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Desorption of crown ether–alkali metal ion complexes in liquid secondary ion mass spectrometry (LSIMS)

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The liquid secondary ion mass spectra of crown ether solutions containing an equimolar mixture of alkali halides display large differences in the relative abundances of the crown ether–cation complexes formed, depending on various desorption yields. The results presented here show that from dilute solutions of samples, the less solvated ion species lead to better sensitivities. At higher concentrations, the matrix hydrophilicity plays an important role by discriminating between the mixed complexes in favour of those possessing both a surface activity and limited interactions with the solvent. The desorption of other ions is delayed by a slower desolvation, thus increasing the ion pairing by recombination with the anions present. This leads to an ion signal suppression in the case of strongly solvated complexes (lithium complexes) or anions (chlorides). Use of hydrophobic matrices limits considerably the solvation energy of the dissolved complexes thus reducing the discrimination between the complexes towards the desorption process. Provided that an appropriate choice of matrix, counteranion and other experimental parameters has been made, the desorption of crown ether–alkali cations does not suffer from any discriminatory effect.

Mass spectrometry using a fast-atom bombardment or a cesium ion beam as ionizing agent (FAB and LSIMS) has gained an increasingly important role by virtue of its ability to transfer polar and involatile chemical substances introduced in a liquid matrix into the gas phase.[1] The processes of energy transfer from the fast incident particles to the molecules dissolved in the matrix and the mechanisms leading to isolated ions in the gas phase are not fully understood. Instead of a unique desorption model, several processes would account for different experimental situations responsible for the diversity of the secondary ions produced: molecular ions ($M^{+\bullet}$), protonated molecules ($[M + H]^+$), 'cationized' molecules ($[M + C]^+$, where M is a molecule and C a metal cation) and ions arising from chemically modified molecules.[2]

The gas-phase transfer, from a dissolved sample, of cationized molecules $[M + C]^+$ gave rise to a growing interest for mass spectrometric studies of the interactions between organic molecules and metal salts. Although the 'cationisation' mechanism remains unknown,[3] some experimental results suggest that the mass spectra may reflect the equilibrium established in the matrix solution.[4] This assumption has been developed for studying crown ethers and other macrocyclic ligands of metallic cations allowing metal cation selectivity measurements[5] and, in some cases, an evaluation of the corresponding stability constants.[6] These investigations make use of the $[M + C]^+$ relative intensities which are expected to be proportional to the complex concentrations in the matrix. Various strategies have been proposed: (i) comparison of various ligand to metal concentration ratios of the $[M + C]^+$ relative abundance with respect to that of the protonated molecule $[M + H]^+$; (ii) observation of the variations of the complex ion intensity relative to that of an internal reference (a matrix ion for example); (iii) comparison of the relative intensities of complex ion peaks produced by competitive binding of metals in equimolar amounts by a limited quantity of ligand. Although the formation of ligand–cation complexes in the solution phase is in no doubt,[7] especially in the case of high cationic affinity ligands such as crown ethers,[8] the different behaviour of complexes mixed together in the matrix towards the desorption process are generally considered as a minor parameter or even ignored. Recently, we have shown that the desorption efficiency of complexes formed by 15-crown-5 with sodium cations was twenty-fold lower than that of the 15-crown-5–potassium complex when using a glycerol matrix.[6b] The dramatic effect of the liquid matrix on the desorption rates of the $[M + C]^+$ complexes was underlined recently by G. J. Langley *et al.*[9] These authors also observed that the relative abundances of $[M + H]^+$ and $[M + C]^+$ ions 'differ enormously'. Hence, a better knowledge of the factors influencing the desorption of cationized molecules from the solution phase is desirable for both the theoretical and analytical purposes.

From a practical point of view, the cationized molecules are often produced in a high yield and seem to be particularly stable as demonstrated by their limited fragmentation. Thus, these ion species are good candidates for collision-induced dissociation studies (CID). The fragmentations activated by collision of molecules cationized by alkali, alkaline earth and transition metal ions are of structural interest for many types of compounds (peptides, oligosaccharides, aliphatic acids, *etc.*).[10]

In this paper, we propose to examine the influence on the desorption efficiency of crown ether–alkali metal ions complexes of some experimental factors such as the complex concentration in the matrix, the cesium bombardment duration, the cation size relative to the crown ether diameter, the matrix hydrophilicity and the type of anion present in the matrix. All these parameters seem to play a very significant role in the desorption process of the complex ions formed in the solution phase. They provide some indications on the mechanism of $[M + C]^+$ ions desorption and suggest also experimental protocols convenient for mass spectrometric analysis of ligand–cation complexes.

Results and discussion

Influence of the concentration of 18-crown-6–alkali cation complexes on their desorption efficiency

Our strategy is essentially based on the study of the ion peak intensities of crown ether–cation complexes of three different alkali metal ions introduced together in a liquid matrix

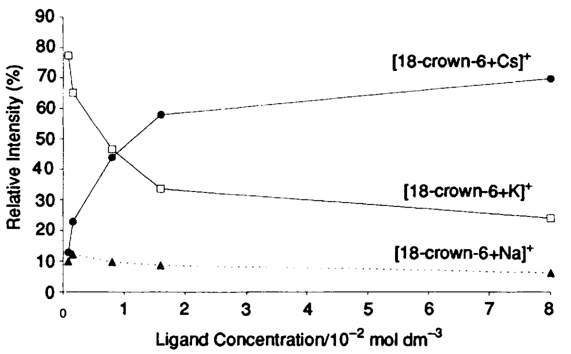

Fig. 1 Relative intensities of the ion peaks corresponding to the sodium, potassium and cesium complexes formed with 18-crown-6 at different concentrations

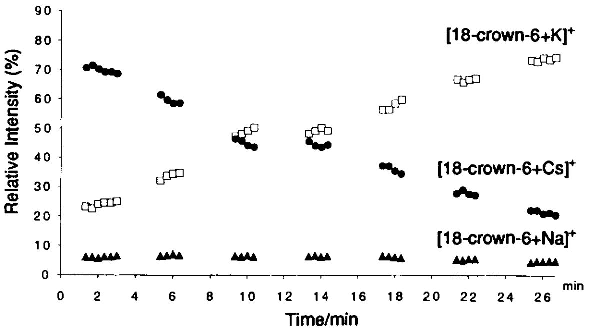

Fig. 2 Relative intensities of the ion peaks corresponding to the sodium, potassium and cesium complexes formed with 18-crown-6 as a function of the bombardment duration

containing a fixed amount of crown ether, in the same way as the pioneering works of Johnstone *et al.*[5a–c]

The stability constants of 18-crown-6–alkali cations complexes are known to be sufficiently large such that alkali cations mixed with an excess of 18-crown-6 could be considered as totally complexed by the ligand.[11] By using an equimolar mixture of three alkali metal cations (Na^+, K^+, Cs^+) in the presence of an excess of crown ether, each complex should be formed in the same concentration ($[M + Na]^+ = [M + K]^+ = [M + Cs]^+$). Consequently, the differences of ion peak intensities observed in the mass spectra of such complex mixtures should be related to different desorption behaviour of the complexes rather than to different concentrations in the matrix. In practice, we have maintained the concentration of salts to half of the ligand concentration. However, some experimental precautions must be taken: (i) no contamination of the analyte or the matrix by metal cations, (ii) no competitive complexation of the cations by the matrix, (iii) no formation of dimeric 'sandwich-type' complexes. These prerequisites dictate the choice of several parameters such as the matrix used or the concentration range of both the ligand and the alkali metal salts.

Fig. 1 shows the relative intensities of the ion peaks of the sodium, potassium and cesium complexes formed with 18-crown-6 at different concentrations {in this paper, the relative intensity values correspond to the ratio $[M + C_i]^+/([M + C_1]^+ + [M + C_2]^+ + [M + C_3]^+)$}. The desorption efficiency of the potassium complex is higher than those of cesium and sodium complexes only for the lower complex concentrations. In this case, the relative abundances can be correlated with the hydration numbers of the alkali metal–18-C-6 complexes (potassium 0, cesium 0.9 and sodium 1.3)[12] or to the free energies of transfer from water to methanol of these cations complexed by 18-crown-6 [-1.77, -1.33 and -1.56 kcal mol^{-1} (1 cal = 4.184 J) for the potassium, cesium and sodium complexes, respectively].[13] This can be explained by the lower solvation energy of the potassium complex, which is expected to play a significant role in a hydrophilic matrix (glycerol was used in this experiment). By comparison with the potassium complex and with the 18-crown-6–lithium complex which does not appear at all in such matrix and concentration conditions, the sodium and cesium complexes behave similarly with an intermediate desorption efficiency.

However, by increasing the complex concentrations, the ion current of the potassium complex decreases suddenly in favour of the cesium complex, whereas the sodium complex relative intensity remains almost constant. This spectacular reversal suggests that, for more concentrated solutions, factors other than the solvation energy are involved in the desorption process. For example, the surface activity of the sample proved to be an important factor of the desorption rate in fast-atom bombardment mass spectrometry.[14] Thus, previous works showing a strong dependence of secondary ion emission from solutions on surface phenomena on the one hand, and the role of surface activity appearing to vary with time on the other hand,[15] prompted us to investigate the effect of bombardment duration on the desorption rates of 18-crown-6–alkali metal ions complexes.

Influence of the bombardment duration on the desorption of 18-crown-6–alkali cation complexes

Fig. 2 displays the time dependence of the $[M + C]^+$ ions formed by complexation of Na^+, K^+ and Cs^+ with 18-crown-6 at a concentration ratio of 0.5 (total salt concentration/crown concentration). The initial concentration of 18-crown-6 was 8×10^{-2} mol dm^{-3}, the highest concentration reported in Fig. 1. While the signal of the cesium complex decreases with time, the relative intensity of the potassium complex increases. This behaviour is likely to be due to the surface effects investigated earlier by other authors.[15] The more surface active species are uniformly dispersed across the surface and the excess of analyte is removed by sputtering thus resulting in high ion currents during the first minutes of the bombardment. Progressively, the less surface-active compounds are forced to the surface both by sputtering and evaporation of the upper layers of the matrix. Their ion signals then increase with time and dominate the spectra toward the end of the experiment.[15]

In the case of 18-crown-6–alkali metal ions complexes, such a surface heterogeneity is also supported by the fact that the spectacular decrease of the cesium complex relative intensity with time was only observed by using a high-voltage ion source. The data displayed in Fig. 2 were indeed obtained with a sector instrument operating at 4 kV. By performing the same experiment on a quadrupole instrument at only 20 V of accelerating voltage, no significant changes in the relative intensities of the different $[M + C]^+$ ions were observed during the twenty minutes of the experiment. This can be explained by the fact that the residual electrostatic field near the matrix surface is quite negligible in this experiment by contrast with the high-voltage ion source. As the extraction voltage exerts its force in a very small distance within the 'selvedge' (the selvedge is the high density hot gas located at or near the surface),[7] its effect on the desorption of the cesium complex reinforces the hypothesis of a better surface activity of this complex relative to that of the sodium or potassium complexes. The over-concentration of the 18-crown-6–cesium complex in the upper layers of the matrix could be explained by the principal characteristic of this complex, that is to say, the large cesium cation size relative to the crown ether 'cavity' diameter (Table 1). The position of cesium out of the plane of the ligand should lead to a structure composed of a hydrophilic region containing the cation and the co-ordinating oxygen atoms and a hydrophobic moiety comprising the methylene groups of the ligand. This could confer to the complex an amphiphilic behaviour responsible for the surface activity observed in the LSIMS experiments.

Table 1 Ionic diameter/cavity size ratios (R) for various crown ether–alkali cation complexes, and their corresponding $[M + C]^+/[NBA + H]^+$ intensity ratios

Cation	Ionic diameter (Å)[a]	Complex	R	$[M + C]^+/[NBA + H]^+$
Li^+	1.36	$[12\text{-crown-}4 + Li]^+$	1.00	0.14
Na^+	1.94	$[12\text{-crown-}4 + Na]^+$	1.44	6.5
K^+	2.66	$[12\text{-crown-}4 + K]^+$	1.97	0.4
Cs^+	3.34	$[12\text{-crown-}4 + Cs]^+$	2.47	0.14
		$[15\text{-crown-}5 + Li]^+$	0.70	1.95
		$[15\text{-crown-}5 + Na]^+$	1.00	3.5
Crown ether	Cavity size (Å)[a,b]	$[15\text{-crown-}5 + K]^+$	1.36	15.8
12-crown-4	1.2–1.5	$[15\text{-crown-}5 + Cs]^+$	1.71	6.15
15-crown-5	1.7–2.2	$[18\text{-crown-}6 + Li]^+$	0.46	1.85
18-crown-6	2.6–3.2	$[18\text{-crown-}6 + Na]^+$	0.67	3.2
		$[18\text{-crown-}6 + K]^+$	0.92	3.7
		$[18\text{-crown-}6 + Cs]^+$	1.15	7.6

[a] Ref. 16. [b] R ratios were calculated by using the mean value of cavity size.

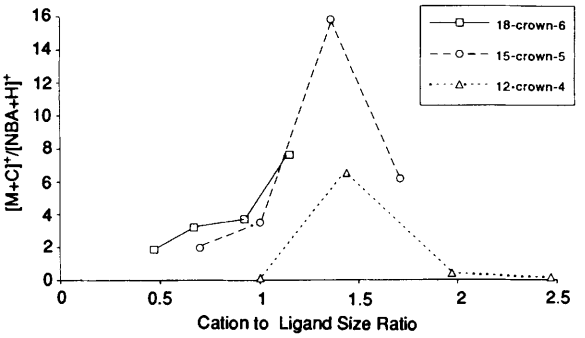

Fig. 3 Dependence of the $[M + C]^+/[NBA + H]^+$ intensity ratio on the cation to ligand size ratio of complexes formed with M = 18-crown-6, 15-crown-5 or 12-crown-4, and C = Li, Na, K or Cs (the data are listed in Table 1)

Influence of the cation size relative to the 'host' cavity diameter on the desorption of crown ether–alkali cation complexes

The surface activity of the 18-crown-6–cesium complex, if related to the size of the cesium relative to the crown ether cavity diameter, should be observed in other cases where the cation sizes exceed those of the crowns. For this purpose, we have compared the desorption efficiency of complexes formed by three different crown ethers (18-crown-6, 15-crown-5 and 12-crown-4) with four alkali cations (Li^+, Na^+, K^+, Cs^+). Equimolar mixtures of three cations, among the four investigated, were added to the crown solutions so that the total concentration of cations was maintained at half the ligand concentration in the matrix (8×10^{-2} mol dm^{-3}). The choice of *meta*-nitrobenzyl alcohol (NBA) as the matrix was dictated by the required sensitivity and reproducibility of ion peak intensities of all the studied complexes (the desorption efficiencies of lithium complexes or of complexes formed with 12-crown-4 are often weak and unreproducible in other matrices).

In order to compare the desorption rates of complexes formed by the different ligands, we have used the relative intensities of each of their corresponding ion peaks with respect to a common ion arising from the matrix ($[NBA + H]^+$ at m/z 154). We made this choice because the formation of the protonated matrix molecule should not be influenced by the change of one crown to another and because cation complexation by the matrix, which could be competitive to the protonation process, does not occur. The spectra were recorded during the first minutes of the cesium bombardment.

The results are shown in Fig. 3. They demonstrate a strong dependence of the desorption efficiency on the ion to ligand size ratio (R). The better desorption yields are observed for R exceeding 1. This is the case for the 18-crown-6–cesium (R = 1.15), 15-crown-5–potassium (R = 1.36) and 12-crown-4–sodium (R = 1.44) complexes. For higher cation to ligand size ratios, the desorption efficiencies of complexes fall spectacularly (15-crown-5–Cs^+, 12-crown-4–K^+, 12-crown-4–Cs^+). With a cation external to the ligand, the interactions with the counter-ion and the solvent are much stronger. This can lead either to neutralization of the cation charge by ion pair formation with the counter-anion or to an increase of the solvation energy responsible for a delayed desorption. Thus, the better desorption efficiency of crown ether–alkali cation complexes is obtained when a good compromise between the solvation forces and the surface activity, implying an eccentric position of the cation, is obtained.

It is noteworthy that the optimal cation to ligand size ratios remain the same when glycerol is used as solvent in place of NBA. However, some important differences are observed: (i) the lithium complexes can not be detected in glycerol, (ii) the differences of desorption rates are much larger in glycerol than in NBA. Therefore, the matrix hydrophilicity seems to play a significant role by increasing the discrimination in favour of the most surface-active complexes against the heavily solvated and the surface-inactive complexes.

Influence of solvation and ion pairing on the desorption of crown ether–alkali cation complexes

The discrimination towards the desorption process between complexes at the same concentration can be measured by use of the product (P) of their relative desorption rates (D_i). The relative desorption rate of a complex $[M + C_i]^+$ corresponds to the ratio between its relative intensity (I_i) and its relative concentration (c_i) in the matrix:[6b]

$$D_i = I_i/c_i$$

The relative concentration c_i is assumed to be 33.3% in the case of equimolar mixtures of three cations. Knowing that the sum of the relative intensities ($I_1 + I_2 + I_3$) is equal, by definition, to 100%, the product of the relative desorption rates D_i tends to 1 if no discrimination occurs ($I_1 = I_2 = I_3 =$ 33.3%) and to zero if one complex $[M + C_i]^+$ does not appear on the spectrum ($I_i = 0$). Thus, the value P is of interest for determining the influence of some experimental parameters such as the matrix hydrophilicity or the type of counteranion on the desorption discrimination.

In the case of complexes formed by 18-crown-6 with the sodium, potassium and cesium cations, we have compared the P values calculated from spectra obtained by using glycerol, diacetylglycerol and triacetylglycerol. The results, shown in Table 2, are remarkable since the discrimination measured by a low P value in glycerol disappears in its acetylated analogues with P values close to unity (P = 0.9 and 0.8 in diacetylglycerol and triacetylglycerol, respectively).

Table 2 Relative desorption rates (D_i) of 18-crown-6–alkali cation complexes formed by FAB in various matrices: glycerol (G), diacetylglycerol (DAG) and triacetylglycerol (TAG)

Cation	G	DAG	TAG
Na^+	0.16	1.00	0.96
K^+	0.36	0.90	0.90
Cs^+	2.47	1.00	0.94
$P = D_{Na} \times D_K \times D_{Cs}$	0.14	0.90	0.81

Table 3 Relative desorption rates (D_i) of 18-crown-6–alkali cation complexes formed by FAB in glycerol in the presence of various counteranions (Cl^-, Br^-, I^-)

Cation	Cl^-	Br^-	I^-
Na^+	0.16	0.26	0.20
K^+	0.36	0.70	1.30
Cs^+	2.47	2.40	1.50
$P = D_{Na} \times D_K \times D_{Cs}$	0.14	0.44	0.39

These results are consistent with the 'surface effect' observed in glycerol in favour of the 18-crown-6–cesium complex which should be much less relevant in apolar solvents for which the hydrophilic interactions with the alkali cations are considerably reduced. Another explanation refers to the role assigned by Sunner to the ion solvation on the desorption process.[2] The transfer of a 'preformed' ion from the matrix to the gas-phase is a gradual process involving a progressive lowering of the ion solvation during the desorption event. The energy and the time scale required by a complete desolvation of an ion are likely to be as much larger as the ion–solvent interactions are stronger. The principal effect of desolvation on the secondary ion yield is the neutralization of the ion species by recombination or ion pairing which are very extensive in FAB. Thus, the cationic species which are separated from the anions in a solvent of high dielectric constant such as glycerol are destabilized during the desolvation step and form contact ion pairs with vicinal anions present in the selvedge.[17] The discrimination between different complexes dissolved in a polar matrix such as glycerol could therefore be explained by a slower desolvation of the more solvated species which undergo an increased ion pairing. This was suggested as an explanation for the low sensitivity of the 18-crown-6–lithium complex in previous electrohydrodynamic mass spectrometric studies using a glycerol matrix.[18] Under conditions of reduced ion solvation (with a diacetyl- or triacetyl-glycerol matrix), no significant differences in the desolvation efficiency are expected; all complexes desorb rapidly with a high efficiency, including the lithium complexes which lead also to intense ion peaks. From a practical viewpoint, this observation signifies that the relative intensities of ion peaks in the mass spectra directly reflect the relative concentrations of the complexes in the matrix. This implies also that an apolar matrix such as diacetyl- or triacetyl-glycerol must be recommended when the production of lithium complexes is needed. Scrutiny of the literature demonstrates an extensive but empirical use of the NBA hydrophobic matrix for analysing organometallic complexes, as pointed out by Barber and co-workers.[19]

Various anions arising from the alkali halides or from the matrix and sample molecules are transferred together with the positive ions into the gas phase. If ion pairing was responsible for the desorption discrimination in FAB, the nature of the counteranion present in the matrix should logically affect the results. Indeed, although less dramatic than the matrix polarity changes, significant effects on the desorption discrimination have been evidenced by comparative studies of the counterion present in the matrix (Table 3). In glycerol, the discrimination in favour of the 18-crown-6–cesium complex ($P = 0.14$), observed when using mixtures of alkali chlorides, is significantly reduced by using bromides or iodides ($P = 0.44$ and 0.39, respectively). Two complementary explanations account for these results. First, the higher solvation energies can be attributed to the smaller halide anions,[20] their desorption should be affected in the same way as the more solvated cations with which they are able to desorb and recombine. Secondly, despite the lack of thermodynamic data on the formation of crown ether–cation/anion entities, if we consider that the ion pairing process depends on the alkali halides formation energies, the gas phase recombination between complexes and anions is expected to be more efficient for chlorides than for bromides or iodides.[21] These results help to understand an observation made by Miller and co-workers on the variations in sensitivities of tris(3,6-dioxaheptyl)amine–alkali cation complexes formed by FAB.[5f] These complexes, obtained by mixing individual alkali halides with the ligand, led to much better sensitivities in terms of total ion current percentage when iodides or bromides were used, by comparison with chlorides and especially fluorides which gave only very poor ion signals. In our own experiment, no significant increase of the overall sensitivity but only a reduced desorption discrimination was observed by using the heavier anions.

Conclusions

In summary, from diluted solutions of 18-crown-6–alkali cations complexes, the less solvated ion species lead to more intense ion signals (K > Na, Cs > Li). At a higher concentration, the matrix hydrophilicity plays the principal role. A hydrophilic matrix such as glycerol facilitates the desorption of complexes possessing simultaneously a certain surface activity and a limited degree of solvation. These ions desorb rapidly and are observed essentially during the first minutes of the bombardment. The ions which are 'enclosed' in the bulk and are strongly solvated undergo a progressive and slow desolvation in the selvedge. Their desorption is either simply delayed for the less solvated among them or sufficiently slow so that an extensive ion pairing process occurs. In this context, the nature of the counteranion is significant. The use of hydrophobic matrices such as *meta*-nitrobenzyl alcohol or the acetylated derivatives of glycerol limits greatly the influence of solvation on the desorption of the dissolved ion species. Under these conditions, the surface activity effects and the recombination of ion pairs are reduced.

Thus, in spite of the complexity of the desorption process in which many factors are involved, it seems possible to improve the quality of the ligand–metal complexes analysis. In particular, the absence of an expected ion signal does not systematically imply that the complex is not formed in the matrix. Mere change of concentration, counteranion, matrix, *etc.*, could considerably improve the results.

Experimental

The crown ether samples were dissolved directly in the matrix (glycerol, diacetylglycerol, triacetylglycerol or *meta*-nitrobenzyl alcohol). The equimolecular mixtures of alkali-metal salts were dissolved in the solvent glycerol–water (4:1). The use of glycerol as cosolvent of the salts was necessary for obtaining homogeneous solutions with the hydrophobic matrices used in several experiments. For each measurement, 20µl of the ligand solution were mixed with 5µl of each solution of salts. After stirring, 5µl of each aliquot were transferred to the FAB probe copper tip. Usually, the total concentration of salts corresponded to half of the ligand concentration.

The mass spectra were acquired with a Kratos MS80RF double focusing mass spectrometer of Nier-Johnson geometry at an accelerating voltage of 4 kV and a post acceleration voltage of 8 kV in the liquid-secondary ionization (LSIMS) mode. A Phrasor Scientific cesium ion gun was used, operating at 20 kV and 5 μA. The mass range from 1300 to 30 was scanned at 10 s/decade. The resolution of the mass spectrometer was 1000.

Crown ethers were purchased from Janssen Chimica (Noisy-le-Grand, France); NBA was obtained from Aldrich (Sigma-Aldrich Chimie, Saint-Quentin Fallavier, France); diacetylglycerol and triacetyl glycerol were purchased from Prolabo (Paris, France). All compounds were used without further purification.

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