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Cation-coordinating properties of perfluoro-15-crown-5

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ABSTRACT

The coordinative properties of perfluoro-15-crown-5 with monocations were investigated using ^{19}F NMR spectroscopy and ion-selective electrodes with perfluoro-15-crown-5 as the matrix of their sensor membranes and the fluorophilic tetrakis[3,5-bis(perfluorohexyl)phenyl]borate as ion exchanger site. The results show that perfluoro-15-crown-5 interacts weakly but significantly with Na^+ and K^+. Assuming 1:1 stoichiometry, the formal complexation constants were determined to be 5.5 and 1.7 M^{-1}, respectively. This weak binding is consistent with the strong electron withdrawing nature of the many fluorine atoms in the perfluorocrown ether. While perfluorinated crown ethers have been known to form host–guest complexes with the anions O_2^- and F^- in the gas-phase, this is the first study that quantitatively confirms cation binding to a perfluorocrown ether.

1. Introduction

Due to their unique properties, a wide range of perfluorinated organic compounds has been developed and is now used routinely in application fields as diverse as the electronics industry, aerospace engineering, medical sciences, and the cosmetic industry. Surprisingly, the coordinative properties of perfluorinated compounds with functional groups such as amino and ether groups are still poorly known, even though they are important factors in the performance of these compounds. For example, the coordinative properties of perfluorocrown ethers may affect their use as probes for nuclear magnetic resonance imaging of oxygen in the human body [1,2], and the coordinative properties of perfluoropolyethers have been associated with the degradation of hard disk lubricants [3]. It is generally assumed that the strong electron withdrawing perfluorinated moieties render ether groups rather inert, but only little is known quantitatively about the extent of this inertness.

An early computational study suggested that the Lewis acid BF_3 does not form a complex with perfluoro(diethyl ether), which was confirmed experimentally by infrared spectroscopy [4]. Moreover, computational evidence suggested that the proton affinity of the oxygen atom of perfluoro(diethyl ether) exceeds the proton affinity of methane only slightly [5,6]. Interestingly, the proton affinity of the fluorine atoms of this ether was assessed to be 6–13% lower than for the oxygen. Unfortunately, attempts to confirm these results by mass spectrometry were not successful due to the prominent formation of HF.

More recently, our group reported quantitative data for proton binding to perfluorotripentylamine and several partially fluorinated trialkylamines, as determined with fluorous liquid-membrane cation-selective electrodes doped with fluorophilic tetrakis[3,5-bis(perfluorohexyl)phenyl]borate salts. The result showed that the amine did not undergo measurable association with any ion tested, and its formal pK_a was shown to be smaller than -0.5 [7]. In contrast, the amines with different $(CH_2)_n$ spacers between the nitrogen atom and the perfluorinated ponytails were found to be excellent H^+ ionophores with pK_a values in the wide range from 3.6 to 15.4 [8]. Using the same technique, 2*H*-perfluoro-5,8,11-trimethyl-3,6,9,12-tetraoxapentadecane (a fluorinated tetraether) was found to interact very weakly with Na^+ and Li^+. Assuming 1:1 stoichiometry, formal complexation constants were determined to be 2.3 and 1.5 M^{-1}, respectively [7]. Also, the perfluorinated, dioxole group-containing polymer Teflon AF2400 was found to coordinatively interact with Na^+ and K^+ with a very similar binding strength, i.e., 1.9 and 2.6 M^{-1}, respectively [9]. However, while there are many reports on the complexation of hydro crown ethers with alkali metal ions, organic ammonium ions, and even neutral molecules [10–16], little has been reported about cation binding to perfluorinated crown ethers. While a gas-phase study with several perfluorocrown ethers has shown that these macrocycles bind O_2^- and F^- with complexation energies in the range of 40–60 kcal, the same investigation could not confirm binding of cations. It was speculated that, due to the strong electron withdrawing effect of the CF_2 groups, the base character in perfluorinated macrocycles may be non-existent [17].

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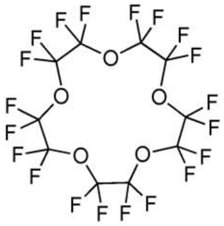

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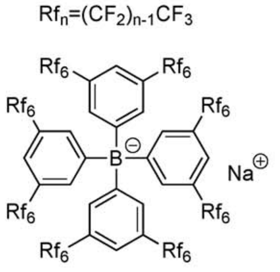

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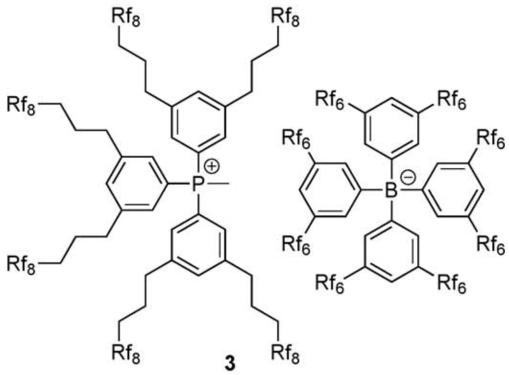

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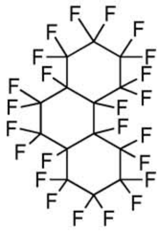

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In the work described here, monocation binding to perfluoro-15-crown-5, **1**, has been studied with ^{19}F NMR spectroscopy and ion-selective potentiometry. This compound has only one resonance from the 20 magnetically equivalent fluorines, which makes it a very sensitive probe for in vivo NMR imaging of O_2 based on the strong dependence of the relaxation time T_1 of the ^{19}F nucleus to molecular oxygen [18,19]. The liquid **1** is more suitable for this purpose than perfluoro-12-crown-4, which has a low vapor pressure that readily causes embolism. Also, unlike perfluoro-18-crown-6, it does not readily precipitate in crystalline form.

2. Results and discussion

Preliminary experiments with NMR spectroscopy were performed to explore the strength of interactions between perfluoro-15-crown-5 and alkaline cations. Attempts to dissolve sodium tetraphenylborate and potassium tetrakis[*p*-chlorophenyl]borate in $CDCl_3$ solutions of the perfluorocrown ether failed to show any ^{1}H NMR signals indicative of the presence of the anions, giving a first confirmation that the interaction between the cations and the perfluorocrown ether is indeed weak. Further experiments were performed in perfluoro-15-crown-5 as the solvent. Even though the saturation concentration of the fluorophilic sodium salt **2** in the perfluorocrown ether was found to be much lower (0.48 ± 0.16 mM) than the concentration of the perfluoro-15-crown-5 itself (3.07 M), the lack of any observable shift of the ^{19}F NMR shifts seemed to be a further indication that the host–cation interactions are weak at most, in particular in view of ^{19}F NMR shifts as large as 40 ppm upon metal cation binding to macrocycles with only one or few fluorine atoms [20]. Additional evidence to confirm this conclusion comes from the fact that the concentration of a saturated solution of sodium salt **2** in perfluoro-15-crown-5 is 2.9 times lower than the concentration of a saturated solution of **2** in perfluoroperhydrophenanthrene [7]. This is surprising since a higher solubility of **2** would be expected if the interaction between the sodium ion and oxygen atoms of **1** was strong. Because the potentiometric experiments discussed below show that the sodium ion does interact, although very weakly, with the perfluorocrown ether, it appears that the somewhat higher solubility of **2** in perfluoroperhydrophenanthrene is the result of the slightly more favorable solvation of the tetrakis[3,5-bis(perfluorohexyl)phenyl]borate anion in perfluoroperhydrophenanthrene, and is not related to the Na^+ cation.

To further explore the strength of interactions between **1** and the cations and assess the weak binding quantitatively, ion-selective electrodes (ISEs) were used. ISEs have been used for many years to study host–guest complexation in aqueous solution. In a typical application, the host is dissolved in an aqueous solution, increments of guests are added, and a titration curve is obtained either by measuring the ionic host directly with a host-selective ISE or – in cases where H^+ competes with the ionic guest – by measuring changes in pH with a glass electrode [21]. Complex constants and stoichiometries are obtained by fitting of the titration curve. Unfortunately, this approach is not only unsuitable for hosts that are insufficiently soluble in polar solvents, but it also requires large samples of host. The recent development of a quantitative theory to explain the selectivity of host-based ISEs has made it possible to overcome these problems [22,23]. The amount of host can be drastically reduced by its incorporation into the hydrophobic ion-selective membrane, which even without miniaturization has a volume of only a few microliters (See Fig. 1). This approach requires that the tested host is hydrophobic enough that it remains in the sensor membrane and does not appreciably leach out into the sample solution during measurements [24–26].

In this work, the stabilities of cation complexes with perfluoro-15-crown-5 were determined by a quantitative comparison of the ion selectivities of sensing membranes consisting of 98.6% perfluorocrown ether with those of analogous membranes based on the tricyclic and oxygen-free perfluorocarbon perfluoroperhydrophenanthrene. In both cases, the perfluorinated compound is the liquid matrix in which the fluorophilic sodium salt **2** is dissolved as ion exchanger to provide the sensor membrane with permselectivity for cations [27]. Since the concentration of **2** saturated in **1** is only 0.48 ± 0.16 mM, as determined in the ^{1}H NMR experiments described above, and since ion pairing in fluorous phases is known to be very strong [28], the ionic conductivity of a saturated

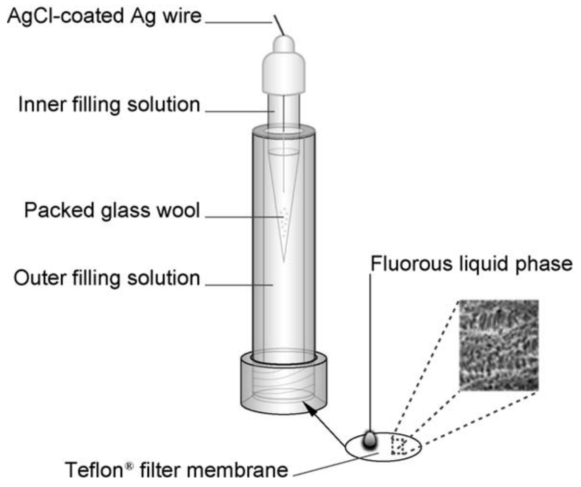

Fig. 1. Schematic of an ISE based on a liquid perfluoro-15-crown-5 sensor membrane supported by an inert porous filter.

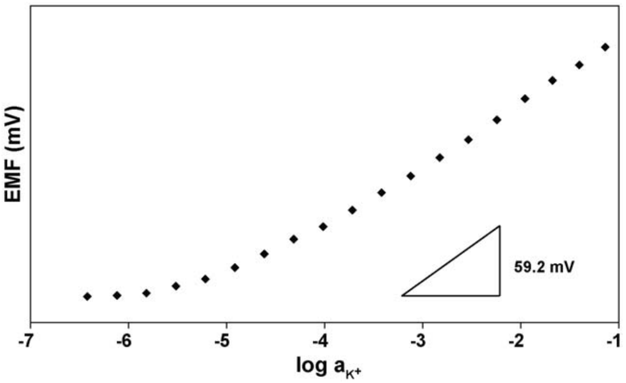

Fig. 2. Potentiometric K^+ response of an ISE with a perfluoro-15-crown-5 membrane.

solution of **2** in **1** was not surprisingly found to be extremely low. This made it impossible to use sensor membranes doped only with **2** for accurate and sufficiently noise-free measurements of the potentiometric responses. Therefore, the fluorophilic inert electrolyte **3** was added to the solutions of **2** in **1** to increase the conductivity. As expected, the addition of 3.6 mM electrolyte lowered the electrical resistance (i.e., the inverse of the conductivity) of the sensor membrane from about 200 GΩ down to 10 MΩ.

The first experimental step towards the potentiometric determination of stability constants is the measurement of the potentiometric responses of these sensors to the ion of interest. Fig. 2 shows, as an example, the potentiometric response of the electrode with the perfluoro-15-crown-5 membrane to the cation K^+. The response slope of 59.2 mV/decade is the theoretically expected response slope, which shows (i) that the electrode membrane is leak-free, (ii) that within the range of this linear slope the sensing membrane responds exclusively to K^+, and (iii) that at the time of measurement thermodynamic equilibrium has been reached at the interface between the aqueous sample and the fluorous phase. Responses of electrodes based on perfluoro-15-crown-5 to all other monocations under investigation were measured too, and Nernstian responses with 59.2 mV/decade slopes were obtained for all those ions.

The second step towards the determination of complex stabilities is the measurement of the potentiometric selectivities of these sensor membranes. The selectivity coefficients, $K_{I,J}^{pot}$, are determined by measurements of the potentiometric responses to mixed solutions of I and J and express the selectivity of the sensor membrane for ion J with respect to ion I [29,30]. They are defined in the case of monovalent cations by the following equation, where EMF is the sensor response, E° is a constant value obtained from a calibration curve, a_I and a_J are the activities of the two ions, respectively, and $K_{I,J}^{pot}$ is the selectivity coefficient:

$$\mathrm{EMF} = E^\circ + RTF^{-1}\ln(a_I + K_{I,J}^{pot}a_J)$$

R, *T*, and *F* are the universal gas constant, temperature, and Faraday constant, respectively.

The selectivity coefficients for a series of monocations with reference to K^+ are shown in Table 1. The electrodes based on perfluoro-15-crown-5 exhibit selectivities that span a wide range of 18 orders of magnitude, which is much wider than for typical non-fluorous organic sensing membranes. For example, this range is 10 orders of magnitude larger than for electrodes based on the very common ISE matrix consisting of ≈33% poly(vinyl chloride) and ≈66% *o*-nitrophenyl octyl ether [7]. This wide selectivity range is similar to the one found previously for fluorous membrane formulations based on perfluoroperhydrophenanthrene, **4** (also shown in Table 1), perfluorotripentylamine and 2*H*-perfluoro-5,8,11-trimethyl-3,6,9,12-tetraoxapentadecane, which all showed selectivities ranges of at least 16 orders of magnitude [7].

Formal complexation constants, K'_{JL}, for binding of ion J to host L can be obtained from formal ion exchange constants, *K*, that describe the exchange of ions I and J between a reference phase 'ref' lacking coordinating oxygen groups (i.e., in this case the perfluoroperhydrophenanthrene phase) and a phase 'co' with the coordinating host compound.

$$I^{ref} + J^{co} \rightleftarrows I^{co} + J^{ref}$$

Experimentally, the two fluorous phases cannot be equilibrated with one another by direct contact since they are miscible with one another. However, the two fluorous phases can be equilibrated separately with the same type of aqueous solution containing the ion I, and potentiometric selectivities, $K_{I,J}^{pot,co}$ and $K_{I,J}^{pot,ref}$, can be determined with ISE sensor membranes consisting of the respective phases. Thereby, equilibration of the two fluorous phases with respect to ion I may be achieved without the two fluorous phases having to contact one another directly. As shown in the literature [7,31], the logarithm of the formal ion exchange constant, *K*, can then be obtained from

$$\log K = \log K_{I,J}^{pot,co} - \log K_{I,J}^{pot,ref} \qquad (1)$$

If only ion J but not ion I interacts specifically with one of the two fluorinated phases, *K* equals the so-called formal single ion distribution coefficient, k_J. Ions with a large size and a bulky structure, such as tetrabutylammonium or tetraphenylphosphonium, are typically considered not to interact specifically with the solvent [7,31]. Finally, in order to facilitate the interpretation of the ion–host interaction at the molecular level, a formal complexation constant, K'_{JL}, for binding of cations to host can be obtained if 1:1 complex stoichiometry is assumed: [7,31]

$$K'_{JL} = \frac{K_{I,J}^{pot,co}/K_{I,J}^{pot,ref} - 1}{[L]} \qquad (2)$$

where [L] is the concentration of the host that interacts with the ion.

The coefficients for single ion distribution between reference solvent **4** and perfluoro-15-crown-5 for different ions, as calculated based on Eq. (1), are shown in Table 2. The tetraphenylphosphonium cation, PPh_4^+, is assumed to be the ion that does not interact specifically with either **1** or **4**. Consequently, the log *k* values for PPh_4^+ are 0.00. Within experimental error, there is no evidence for an interaction between perfluoro-15-crown-5 and the larger ions NBu_4^+ and NH_4^+ and the smallest ion, Li^+. In particular, the result for NBu_4^+ is consistent with its bulky structure, which does not suggest a strong interaction with the

Table 1
Logarithmic selectivity coefficients, $\log K_{I,J}^{pot}$, of fluorous membrane cation-selective electrodes, referenced to K^+.

Membrane components			$\log K_{I,J}^{pot}$					
	[**2**] (mM)	[**3**] (mM)	PPh_4^+	NBu_4^+	NH_4^+	H_3O^+	Na^+	Li^+
1	0.48	3.6	16.3	14.3	−0.58	−1.61	−0.69	−2.07
4[a]	1.0	10	17.1	15.2	0.41	−1.14	−1.20	−0.16

[a] Recalculated with respect to K^+ from Refs. [7,8].

Table 2
Logarithmic single ion distribution coefficients, log *k*, characterizing distribution between sensor membranes with **1** and membranes with **4**.

	PPh_4^+	NBu_4^+	NH_4^+	H_3O^+	K^+	Na^+	Li^+
log *k*	0.00[a]	−0.13	−0.19	−0.97	0.80	1.43	−0.07

[a] Assumption.

perfluorocrown ether. The smaller ions Na^+ and K^+ weakly but significantly interact with the perfluorocrown ether ($k_{Na} = 17.8 \pm 1.1$ and $k_K = 6.3 \pm 1.3$). Applying Eq. (2) for Na^+ gives a formal complexation constant for the perfluorocrown of $5.5 \pm 0.3\ M^{-1}$. Analogously, a binding constant of $1.7 \pm 0.3\ M^{-1}$ is obtained for K^+. In comparison, the stability constants of the complexes between the non-fluorinated 15-crown-5 and Na^+ and K^+ in acetonitrile are much larger, i.e., 2.0×10^5 and $8.0 \times 10^3\ M^{-1}$, respectively [32]. Notably, both for the perfluorinated and the non-fluorinated crown ether Na^+ is bound more strongly than K^+, which is consistent with a better fit of Na^+ into the host cavity [32]. This seems to confirm that the oxygens are more relevant to Na^+ and K^+ binding than the fluorines. While interactions of metal cations to carbon-bound fluorine have been studied [33], the effect of the added fluorines on binding constants was found to be comparatively small [20]. Moreover, as mentioned above, computational evidence suggests that the proton affinity of the fluorines in the structurally very similar perfluoro(diethyl ether) is 6–13% lower than for the oxygens.

Unexpected are results for H_3O^+ (Tables 1 and 2) as they suggest that this ion has a small but distinct preference for the perfluoroperhydrophenanthrene phase. The reasons for this finding are not clear since nothing about **4** suggests a specific interaction. However, it is notable that in the absence of added electrolyte (**3**) solutions of **2** in **1** are about two orders of magnitude more resistive than solutions of **2** in **4**. Since H_3O^+ forms stronger ion pairs with the fluorophilic anion of **2** than other monovalent cations [28], the small preference of H_3O^+ for the phase with **4** may be related to a different level of ion pairing in the two fluorous media.

3. Conclusions

The coordinative properties of a perfluorocrown ether with cations were studied for the first time quantitatively. Despite the macrocyclic structure of perfluoro-15-crown-5, the formal complexation constants are very similar as for a non-cyclic highly fluorinated tetraether and Na^+ and Li^+ (2.3 and 1.5 M^{-1}, respectively) [7], and for the perfluorinated dioxole group-containing polymer Teflon AF2400 and Na^+ and K^+ (1.9 and 2.6 M^{-1}, respectively) [9]. Due to the very strong electron withdrawing nature of the many fluorine atoms, binding of monocations is very weak but strong enough to be observed in potentiometric measurements with fluorous cation-exchanger electrodes.

4. Experimental

4.1. General experimental procedures

All chemicals were of the highest commercially available purity and were used as received, unless noted otherwise. Perfluoro-15-crown-5 (**1**) was purchased from Oakwood Products (West Columbia, SC, USA). Sodium tetrakis[3,5-bis(perfluorohexyl) phenyl]borate (**2**), and tris[3,5-bis(perfluorooctyl)propyl]phenyl]-methylphosphonium tetrakis[3,5-bis(perfluorohexyl)phenyl]-borate (**3**), were prepared according to previously described procedures [7,28]. Deionized and charcoal-treated water (18.2 MΩ cm specific resistance) obtained with a Milli-Q PLUS reagent-grade water system (Millipore, Bedford, MA, USA) was used for all sample solutions. LiCl, all dihydrogen phosphate salts and tetraphenylphosphonium iodide were from Sigma–Aldrich (St. Louis, MO, USA) and Fluka (Buchs, Switzerland). The concentration of **2** in **1** was determined with ^1H NMR spectroscopy by comparison of the integrals of the aromatic hydrogens of **2** and the ^1H signal from a capillary filled with acetone-d_6. The latter was calibrated using a solution of 2*H*-perfluoro-5,8,11-trimethyl-3,6,9,12-tetraoxapentadecane of known concentration in **1**.

4.2. Membranes

Sensing membranes were prepared to contain 3.6 mM electrolyte salt (**3**) in **1** saturated with **2**. To prepare the membranes, ionic sites were first added into the ether and gently heated to completely dissolve the salt. The solution was allowed to sit overnight and then filtered with glass wool to remove excess ionic sites. The electrolyte salt was added thereafter. The whole mixture was stirred for at least 24 h. Fluoropore™ membrane filters (poly(tetrafluoroethylene) without backing, 47 mm diameter, 0.45 μm pore size, 50 μm thick, 85% porosity) were obtained from Millipore and used as inert support for the fluorous liquid sensing membranes. The Fluoropore™ membrane filters were sandwiched between two note cards and cut with a hole punch to give small disks of 13 mm diameter. Two filter disks were layered on top of each other for all selectivity measurements, except for NBu_4^+ and PPh_4^+, where six layers were used. Upon application of the fluorous solution (about 10–15 μL per membrane filter) with a micropipette to the surface of the porous filter disks, the latter appeared translucent.

4.3. Electrodes

The thus prepared fluorous membranes were mounted into custom-machined electrode bodies made from poly(chlorotrifluoroethylene). A screw cap with a hole (8.3 mm diameter) in the center was screwed onto the electrode body, securing the membrane in between the electrode body and the cap but leaving the center of the membrane exposed (see Fig. 1). An outer filling solution (in contact with the backside of the sensing membrane) and an inner filling solution (in contact with an AgCl-coated Ag wire) were used for each electrode, and were separated by a small glass wool plug that was tightly packed into a tapered plastic pipette tip. The inner filling solution was always 1 mM LiCl and 1 mM LiH_2PO_4. For selectivity measurements, the outer filling solution contained the $H_2PO_4^-$ salt (1 mM) of the cation used as the constant background in the sample solution. Prior to measurements, all electrodes were conditioned in the sample solution containing the target ions for 3–4 h; during this time period, the target ions enter the fluorous membrane by replacing the sodium ions introduced with **2**. Successful ion exchange was confirmed by monitoring the EMF throughout this conditioning process. During conditioning, the fluorous membranes also absorb a very small amount of water, which is limited by the very low solubility of water in the fluorous phase.

4.4. Potentiometric measurements

Potentials were monitored with an EMF 16 potentiometer controlled with EMF Suite 1.02 software (Lawson Labs Inc., Malvern, PA, USA) at room temperature (25 °C) and with stirred solutions. The external reference electrode (DX200, Mettler Toledo, Greifensee, Switzerland) consisted of a double-junction Ag/AgCl electrode with a 1.0 M LiOAc bridge electrolyte and 3.0 M KCl saturated with AgCl as inner filling solution. Potentials were recorded after equilibrium at the membrane/sample interface had been reached, as assessed by the observation of the potentiometric signal. Calibration curves were measured by successive dilution of a concentrated solution while continuously measuring the EMF. Selectivity coefficients were determined with the fixed interference method, except for NBu_4^+ and PPh_4^+, for which the fixed primary ion method was applied [29]. Nernstian responses were confirmed for all ions in the concentration range where selectivities were measured. Activity coefficients were calculated with a two-parameter Debye–Hückel approximation [34]. DC resistances of sensing membranes were determined using the method of potential reduction by a known shunt, as in our previous work [24,35].

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