152. Stereoselective Formation of Ternary Copper(II) Complexes of (*S*)-Amino-acid Amides and (*R*)- or (*S*)-Histidine and (*R*)- or (*S*)-Tyrosine in Aqueous Solution

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Formation constants of ternary complexes of Cu^{II} with (*S*)-amino-acid amides ((*S*)-phenylalaninamide, (*S*)-prolinamide, and (*S*)-tryptophanamide) and (*R*)- or (*S*)-histidine and (*R*)- or (*S*)-tyrosine were determined potentiometrically in aqueous solution. Significant stereoselectivity was presented by all three amides towards histidine, the diastereoisomeric complexes with 'heterochiral' ligands being more stable than those with 'homochiral' ligands (see *Table 3*). The stereoselectivity observed with (*S*)-phenylalaninamide and (*S*)-tryptophanamide may be explained on the basis of hydrophobic stacking interactions between 1*H*-imidazole and the aromatic side chain, favoured by the terdentate behaviour of histidine (see *Fig. 2*), whereas repulsive effects seem to be prevalent with (*S*)-prolinamide. Only (*S*)-prolinamide and (*S*)-phenylalaninamide show appreciable stereoselectivity with tyrosine, which is bidentate, probably on account of repulsive interactions. The present results on the stability of ternary complexes in solution allow to draw some conclusions on the mechanism of chiral discrimination performed by Cu^{II} complexes of (*S*)-amino-acid amides added to the mobile phase in HPLC (reversed phase).

1. Introduction. – Stereoselectivity in mixed-complex formation of copper(II) with amino acids and peptides plays an important role in the activity of biological systems [1], the stereospecific noncovalent interactions being responsible for chiral recognition. The subject has been approached mainly by model systems within the general field of supramolecular chemistry [2].

Diastereoisomeric mixed-complex formation is also involved in chiral discrimination in HPLC, where Cu^{II} complexes of (*S*)-amino acids either covalently linked or dynamically adsorbed on the stationary phase or added to the mobile phase have been used as selectors for the separation of α-amino acids, hydroxy acids, *etc.* according to a mechanism of ligand exchange (LEC; *l*igand-*e*xchange *c*hromatography) [3]. In particular, it was reported that Cu^{II} complexes of (*S*)-amino-acid amides, added to the mobile phase, were able to give enantiomeric separation of dansyl-amino acids [4], unmodified amino acids [5], and hydroxy acids [6] in HPLC (reversed phase). Chiral discrimination was assumed to involve several equilibria: *i*) formation of mixed complexes in aqueous solution, *ii*) formation of mixed complexes on the column stationary phase, *iii*) partition of the species between the aqueous and the stationary phases [7].

In a previous paper [8], we approached the first point, *i.e.*, whether the equilibria of mixed-complex formation in solution are involved in the chromatographic stereoselective separation: in this case, the elution order of the enantiomers should depend on the stability of the diastereoisomeric complexes, and the more stable complex should elute first. In particular, we studied the equilibria of copper(II) with (*S*)-amino-acid amides (prolinamide (Pro-NH_2), phenylalaninamide (Phe-NH_2) and tryptophanamide (Trp-NH_2)) used as selectors and (*R*)- or (*S*)-amino acids (valine (Val), proline (Pro), phenylalanine (Phe), and tryptophan (Trp)) as selectands. Significant stereoselectivity was found for the systems (*S*)-Pro-NH_2/Trp, (*S*)-Phe-NH_2/Pro, and (*S*)-Trp-NH_2/Pro, the diastereoisomeric complexes with 'homochiral' ligands being more stable than those with 'heterochiral' ligands. However, this was in contrast with the elution order observed in HPLC ($k_R < k_S$) [5], thus leading to the conclusion that the equilibria of ligand exchange occurring in aqueous solution do not account for the overall chromatographic discriminative process, but that the affinities of the mixed complexes for the reversed-phase column determine the relative elution order of the enantiomers.

In this work, we report the formation equilibria of the ternary Cu^{II} complexes of the same (*S*)-amino-acid amides, (*S*)-Pro-NH_2, (*S*)-Phe-NH_2, and (*S*)-Trp-NH_2, with two amino acids, *i.e.*, (*R*)- or (*S*)-histidine ((*R*)- or (*S*)-His), which is potentially terdentate, and (*R*)- or (*S*)-tyrosine ((*R*)- or (*S*)-Tyr), which gave different elution orders in the chromatographic separation ($k_S < k_R$ for His and $k_R < k_S$ for Tyr) [5].

Solution studies concerning the stereoselectivity of ternary Cu^{II} complexes of (*R*)- or (*S*)- histidine and amino acids bearing aliphatic or aromatic side chains have already been reported in the literature [9–11]. When the amino acid contains an aromatic ring (Phe or Trp), the 'heterochiral' species is significantly more stable than that containing ligands with the same chirality. With aliphatic amino acids (Ala, Val, Leu, Pro, Ser, Thr), stereoselectivity is either insignificant or slightly in favour of the 'heterochiral' complex. On the basis of both enthalpic and entropic data, it was demonstrated that the terdentate coordination mode exhibited by histidine was the key point for the thermodynamic stereoselectivity observed with phenylalanine and thryptophan, interpreted in terms of noncovalent interactions between *1H*-imidazole and the aromatic residues of the two amino acids [11]. Moreover, electrostatic ligand-ligand interactions or intramolecular H-bonding have been invoked to explain the thermodynamic stereoselectivity of ternary Cu^{II} complexes with histidine and (*S*)-α-amino acids bearing amino, amidic, or hydroxy groups in the side chain [10]. The isolation of diastereoisomeric ternary complexes and the optical resolution of (*RS*)-His were interpreted in terms of the solubility differences induced by the intramolecular H-bonding between the carboxylate of His and the amide group present in the amino-acid side chain, *e.g.*, in (*S*)-citrulline [12].

With regard to the ternary system Cu^{II}-tyrosine/α-amino acids, significant stereoselectivity has been reported with Pro where the 'homochiral' complex is more stable than the 'heterochiral' one, and with Val which shows an opposite behaviour and a smaller stereoselectivity effect [13].

Results and Discussion. – Potentiometric titrations were performed with (*S*)-Pro-NH_2, (*S*)-Phe-NH_2, and (*S*)-Trp-NH_2 in the presence of Cu^{II} and (*R*)- or (*S*)-His and (*R*)- or (*S*)-Tyr, respectively. Protonation and Cu^{II} complex formation constants of (*S*)-His and (*S*)-Tyr were taken from the literature [14] [15] and are reported in *Table 1*, whereas those referred to the (*S*)-amino-acid amides were previously determined by us [8] [16] and are reported in *Table 2*.

Table 1. *Literature Values for Protonation and Cu^II Complex Formation Constants* ($\log\beta$) *of (S)-Histidine* (His) *and (S)-Tyrosine* (Tyr) *Used in the Calculations.* $T = 25°$, $I = 0.1$ M

	His[a])		Tyr[a])
HA	9.09	HA^-	10.11
H_2A^+	15.11	H_2A	19.15
H_3A^{2+}	16.81	H_3A^+	21.32
$[CuAH]^{2+}$	14.13	$[CuAH]^+$	17.91
$[CuA_2H]^+$	23.80	$[CuA_2H_2]$	34.92
$[CuA]^+$	10.16	$[CuA_2H]^-$	25.75
$[CuA_2]$	18.10	$[CuA_2]^{2-}$	15.69
$[Cu_2A_2H_{-2}]$	8.00		
$[CuA_2H_{-1}]^-$	6.80[b])		

[a]) From [14]. [b]) From [15].

Table 2. *Logarithms of Protonation and Cu^II Complex Formation Constants* ($\beta_{pqr} = [[Cu_pL_qH_r]]/[Cu]^p[L]^q[H]^r$) *of (S)-Tryptophanamide* (Trp-NH_2), *(S)-Phenylalaninamide* (Phe-NH_2), *and (S)-Prolinamide* (Pro-NH_2). $T = 25°$, $I = 0.1$ M (KCl). Standard deviations are given in parentheses.

	Trp-NH_2[a])	Phe-NH_2[b])	Pro-NH_2[b])
HL^+	7.49(1)	7.26(1)	8.69(1)
$[CuL]^{2+}$	4.70(1)	4.42(1)	5.74(1)
$[CuL_2]^{2+}$	8.86(1)	7.84(2)	10.36(3)
$[CuLH_{-1}]^+$	−1.99(4)	−2.08(3)	−0.86(2)
$[CuL_2H_{-1}]^+$	2.73(1)	1.90(2)	3.87(2)
$[CuL_2H_{-2}]$	−4.93(1)	−5.46(2)	−3.62(1)

[a]) From [8]. [b]) From [16].

Ternary Systems Cu^II/(S)-Amino-acid Amide/(R)- or (S)-Histidine. The treatment of the potentiometric data by the program HYPERQUAD [17] revealed the formation of the species $[CuLA]^+$ and $[CuLH_{-1}A]$, (L = amide, HA = His), as reported for Gly-NH_2 [18]. Another complex, $[CuLAH]^{2+}$, included in the model, was rejected during the refinement. The stability constants obtained for (*S*)-Pro-NH_2, (*S*)-Phe-NH_2, and (*S*)-Trp-NH_2 are reported in *Table 3*. A species distribution diagram for the Cu^{II}/(*S*)-Phe-NH_2/(*R*)-His system as a function of pH is presented in *Fig. 1*.

The enantioselectivity can be evaluated by considering the difference between the $\log\beta$ values of the diastereoisomeric complexes formed by each (*S*)-amide with the (*R*)- ($\log\beta_{SR}$) and with the (*S*)-amino acid ($\log\beta_{SS}$):

$$\Delta\log\beta = \log\beta_{SR} - log\,\beta_{SS}$$

All the (*S*)-amino-acid amides examined present significant stereoselectivity towards (*R*)- and (*S*)-His with a $\Delta\log\beta$ always positive, both for $[CuLA]^+$ and $[CuLH_{-1}A]$ (*Table 3*). The results are consistent with a terdentate behaviour of His with (*S*)-amides. A terdentate coordination mode of His in ternary Cu^{II} complexes with some amino acids is supported by solution [9–11] and solid-state [19] [20] studies. The complexes reported present a distorted pyramidal tetragonal geometry with *cis* configuration in the plane and a carboxylate O-atom at the apical position. On the ground of calorimetric studies [11], it has been proposed that also in solution, the *cis* structure is favoured for the mixed

Table 3. *Formation Constants* ($\log \beta_{pqrs} = [[Cu_pL_qA_rH_s]]/[Cu]^p[L]^q[A]^r[H]^s$) *of the Ternary Cu^{II} Complexes of (R)- or (S)-Histidine and (R)- or (S)-Tyrosine with (S)-Pro-NH$_2$, (S)-Phe-NH$_2$, and (S)-Trp-NH$_2$.* $T = 25°$ and $I = 0.1$ M (KCl). Standard deviations are given in parentheses. L = Amino-acid amide, A = Amino acid.

	(*S*)-Pro-NH_2			(*S*)-Phe-NH_2			(*S*)-Trp-NH_2		
	(*R*)-His	(*S*)-His	$\Delta\log\beta$[a])	(*R*)-His	(*S*)-His	$\Delta\log\beta$[a])	(*R*)-His	(*S*)-His	$\Delta\log\beta$[a])
$[CuLA]^+$	15.43(1)	15.37(1)	0.06(1)	14.65(1)	14.45(1)	0.20(1)	15.66(1)	15.22(1)	0.44(1)
$[CuLH_{-1}A]$	7.54(1)	7.31(2)	0.23(2)	6.93(1)	6.74(1)	0.19(1)	7.63(1)	7.27(2)	0.36(2)
s^2 [b])	0.92	1.88		0.96	0.66		0.88	0.66	
n	410	469		345	329		419	411	
	(*S*)-Pro-NH_2			(*S*)-Phe-NH_2			(*S*)-Trp-NH_2		
	(*R*)-Tyr	(*S*)-Tyr	$\Delta\log\beta$[a])	(*R*)-Tyr	(*S*)-Tyr	$\Delta\log\beta$[a])	(*R*)-Tyr	(*S*)-Tyr	$\Delta\log\beta$[a])
$[CuLAH]^+$	23.04(2)	23.23(2)	−0.19(3)	21.80(2)	21.75(2)	0.05(3)	22.27(2)	22.33(2)	−0.06(3)
[CuLA]	16.24(1)	16.53(1)	−0.29(1)	15.09(1)	15.05(1)	0.04(1)	15.24(2)	15.33(2)	−0.09(3)
$[CuLH_{-1}A]^-$	6.67(1)	6.77(1)	−0.10(1)	5.58(2)	5.34(2)	0.24(3)	5.66(2)	5.62(2)	0.04(3)
s^2 [b])	1.32	1.80		2.40	1.49		1.90	2.37	
n	460	360		511	442		478	462	

[a]) $\sigma(\Delta\log\beta) = [\sigma^2(\log\beta_{SR}) + \sigma^2(\log\beta_{SS})]^{1/2}$. [b]) $s^2 = \Sigma\, w_i\,(E_i^o - E_i^c)^2/(n-m)$ = sample variance; $w_i = 1/\sigma_i^2$, where σ_i is the expected error on each experimental *e.m.f.* value (E_i^o); *n* = number of observations; *m* = number of parameters refined.

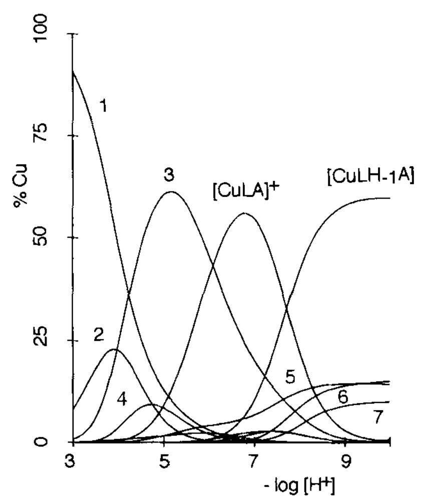

Fig. 1. *Species distribution for the Cu^{II}/(S)-Phe-NH$_2$/(R)-His 1:1:1 system, with $c_{Cu} = 0.001$M, as a function of $-\log[H^+]$.* Curve *1*: Cu^{2+}; *2*: $[CuAH]^{2+}$; *3*: $[CuA]^+$; *4*: $[CuA_2H]^+$; *5*: $[CuA_2]$; *6*: $[CuL_2H_{-2}]$; *7*: $[Cu_2A_2H_{-2}]$.

His/Phe and His/Trp complexes [CuLA], and the positive stereoselectivity ($\Delta\log\beta > 0$) has been attributed to intramolecular noncovalent stacking interactions between the side chains of the two amino acids. The present data for Phe-NH_2 and Trp-NH_2 show a similar behaviour ($\Delta\log\beta > 0$), both for $[CuLA]^+$ and $[CuLH_{-1}A]$, and it seems, therefore, reasonable to suggest that solvophobic stacking interactions between the 1*H*-imidazole ring and the aromatic residue are also operative in our systems. Inspection of molecular models shows that only in the *cis*-$[CuLH_{-1}A]$ isomer, the indole moiety of (*S*)-Trp-NH_2

(*Fig. 2*) or the aromatic ring of (*S*)-Phe-NH_2, can give a hydrophobic stacking interaction with the 1*H*-imidazole group of (*R*)-His, which, in the case of (*S*)-His, is prevented by the presence of the carboxylate group in the apical position.

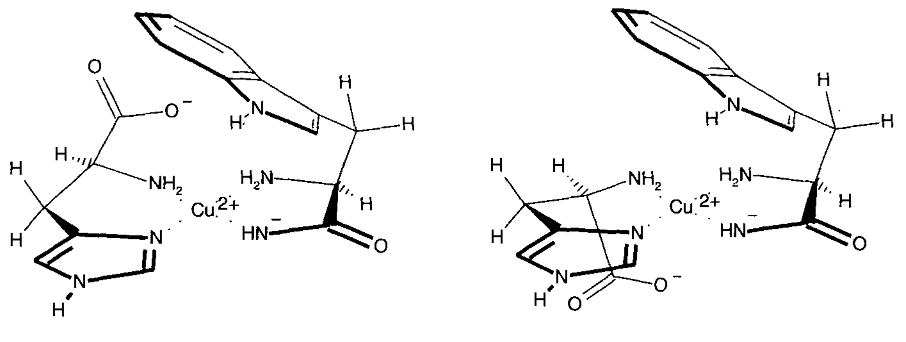

Fig. 2. *Proposed structures for the two diastereoisomeric ternary complexes* cis-*[$CuLH_{-1}A$], where L = (*S*)-Trp-NH_2 and A = (*R*)- or (*S*)-His*

Significant stereoselectivity ($\Delta \log \beta = 0.23$) is also found for (*S*)-Pro-NH_2, though only for the species [$CuLH_{-1}A$], in contrast with what was observed with the corresponding amino acid (*S*)-Pro ($\Delta \log \beta = 0$) [10]. In this case, only repulsive interactions between the pyrrolidine ring of (*S*)-Pro-NH_2 and the (*S*)-His carboxylate appear to be responsible for the stereoselectivity observed.

*Ternary Systems Cu^{II}/(*S*)-Amino-acid Amide/(*R*)- or (*S*)-Tyrosine.* The model which best fitted the experimental data obtained with the three amides (L) consists of the complexes $[CuLAH]^+$, [CuLA], and $[CuLH_{-1}A]^-$, as reported in *Table 3*. An example of the species distribution diagram for Cu^{II}/(*S*)-Pro-NH_2/(*R*)-Tyr is presented in *Fig. 3*. We can write the formula of the complex [CuLA], which is formed between pH 7 and 9, as [$CuLH_{-1}(AH)$], where AH^- represents Tyr with the protonated phenolic group. If we compare the equilibrium of *Eqn. 1* for Tyr with the equilibrium of *Eqn. 2* for Phe [8], nearly the same log *K* values (−6.8 and −7.0, resp.) are obtained, which are indicative of the deprotonation of an amidic group in both cases. In fact, the dissociation of the phenolic group in [$CuLH_{-1}(AH)$] occurs above pH 9, as supported by the constants of the equilibrium of *Eqn. 3* which are close (in the log *K* range between −9.5 and −9.7) to the values reported (between −9.5 and −9.6) for the mixed complexes Cu^{II}/Tyr/amino acid [21].

$$[CuLAH]^+ = [CuLA] + H^+ \quad (1)$$

$$[CuLA]^+ = [CuLH_{-1}] + H^+ \quad (2)$$

$$[CuLH_{-1}(AH)] = [CuLH_{-1}A]^- + H^+ \quad (3)$$

From the $\Delta \log \beta$ values of *Table 3*, it appears that (*S*)-Pro-NH_2 and (*S*)-Phe-NH_2 (in $[CuLH_{-1}A]^-$) show stereoselectivity towards (*R*)- and (*S*)-Tyr, whereas (*S*)-Trp-NH_2 does not present appreciable stereoselectivity. In particular, with (*S*)-Pro-NH_2 the 'homochiral' species (*S,S*) is more stable than the 'heterochiral' (*S,R*), whereas with (*S*)-Phe-NH_2, the opposite happens. It is worth noting that the stereoselectivity observed for

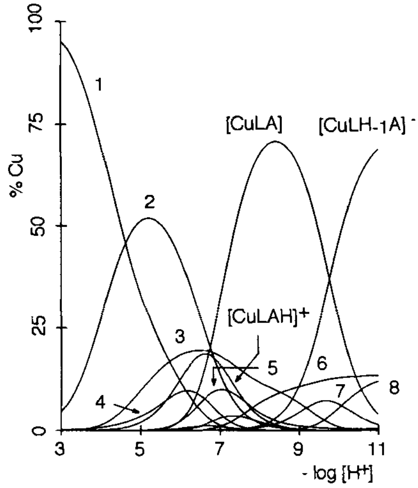

Fig. 3. *Species distribution for the Cu^{II}/(S)-Pro-NH_2/(S)-Tyr 1:1:1 system, with c_{Cu} = 0.001 M, as a function of* $-\log[H^+]$. Curve *1*: Cu^{2+}; *2*: $[CuAH]^+$; *3*: $[CuA_2H_2]$; *4*: $[CuL]^{2+}$; *5*: $[CuLH_{-1}]^+$; *6*: $[CuL_2H_{-2}]$; *7*: $[CuA_2H]^-$; *8*: $[CuA_2]^{2-}$.

Cu^{II}/(*S*)-Pro-NH_2/Tyr is analogous ($\Delta \log \beta < 0$) to that reported [13] for Cu^{II}/Pro/Tyr (−0.19, [CuLAH], L = Pro, AH^- = tyrosinate). In agreement with the results reported in the literature, the phenolate group of Tyr does not coordinate to the Cu^{II} ion, so that the formation constant is close to that observed for phenylalanine itself [21]. The complex with (*S*)-Pro-NH_2 is probably *cis*, as already proposed for the mixed complexes with other bidentate amino acids [8], whereas the complex with (*S*)-Phe-NH_2 is *trans*.

In conclusion, the relative stabilities of the diastereoisomeric complexes in solution ($\log \beta_{SR} > \log \beta_{SS}$) do not account for the chromatographic separation of (*RS*)-His by (*S*)-Pro-NH_2 ($k_S < k_R$) ($\log \beta_{SR} > \log \beta_{SS}$). The elution order of (*R*)- and (*S*)-Tyr is the same ($k_R < k_S$) with (*S*)-Pro-NH_2 and (*S*)-Phe-NH_2, whereas the enantioselectivity observed in solution is different ($\log \beta_{SS} > \log \beta_{SR}$ *for* (*S*)-Pro-NH_2; $\log \beta_{SR} > \log \beta_{SS}$ for (*S*)-Phe-NH_2). It appears, once more, that the major factor which determines the elution order in the chromatographic system is the affinity of the mixed complexes for the column. Only in the case of (*S*)-Phe-NH_2, the chromatographic behaviour of Tyr is in agreement with the stereoselectivity observed in solution: the (*S*,*R*)-complex, which has both the side chains of the selector and the selectand in a *trans* position, is more stable and elutes first, mainly on account of the reduced interactions with the column. The (*S*,*S*)-complex, which has both side chains on the same side of the coordination plane, is more strongly retained by the column.

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Experimental Part

Reagents. (*S*)-Phenylalaninamide, (*S*)-prolinamide, and (*S*)-thryptophanamide hydrochlorides (*Sigma*), (*R*)- and (*S*)-histidine, (*R*)- and (*S*)-tyrosine (*Aldrich*) were all of high purity and used as received. The elemental analysis (C, H, N) of all the ligands gave acceptable results. Their purity was checked by means of potentiometric titrations with KOH soln. The ligands were dried (P_4O_{10}) *in vacuo*, and stock solns. (*ca.* 0.2M) were prepared by weight and used within 2–3 days. Cu^{II}, KOH, and HCl solns. were prepared and standardized as already reported [8]. All solns. were prepared with bidistilled freshly boiled H_2O.

Potentiometric Measurements. Computer-controlled titrations were performed using a 5-ml *Metrohm-655-Dosimat* motor-burette and a *Radiometer-PHM64* digital voltmeter equipped with *B2905* glass and *E7786* KCl-sat. calomel *Ingold* electrodes. The electrodic chain was standardized in terms of $[H^+]$ by titrating HCl solns. (0.01M) in a starting volume of 50 ml with standard KOH soln. (*ca.* 0.2M in 0.1M KCl). The PC program BEATRIX [22], based on the *Gran* method [23], was used to calculate the equivalence volume, v_e, the electrode couple standard potential, E^o, and pK_w (13.77(1)). The experiments were carried out at 25.0 + 0.1° and $I = 0.1$M (KCl) under an N_2 stream previously saturated with H_2O vapor in 0.1M KCl.

Appropriate aliquots of the soln. of the ligands, Cu^{II}, and HCl were added in the cell, and the volume was adjusted to 50 ml with H_2O.

For each of the ternary systems considered, five or six alkalimetric titrations were performed with Cu/L/A ratios 1:1:1 and 1:2:1 ($c_{Cu} = 0.001$–0.002M). The pH range explored varied between *ca.* 3.0 and 10.0 for histidine, and between *ca.* 3.0 and 10.8 for tyrosine.

Calculations. The stability constants were calculated by the computer program HYPERQUAD [17], which employs the sum of the weighted squares of the residuals between observed and calculated *e.m.f.* values as the optimization function. The weighting of the exper. observations takes into account the errors of both *e.m.f.* and titrant volume, they were estimated as 0.2 mV and 0.008 ml, resp. During the refinement of the trial, $\log\beta$ values for the ternary complexes, the protonation and binary Cu^{II} complexation constants were fixed. For each system, the data from different titrations were treated in a unique batch.

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