	15.29	12.91	5.6	11.75	14.20	5.5	8.14	15.63	5.6	4.22	17.38	5.5
28.78	-8.24	13.57	19.31	5.7	10.39	21.21	5.5	7.11	23.37	5.5	3.70	25.84	5.5
37.9	-8.34	12.76	25.5	5.7	9.78	27.9	5.6	6.73	30.7	5.6	3.55	33.9	5.7
51.1	-8.37	11.90	34.7	5.7	9.08	38.0	5.5	6.22	41.7	5.4	3.26	46.0	5.5
68.0	-8.59	11.29	46.4	5.6	8.61	50.8	5.5	5.91	55.6	5.4	3.11	61.2	5.5
88.0	-8.90	10.83	60.3	5.6	8.24	66.0	5.4	5.66	72.2	5.3	2.97	79.3	5.4
124.7	-9.52	10.23	86.4	5.4	7.77	94.4	5.3	5.33	103.0	5.2	2.76	112.9	5.2
163.6	-10.22	9.75	114.7	5.3	7.41	124.9	5.1	5.06	136.0	5.0	2.61	148.7	5.0
206.0	-11.00	9.32	146.1	5.1	7.08	158.7	4.9	4.82	172.4	4.8	2.48	188.0	4.8
253.7	-11.92	8.90	182.2	4.9	6.73	197.5	4.7	4.63	213.6	4.7	2.37	232.3	4.6
299.2	-12.87	8.46	218.1	4.6	6.38	235.7	4.4	4.36	254.2	4.4	2.21	275.5	4.3
340	-13.67	8.20	250	4.5	6.21	269	4.3	4.25	290	4.3	2.15	314	4.2
374	-14.35	7.95	277	4.3	6.02	298	4.2	4.07	321	4.1	2.06	346	4.0
449	-16.03	7.60	337	4.1	5.57	364	3.9	3.81	389	3.8	1.87	418	3.6
561	-18.61	7.01	430	3.8	5.06	463	3.5	3.51	491	3.5	—	—	—
660	-20.88	6.44	517	3.4	4.58	555	3.1	3.18	585	3.2	—	—	—
748	-22.92	5.87	598	3.1	4.16	639	2.8	2.86	671	2.9	—	—	—

ever, fitted well with those obtained at larger C_M -values and were consequently included in the calculations.

No indication of polynuclear complexes was found. The $\bar{n}/[L]$ -values were independent of C_M , which is illustrated in Fig. 2 for smaller [L]-values.

The β_n -values and estimates of the errors in the determination were obtained by the same method as in the ethoxyacetate system. The results were

$$\begin{aligned}\beta_1 &= (5.5 \pm 0.3) M^{-1} \\ \beta_2 &= (16 \pm 1) M^{-2} \\ \beta_3 &= (14 \pm 3) M^{-3}\end{aligned}$$

Measurements were also made at $C_M = 60$ mM with a buffer with $\delta = 0.493$ in order to check if the concentration of free (ethylthio)acetic acid influenced the result of the investigation. As can be seen from Fig. 2 the $\bar{n}/[L]$ -values agreed well with those found in the main investigation. The small deviation at $[L] < 25$ mM is hardly significant. This difference, however, was considered in the estimation of the errors in the β_n -values.

DISCUSSION

In the ethoxyacetate system the experimentally determined \bar{n} reached a value of 2.0 and in the (ethylthio)acetate system a value of 1.9. This is shown

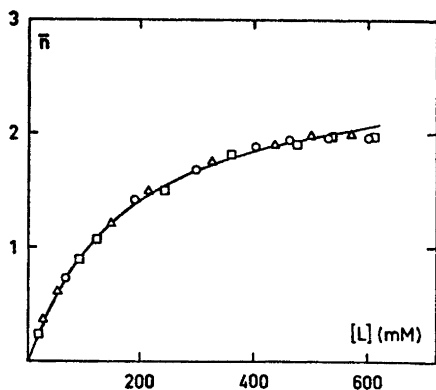


Fig. 3. Some of the experimentally obtained \bar{n} -values in the ethoxyacetate system. $C_M=80$ mM (O), 60 mM (Δ), 40 mM (\square). The full-drawn curve is calculated from the β_n -values listed in Table 5.

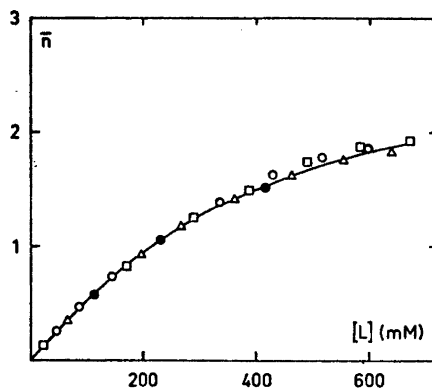


Fig. 4. Some of the experimentally obtained \bar{n} -values in the (ethylthio)acetate system. $C_M=80$ mM (O), 60 mM (Δ), 40 mM (\square), 20 mM (\bullet). The full-drawn curve is obtained by means of the calculated β_n -values in Table 5.

in Figs. 3 and 4. Thus the formation of at least two complexes is indicated in both systems.

In the ethoxyacetate system the relationship between X_1 and $[L]$ was linear at $[L]<40$ mM. For larger $[L]$ -values the X_1 -graph showed a marked curvature, thus indicating that a third complex is formed in an appreciable amount in this system at $[L]>40$ mM. In the (ethylthio)acetate system the X_1 -graph was linear at $[L]<100$ mM. This indicates that the formation of a third complex in this system is not observable until $[L]$ is larger than 100 mM.

For both systems the graph of the X_2 -function was a straight line in the region $100<[L]<600$ (mM). In both systems the β_2 -value obtained from the slope of the X_1 -plot was in good agreement with that obtained from the X_2 -plot.

Thus it is found by the graphical treatment that three complexes are formed in both systems, if the entire material from the measurements is taken into consideration. In both cases, however, the calculation of the third stability constant had to be based on rather small E_L -values corresponding to $[L]>100$ mM. Hence it is obvious that the determination of the stability constants of the third complexes might be influenced by an unknown change in the liquid junction potential and in the activity coefficients caused by the exchange of a considerable part of the perchlorate ions for the ligand ions. The significance of the calculated β_3 -values may therefore be much less than expressed by the stated limits of error, which refer to the scatter in the experimental material.

The calculated stability constants, β_n and K_n , are collected in Table 5. The complexity is weak. The magnitude of the constants and of the quotients between them indicates that the ligands act mainly monodentately. All the β_n -values in the ethoxyacetate system, however, are significantly larger than in the (ethylthio)acetate system. This is in contrast to earlier findings on the

Table 4. X-Values obtained by graphical integration of the $\bar{n}/[L]$ -function for the zinc (ethylthio)acetate system.

$\frac{[L]}{M}$	X([L])	X_1 M ⁻¹	X_2 M ⁻²	X_3 M ⁻³
0	1	5.5	16	14
0.015	1.088	5.9		
0.020	1.118	5.9		
0.030	1.183	6.1		
0.040	1.251	6.3		
0.050	1.322	6.4		
0.060	1.397	6.6		
0.070	1.476	6.8		
0.080	1.558	7.0		
0.100	1.732	7.3		
0.120	1.921	7.7		
0.140	2.13	8.1		
0.170	2.47	8.6	18	
0.200	2.85	9.3	19	
0.250	3.59	10.4	20	16
0.300	4.46	11.5	20	13
0.360	5.70	13.1	21	14
0.420	7.18	14.7	22	14
0.480	8.93	16.5	23	15
0.540	11.0	18.4	24	15
0.600	13.3	20.4	25	15
0.660	15.9	22.5	26	15

complex formation between these ligands and bivalent Cu-, Cd-, and Ni-ions.^{9,10,7} It also differs from the results published by Suzuki and Yamasaki⁵ on the zinc complexes of phenoxy- and (phenylthio)-acetate. On the other hand it is in agreement with the results from investigations on the zinc complexes with more complicated ligands.^{1,2,4}

Since ethoxyacetic acid is stronger than (ethylthio)acetic acid it should be reasonable to ascribe the greater stability of the zinc ethoxyacetate complexes to a certain degree of chelation through the ether oxygen.

Table 5. The stability constants for the ethoxyacetates and (ethylthio)acetates of bivalent zinc and nickel.

	β_1 M ⁻¹	β_2 M ⁻²	β_3 M ⁻³	K_1 M ⁻¹	K_2 M ⁻²	K_3 M ⁻³	$\frac{K_1}{K_2}$	$\frac{K_2}{K_3}$
Zn ²⁺ /C ₂ H ₅ ·O·CH ₂ ·COO ⁻	13.5	74	60 ^a	13.5	5.5	0.8	2.5	7
Zn ²⁺ /C ₂ H ₅ ·S·CH ₂ ·COO ⁻	5.5	16	14 ^a	5.5	2.9	0.9	1.9	3
Ni ²⁺ /C ₂ H ₅ ·O·CH ₂ ·COO ^{-b}	10.5	32	(17)	10.5	3.0	(0.5)		
Ni ²⁺ /C ₂ H ₅ ·S·CH ₂ ·COO ^{-b}	11.0	65	190	11.0	5.9	2.9		

^a cf. the discussion. ^b see Ref. 7.

For the sake of comparison the stability constants of the nickel(II) complexes with the ligands under investigation are included in Table 5. It is evident that the ethoxyacetate ion forms stronger complexes with the zinc ion than with the nickel(II) ion, while the (ethylthio)acetate ion shows larger affinity to the nickel(II) ion than to the zinc ion. In this respect too the ligands under investigation show a clear parallelism to the pair oxydiacetate and thiodiacetate.

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