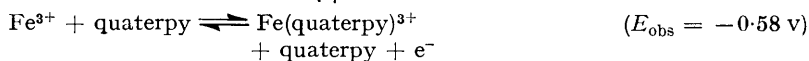
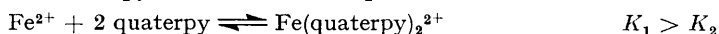
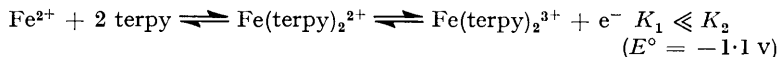
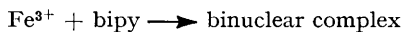
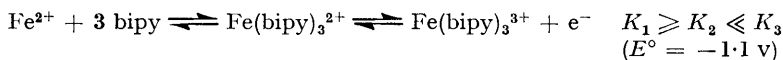


### 304. Complexes of 2,2',2'',2'''-Quaterpyridine with Ferrous and Ferric Ions.

By ARPAD BERGH, PETER O'D. OFFENHARTZ, PHILIP GEORGE,  
and G. P. HAIGHT, jun.

2,2',2'',2'''-Quaterpyridine forms mono- and bis-complexes with  $\text{Fe}^{2+}$ , and a mono-complex with  $\text{Fe}^{3+}$ , with properties which differ from those of 2,2'-bipyridine and 2,2',2''-terpyridine complexes in reactivity and in effect of complex formation on the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  electrode potential. Comparisons of reactions of the three ligands yield the following patterns:



It has been found that complexes of  $\text{Fe}^{2+}$  with 2,2'-bipyridine (bipy) and 2,2',2''-terpyridine (terpy) on addition of the third (bipy) ligand or second (terpy) ligand to  $\text{Fe}^{2+}$  become diamagnetic,<sup>1</sup> also that  $K_3 \geq K_2 \leq K_1$  for  $\text{Fe}(\text{bipy})_n^{2+}$  and  $K_2 \geq K_1$  for  $\text{Fe}(\text{terpy})_n^{2+}$ , where  $K$  is the respective step formation constant.<sup>2-5</sup> Morgan and Burstall<sup>6</sup> prepared several complex salts of 2,2',2'',2'''-quaterpyridine (quaterpy), all with only one ligand per metal atom. Since quaterpyridine cannot combine with  $\text{Fe}^{2+}$  to form complexes in which all nitrogen atoms are co-ordinated and all six octahedral valencies of  $\text{Fe}^{2+}$  are used, the properties of ferrous-quaterpyridine complexes should differ from those of the corresponding bi- and terpyridine systems.

This Paper reports the existence in aqueous solution of  $\text{Fe}(\text{quaterpy})^{2+}$ ,  $\text{Fe}(\text{quaterpy})_2^{2+}$ , and  $\text{Fe}(\text{quaterpy})^{3+}$ . The absorption spectra have been determined and used to measure the formation constants. The oxidation potential of  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  in the presence of quaterpyridine has been determined. Results are compared with similar studies in the literature on bipyridine and terpyridine complexes.

#### RESULTS

*Ferrous Complexes.*—It proved impossible to work at  $\text{pH} > 3.7$  since free quaterpyridine was always precipitated. The insolubility of the free base also prevented direct determination of the ionization constants of the acid-forms of quaterpyridine; the ionization constants could not be measured in a spectrophotometer cell (10 cm.), although the total concentration of all forms of quaterpyridine was less than  $5 \times 10^{-6}\text{M}$ . Thus the measured equilibria all involve protonated forms of quaterpyridine, and at any given pH,  $K_{n,\text{obs}} = K_n \cdot [\text{quaterpy}]/T$ , where  $T = [\text{quaterpy}] + [\text{quaterpyH}^+] + [\text{quaterpyH}_2^{2+}]$ . The formation of more highly protonated species is unlikely, since the observation that bipyridine

<sup>1</sup> Basolo and Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454.

<sup>2</sup> Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 55.

<sup>3</sup> Brandt and Wright, *J. Amer. Chem. Soc.*, 1954, **76**, 3083.

<sup>4</sup> Dwyer and Gyarfás, *J. Amer. Chem. Soc.*, 1954, **76**, 6320.

<sup>5</sup> Brandt, Dwyer, and Gyarfás, *Chem. Rev.*, 1954, **54**, 959.

<sup>6</sup> Morgan and Burstall, *J.*, 1938, 1672.

accepts only one proton in up to 0.1M acid<sup>2</sup> indicates that the protons can only be placed on non-adjacent nitrogen atoms. In agreement with this hypothesis, terpyridine accepts two protons, presumably on the non-adjacent nitrogens.<sup>7</sup>

Fig. 1 shows a continuous-variation plot of absorbance of solutions containing  $[\text{Fe}^{2+}] + [\text{total quaterpy}] = 5 \times 10^{-4}\text{M}$  at pH 3. A sharp break at a concentration ratio of 1:2 indicates the formation of the bis-complex. The existence of a mono-complex is inferred from the equilibrium studies. Individual spectra for the complexes were obtained in

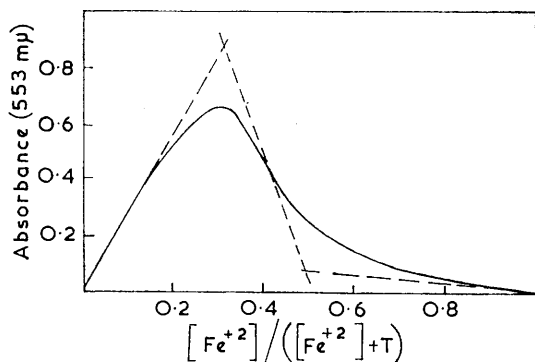


FIG. 1. Job plot showing formation of 1:2 complex  $[\text{Fe}^{2+}] + \text{T} = 5 \times 10^{-4}$  molar.

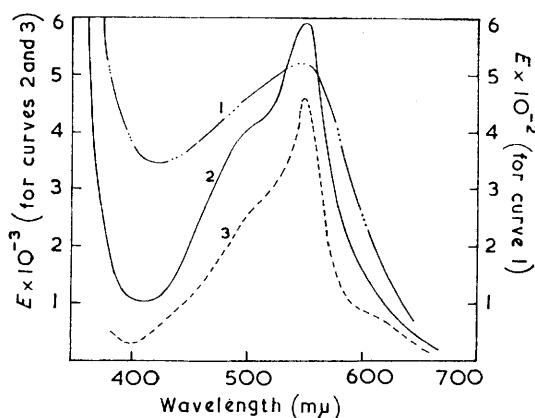


FIG. 2. Visible absorption spectra of (1)  $\text{Fe}(\text{quaterpy})_2^{2+}$ , (2)  $\text{Fe}(\text{quaterpy})_2^{2+}$ , and (3)  $\text{Fe}(\text{terpy})_2^{2+}$ .

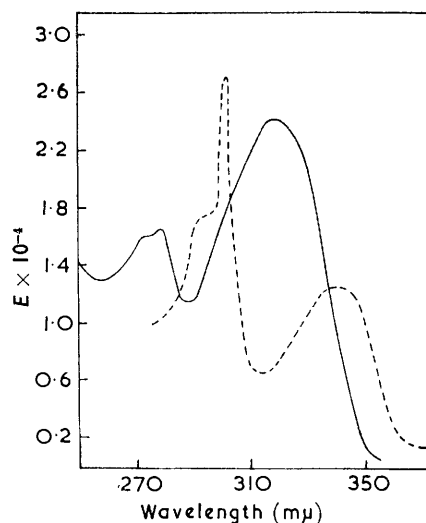


FIG. 3. Ultraviolet absorption spectra of  $\text{Fe}(\text{quaterpy})_2^{2+}$  (solid line) and  $\text{quaterpyH}_2^{2+}$  (dashed line).

solutions containing excess of quaterpyridine (bis) and excess of ferrous ion (mono). Fig. 2 shows the visible absorption spectra of  $\text{Fe}(\text{quaterpy})_2^{2+}$ ,  $\text{Fe}(\text{quaterpy})_2^{2+}$ , and  $\text{Fe}(\text{terpy})_2^{2+}$ . The spectra of the two bis-complexes are strikingly similar. The two quaterpyridine complexes have maxima and minima at very nearly the same wavelengths, but the extinction coefficients for the bis-complex are about ten times those obtained for the mono-complex. For studying equilibria involving both mono- and bis-complexes, measurements were made at 553 and 425  $\text{m}\mu$  and calculations of concentrations were made from the data in Table 1. Fig. 3 shows the ultraviolet spectra of  $\text{Fe}(\text{quaterpy})_2^{2+}$  and  $\text{quaterpyH}_2^{2+}$ . At

<sup>7</sup> Offenhardt, George, and Haight, jun., *J. Phys. Chem.*, 1963, **67**, 116.

TABLE 1.

Wavelength (m $\mu$ ) .....	553	425	410	350
Molar absorbance Fe(quaterpy) <sup>2+</sup> .....	520M	345m	356	9600
Molar absorbance Fe(quaterpy) <sub>2</sub> <sup>2+</sup> .....	5900M	1150	998m	

M = Maximum; m = minimum.

pH *ca.* 2 in the absence of the bis-complex, concentrations of mono-complex and quaterpyH<sub>2</sub><sup>2+</sup> were calculated from absorbances measured at 350 and 315 m $\mu$ . Beer's law is obeyed by all the compounds studied.

*Step Equilibria.*—Table 2 gives data and calculated values of  $K_{2, \text{obs}} = [\text{Fe}(\text{quaterpy})_2^{2+}] / [\text{Fe}(\text{quaterpy})^{2+}]\text{T}$  obtained from solutions containing  $\text{T} = 3[\text{Fe}^{2+}]$  at pH 3.0. It was assumed that all the Fe<sup>2+</sup> is present as either the mono- or the bis-complex in such solutions.

TABLE 2.

Determination of  $K_{2, \text{obs}}$  at 24° for Fe(quaterpy)<sub>2</sub><sup>2+</sup> at pH 3.0.

[Fe <sup>2+</sup> ] mole l. <sup>-1</sup> × 10 <sup>5</sup>	[T] <sub>0</sub> mole l. <sup>-1</sup> × 10 <sup>5</sup>	A <sub>553</sub>	[mono] mole l. <sup>-1</sup> × 10 <sup>5</sup>	[bis] mole l. <sup>-1</sup> × 10 <sup>5</sup>	K <sub>2, obs</sub> l./mole × 10 <sup>4</sup>
5	15	0.210	1.58	3.42	3.3
5	20	0.233	1.15	3.85	3.0
5	25	0.256	0.725	4.28	3.8
5	30	0.262	0.613	4.39	3.5
10	40	0.527	1.17	8.83	3.6
12.5	37.5	0.630	2.00	10.5	3.4

 $K_{2, \text{obs}}$  at 50° = 1 × 10<sup>4</sup> (one determination).

TABLE 3.

Determination of  $K_1/K_2$  at 24° for Fe<sup>2+</sup> complexes at pH 3.0.

[Fe <sup>2+</sup> ] <sub>0</sub> mole l. <sup>-1</sup> × 10 <sup>5</sup>	[T] <sub>0</sub> mole l. <sup>-1</sup> × 10 <sup>5</sup>	A <sub>553</sub>	[mono] mole l. <sup>-1</sup> × 10 <sup>5</sup>	[bis] mole l. <sup>-1</sup> × 10 <sup>5</sup>	K <sub>1/K<sub>2</sub></sub>	K <sub>1, obs</sub> l./mole × 10 <sup>6</sup>
100	33.3	0.195	32.4	0.45	35	1.0
150	33.3	0.186	32.8	0.27	35	1.0
35	15	0.090	14.7	0.25	43	1.3
30	20	0.153	18.0	1.00	30	0.9

Table 3 gives data and calculated values of  $K_1/K_2$  and  $K_{1, \text{obs}} = [\text{Fe}(\text{quaterpy})^{2+}] / [\text{Fe}^{2+}]\text{T}$ , obtained from solutions at pH 3.0 containing  $[\text{Fe}^{2+}] = 1.5 \text{ T}$ . It was assumed that all the ligand was present as mono- or bis-complex in such solutions. The values of  $K_1/K_2$  and consequently those of  $K_{1, \text{obs}}$  are only accurate within an order of magnitude since they involve terms for which the accuracy of measurement is severely limited. For example, an error of only 0.001 in the absorbance  $A$ , in Table 3 changes  $K_1/K_2$  by 5–10%.

At pH 2.0, the formation of Fe(quaterpy)<sub>2</sub><sup>2+</sup> was more easily suppressed and direct measurement of  $K_{1, \text{obs}}$  was possible. Absorbance at 553 m $\mu$  of solutions  $4 \times 10^{-5}\text{-M}$  in both Fe<sup>2+</sup> and quaterpyridine was virtually nil, indicating the absence of bis-complex.  $K_{1, \text{obs}}$  could be determined directly at this pH as shown in Table 4. From  $K_{1, \text{obs}}$  values

TABLE 4.

Sample data for  $K_{1, \text{obs}}$  at pH 2.0 at 21°.

Species at concn. $4 \times 10^{-5}\text{M}$	A <sub>553</sub>	A <sub>350</sub>	Species at concn. $4 \times 10^{-5}\text{M}$	A <sub>553</sub>	A <sub>350</sub>
Bis-complex .....	0.237	—	Quaterpyridine(T) .....	0.000	0.032
Mono-complex .....	0.020	0.384	Fe <sup>2+</sup> .....	0.000	0.000
			Fe <sup>2+</sup> + quaterpyridine(T) ...	0.010	0.146

 $K_{1, \text{obs}} = 1.77 \times 10^4 \text{ l. mole.}$  and is independent of temperature between 9 and 44°.

at pH 2 and 3, it can be shown that the first dissociation constant for quaterpyH<sub>2</sub><sup>2+</sup> is about  $6 \times 10^{-4}$ , quaterpyridine being assumed to be present only as mono- and di-protonated species. This compares with  $5.4 \times 10^{-4}$  found for the first dissociation of terpyH<sub>2</sub><sup>2+</sup>.<sup>7</sup>

At pH 3, the dissociation of Fe(quaterpy)<sub>2</sub><sup>2+</sup> was quite slow in the presence of excess of ferrous ion, while in more acidic solutions the reaction was considerably faster, indicating

that the bis-complex is relatively inert to attack by the ferrous ion, but labile to attack by the hydrogen ion.

*Ferric Complex.*—Fig. 4 shows the absorption spectrum of  $\text{Fe}(\text{quaterpy})^{3+}$ . This complex is formed by direct combination of ferric ion with quaterpyridine in contrast to the observed formation of polynuclear complexes when the ferric ion reacts directly with bipyridine or terpyridine. Oxidation of  $\text{Fe}(\text{quaterpy})_2^{2+}$  with air (slow) or bromine (fast) gives  $\text{Fe}(\text{quaterpy})^{3+}$  and not the bis-complex as with terpyridine. At pH 2.7, the complex dissociates too little to permit study of equilibria. Therefore, equilibrium studies were made in 0.02M-nitric acid by measuring the absorbance at 360  $m\mu$  of solutions, containing  $\text{Fe}^{3+}$  and total quaterpyridine between  $10^{-5}$  and  $20 \times 10^{-5}$ M.  $K_{1,\text{obs}} = [\text{Fe}(\text{quaterpy})^{3+}]/[\text{Fe}^{3+}]\text{T}$ , was  $7.1 \pm 0.8 \times 10^6$  at 23.8° and  $8.3 \pm 0.7 \times 10^6$  at 5.8° and pH 1.7.

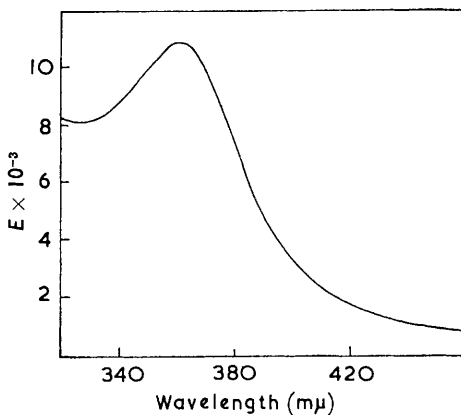


FIG. 4. Absorption spectrum of  $\text{Fe}(\text{quaterpy})^{3+}$ .

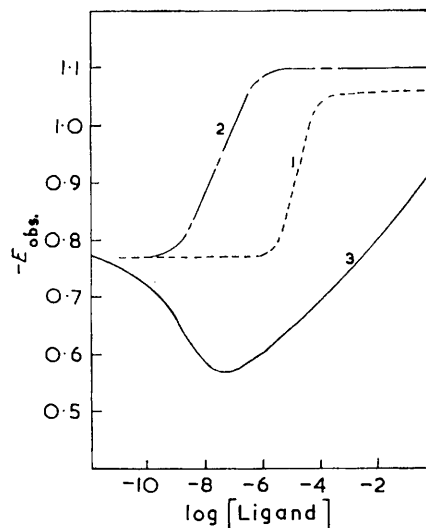


FIG. 5. Plots of  $E$  for  $\text{Fe}^{2+}/\text{Fe}^{3+}$  as a function of concentrations of (1) bi-, (2) ter-, and (3) quater-pyridine.

*Electrode Potential.*—The electrode potential for  $\text{Fe}^{2+}/\text{Fe}^{3+}$  decreases from  $-0.77$  v for the aquo-ions to  $-1.1$  v for the complexed species, when complexes are formed with bi- or ter-pyridine. The effect of quaterpyridine on the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  potential has been calculated by using the equation:

$$E_{\text{obs}} = -0.77 - 0.059 \log \frac{(1 + K_2[\text{quaterpy}] + K_1K_2[\text{quaterpy}]^2)}{(1 + K_1'[\text{quaterpy}])}$$

The graph of this function is shown in Fig. 5. Measurement of the electrode potential with quaterpyridine in excess to give  $\text{T} = 10^{-3}$ M at pH 3 gave a value of  $-0.58$  v, in agreement with the calculated value. The variation of the potential with quaterpyridine concentration does not give the familiar S-shaped curve, since the 1:2 ferric complex is not formed.

#### DISCUSSION

*Thermodynamic Comparisons.*—For comparison of the above results with those obtained with bipyridine and terpyridine, we shall assume that  $pK_1$  and  $pK_2$  for the dissociation of  $\text{quaterpyH}_2^{2+}$  are the same as  $pK_1$  and  $pK_2$  for  $\text{terpyH}_2^{2+}$ , namely 3.3 and 4.7, respectively.

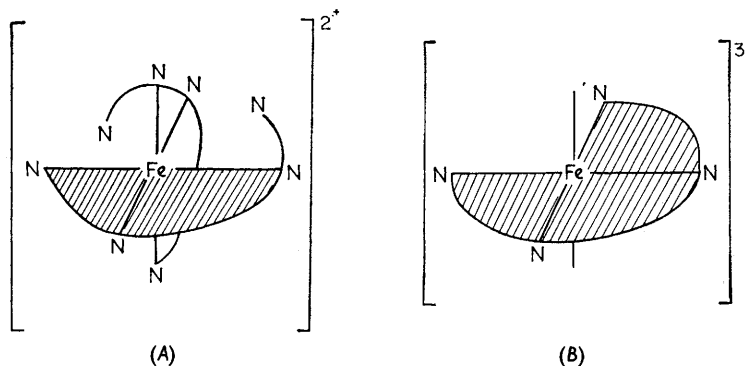
We can thus calculate tentative formation constants for the free base quaterpyridine, and approximate  $\Delta H$  and  $\Delta S$  for reactions as in Table 5.

TABLE 5.

Reaction	$K_{25}$	$\Delta F$ (kcal.)	$\Delta H$ (kcal.)	$\Delta S$ (e.u.)
$\text{Fe(quaterpy)}^{2+} + \text{quaterpyridine} \rightleftharpoons \text{Fe(quaterpy)}_2^{2+}$	$4.5 \times 10^6$	-9.1	-13.5	-15
$\text{Fe}^{2+} + \text{quaterpyridine} \rightleftharpoons \text{Fe(quaterpy)}^{2+}$ .....	$1.5 \times 10^8$	-11.2	-7.5	+12
$\text{Fe}^{3+} + \text{quaterpyridine} \rightleftharpoons \text{Fe(quaterpy)}^{3+}$ .....	$2.5 \times 10^{11}$	-15.6	-9	+22
$\text{Fe}^{2+} + \text{bipyridine} \rightleftharpoons \text{Fe(bipy)}^{2+}$ .....	$2.2 \times 10^4$	-6.0	-7.5	-5.0
$\text{Fe}^{2+} + 3 \text{ bipyridine} \rightleftharpoons \text{Fe(bipy)}_3^{2+}$ .....	$1.15 \times 10^{17}$	-23.1	-24.3	-3.7
$\text{Fe}^{3+} + 3 \text{ bipyridine} \rightleftharpoons \text{Fe(bipy)}_3^{3+}$ .....	$1.6 \times 10^{12}$	-16.4	+1.2	+47.5

The heats of formation of the bi- and quater-pyridine ferrous complexes are similar, but the low entropies for the ferrous bis-complex and the ferric complex of quaterpyridine may indicate strain present in both of these ions. In the ferrous complex, this strain results in an unusually small formation constant, and so  $K_1$  is greater than  $K_2$ . In the ferric complex the strain may permit the bonding of the fourth nitrogen, resulting in unusually high stability.

*Possible Structures for the Quaterpyridine Complexes.*—Molecular models indicate that only three nitrogen atoms of quaterpyridine can join equatorially to octahedral  $\text{Fe}^{2+}$  without severe strain. They also indicate that the fourth pyridine ring should provide steric hindrance for the joining of two quaterpyridine molecules to one  $\text{Fe}^{2+}$ . The fact that a bis-complex is formed and that it gives the same absorption spectrum as  $\text{Fe(terpy)}_2^{2+}$  strongly suggests that the structure is (A)



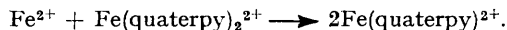
with each nitrogen a part of a pyridine ring. It is just possible that, if the plane of each unco-ordinated pyridine ring is twisted to be parallel to the plane of the other quaterpyridine, a snug fit would be obtained. Such a structure would be consistent with the fact that the bis-complex is labile to proton attack, presumably on the unco-ordinated nitrogen atoms, but inert to  $\text{Fe}^{2+}$  attack since  $\text{Fe}^{2+}$  must co-ordinate with two nitrogen atoms by chelation to form effective bonds.

The failure of  $\text{Fe}^{3+}$  to form either a bis-complex or a binuclear complex could be explained by the formation of a highly-strained porphyrin-like structure with  $\text{Fe}^{3+}$  co-ordinated to all four nitrogens of quaterpyridine in an equatorial plane (B). This would block chelate formation with a second quaterpyridine molecule and prevent the formation of double hydroxyl bridge structures. Oxide bridge structures would still be possible, however.

The possible formation of four co-ordinate links between  $\text{Fe}^{3+}$  and quaterpyridine, and the limit of three quaterpyridine bonds to  $\text{Fe}^{2+}$ , might be explained by recognizing the higher charge density and smaller radius of  $\text{Fe}^{3+}$ , which would tend to reduce the strain imposed on the quaterpyridine ring system.

## EXPERIMENTAL

Quaterpyridine, prepared and kindly donated by F. H. Burstall,<sup>6</sup> was dissolved in 0.03N-nitric acid and insoluble impurities filtered off. Stock solutions of  $\text{Fe}^{2+}$  were prepared by dissolving ferrous ammonium sulphate in 0.01M-sulphuric acid together with small amounts of ascorbic acid to prevent oxidation. A phthalate-hydrochloric acid buffer was used at pH 3. Spectrophotometric studies were made on a Beckman model D.U. spectrophotometer with temperature controlled to  $\pm 0.2^\circ$ . Potential measurements were made with a student potentiometer and a gold *vs.* saturated calomel system of electrodes. Special redistilled water was used which gave no colour when bipyridine and reducing agents were added, assuring the absence of traces of iron.  $\text{Fe}(\text{quaterpy})_2^{2+}$  is oxidized slowly by air, requiring that solutions be protected by ascorbic acid and/or by working under a nitrogen atmosphere. In the study of  $\text{Fe}(\text{quaterpy})_2^{2+}$  at pH 3, reproducible results were obtained only if the order of addition was quaterpyridine,  $\text{Fe}^{2+}$ , buffer, due to the slowness of the reaction



Apparently  $\text{Fe}(\text{quaterpy})_2^{2+}$  forms in the presence of locally high concentrations of quaterpyridine.

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