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Nuclear Magnetic Resonance Studies of Some Paramagnetic Manganese(III) Porphyrins[1]

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The proton nmr spectra of a series of paramagnetic ($S = 2$) manganese(III) porphyrin complexes, [Mn(Por)Cl·H_2O], where Por is etioporphyrin I, mesoporphyrin IX dimethyl ester, protoporphyrin IX dimethyl ester, and methyl pheophorbide *a*, have been investigated at 220 MHz in deuteriochloroform solution. Although resonances are broadened in these species (~350-Hz width at half-height) and lack observable spin-spin coupling, the wide range of chemical shifts has permitted some assignments to be made. Methyl protons attached to the porphyrin rings are shifted ~30 ppm to lower field compared to their positions in the corresponding diamagnetic free ligand, whereas a corresponding methylene group is shifted only ~20 ppm. In contrast, methine-bridge protons are shifted ~20 ppm to higher field. Protons that are three or more σ bonds removed from the macrocycle, however, experience little or no shift. The magnitude of the shift of the methyl protons appears to be dependent on the donor strength of the porphyrin, with the lines for the strongest donor, etioporphyrin I, at the lowest field, while those of the weakest donor, methyl pheophorbide *a*, appear at the highest field. Limited temperature studies have been carried out on [Mn(Etio I)Cl·H_2O]. Curie-law behavior appears to hold for the methyl and methylene protons while an anomalous non-Curie dependence is seen for the methine protons.

Introduction

In the past few years much attention has been given to the study of the nuclear magnetic resonance (nmr) spectra of the paramagnetic iron porphyrins.[2] This results from the obvious relevance of these substances as model compounds in the study of the biologically important heme proteins. However, little or no work has been done on the nmr spectra of other paramagnetic metalloporphyrins. For example, only limited studies of nickel(II)[3a] and cobalt(II)[3b] porphyrins have appeared. Studies on these and other systems would provide valuable data for comparison with the iron porphyrins. In this context examination of analogous paramagnetic manganese(III) porphyrins would be particularly useful. More importantly, such a spectral study could provide information about the electronic structure of the manganese porphyrins which is of interest in its own right.[4] All manganese(III) porphyrins are high-spin complexes ($S = 2$) and no evidence has been presented for spin pairing in these materials.[4] We have, therefore, undertaken a study of the nmr spectra of manganese(III) porphyrin complexes. In this paper we report some results on a series of chloride complexes, [Mn(Por)Cl·H_2O], in which the porphyrin is varied. The materials examined are shown in Figure 1. The chloride salts were chosen since they are readily prepared in a high state of purity.

Experimental Section

Materials. All complexes were prepared and purified as previously described.[5] Elemental analyses agree with the formulations given here. All solvents were vacuum distilled before use. Solutions were prepared with the complexes ~0.03 *M* in $CDCl_3$ and with benzene as an internal standard. The solutions were degassed and sealed off in precision nmr tubes under vacuum.

Spectra. The nmr spectra were obtained with a Varian HR-220 spectrometer operating at 21° in the field sweep mode and equipped with a Varian variable-temperature controller. Temperatures were measured using a standard ethylene glycol sample. Because a single scan did not give suitable spectra in many instances, a Fabri-tek Model SW-71 was used to time-average the spectra.

Results

Table I lists the chemical shifts relative to tetramethylsilane and assignments for the various protons in the complexes. Consistent assignments can be made on the basis of the relative intensities of the lines and comparison of the spectra of the different porphyrins. Figure 2 illustrates the complete nmr spectrum of [Mn(Etio I)Cl·H_2O]. The spectrum shows two lines at low field, a peak at −2.6 ppm, and an additional peak at high field. The peaks at −35.3 and −22.6 ppm can be assigned to the ring methyl and to the ring methylene protons. The HR-220 operates with a 10-kHz field modulation and the side band is usually observed. With the occurrence of large chemical shifts the peaks and side bands sometimes overlap with a diminution of the apparent intensity of the peak. This is the case here for the methylene resonance. The line at −2.6 ppm can be assigned to the β-methyl protons. The upfield resonance at +10.5 ppm can be associated with the meso (methine) protons. It has been pointed out that placement of the metal atom out of the porphyrin plane in high-spin Fe(III) complexes makes the methylene protons diastereotopic.[3b] As a result, in chloro(octaethylporphyrin)iron(III) the nmr spectrum shows two methylene resonances. Although a similar out-of-plane structure is expected[4] for the etioporphyrin complex of Mn(III), the nmr spectrum shows only one methylene resonance. It thus appears that the nonequivalence of the diastereotopic protons in the manganese(III) porphyrins is not great enough to allow resolution into separate resonances. The line widths (at half-height) differ for the various types of protons, *e.g.*, the widths are ~400 Hz for the ring methyl protons, ~350 Hz for the methylene and meso protons, and ~150 Hz for the β-methyl protons. The observation of even these broad lines and the absence of spin-spin coupling in the ethyl groups are indicative of a short electronic relaxation time in these complexes.

For comparison, Figures 3 and 4 illustrate the low-field and high-field portions, respectively, of the nmr spectra of the Mn(III) complexes of etioporphyrin I, mesoporphyrin IX dimethyl ester, protoporphyrin IX dimethyl ester, and methyl pheophorbide *a*. Assignment of the resonances for the mesoporphyrin IX dimethyl ester derivative is straightforward. In etioporphyrin I, the symmetric placement of the substituents results in one magnetic environment for

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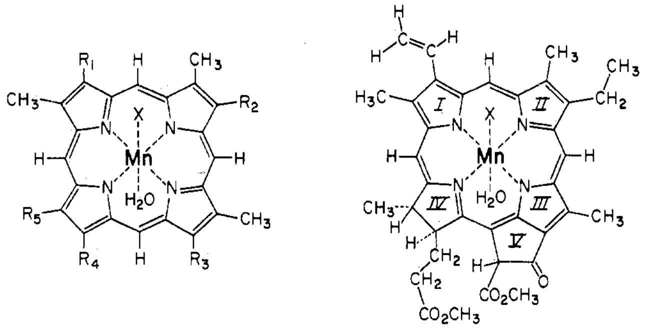
Table I. Chemical Shifts[a] and Assignments for Nmr Spectra of [Mn(Por)Cl·H_2O]

Por	Ring CH_3	α CH_2	β CH_2	β CH_3	Ester CH_3	Meso H	X[b]
Etio I	−35.3	−22.6		−2.6		+10.5	
DMMesoPor	−35.4	−22.9	−3.6	−2.7	−3.6	+10.4	
	−32.5					+13.4	
DMPrPor	−33.7	−25.3	−3.6		−3.6	+7.1	+5.7
	−30.9	−21.4				+7.9	+6.2
	−28.5						
MePheo *a*	−24.9	−14.3	−3.7	−2.6	−3.7	+10.4	+8.6
	−23.6				−3.1	+12.1	−1.3
							−3.1
DMDePor[c]	−39.1	−15.7	−3.5	−2.6	−3.5		
	−36.1	−14.0					
	−33.2						

[a] Chemical shifts, ±0.1 ppm, relative to TMS in $CDCl_3$ solution at 21°. Downfield shifts are marked negative while upfield shifts are marked positive. [b] X = $-CH{=}CH_2$ for DMPrPor; for MePheo *a*, X = ring IV methyl, ring IV proton, and $-CH{=}CH_2$. [c] In DMSO-d_6 solution.



COMPOUND		R_1*	R_2	R_3	R_4	R_5
DEUTEROPORPHYRIN IX DIMETHYL ESTER	DMDepor	H	H	PrM	PrM	M
MESOPORPHYRIN IX DIMETHYL ESTER	DMMesopor	E	E	PrM	PrM	M
PROTOPORPHYRIN IX DIMETHYL ESTER	DMPrpor	V	V	PrM	PrM	M
ETIOPORPHYRIN I	Etio	E	E	E	M	E
METHYL PHEOPHORBIDE *a*	$MePheo_a$	Figure on right				

*M = CH_3; E = CH_2CH_3; V = $CH{=}CH_2$; PrM = $CH_2CH_2CO_2CH_3$

Figure 1. Nomenclature and structures for manganese(III) porphyrins.

each methyl and each ethyl group, and therefore only one nmr line for each kind of proton results. In the case of mesoporphyrin IX dimethyl ester, two of the ethyl groups are replaced by propionic acid methyl ester side chains. The substituents are no longer symmetrically placed and the groups are in nonequivalent environments. Therefore, two equal-intensity ring methyl resonances are seen downfield for [Mn(DMMesopor)Cl·H_2O]. Similar nonequivalence is well established in the metal-free porphyrins.[6] The lines are apparently not resolved in the case of the ethyl groups. The line at −3.6 ppm is assigned to the overlap of lines from β-methylene groups of the propionic side chains and the methyl ester protons. The nonequivalence of the meso protons is partly resolved and two lines appear in the upfield region. The protoporphyrin IX dimethyl ester complex represents a more highly substituted porphyrin with methyl, vinyl, and propionic acid methyl ester side chains. The unsymmetrical nature of the molecule gives rise to three methyl resonances (6:3:3 intensity) and the expected two α-methylene lines (2:2 relative intensity). However, the β-methylene and ester methyl resonances are again not resolved. The meso and vinyl protons show four closely spaced lines upfield at 5.5–8.0 ppm. Although the approximate relative intensities (2:2:3:1) support the assignments given in Table I, the severe overlap of the broad resonance renders the assignments less certain. The expected downfield portions of the vinyl resonances are not seen in the spectrum.[2]

Unfortunately, the deuteroporphyrin IX dimethyl ester complex, [Mn(DMDepor)Cl·H_2O], is not soluble enough in $CDCl_3$ to obtain a spectrum. However, the nmr spectrum of the compound has been obtained in DMSO-d_6. In keeping with the unsymmetrical nature of the porphyrin, this spectrum shows three downfield ring methyls at −39.1, −36.1, and −33.2 ppm in a 3:6:3 intensity pattern. Two equal-intensity α-methylene lines appear at −15.7 and −14.0 ppm while the β-methyl and the β-methylene (and ester methyl) lines are seen at −2.6 and −3.5 ppm, respectively. The meso protons and presumably the pyrrole-ring proton resonances are probably located upfield under a large featureless hump centered at +32 ppm.

The chlorophyll derivative, methyl pheophorbide *a*, is the most highly substituted of the ligands studied. In addition to the methyl, ethyl, vinyl, and propionic acid residue substituents, one of the pyrrole rings is reduced (two additional ring hydrogens) and there is also present an exocyclic ring. The observed spectra are quite complex and only tentative assignments can be made. The nmr spectra show two strongly overlapped broad lines of equal intensity downfield which can be assigned to two of the methyl groups of either ring I, II, or III. The intense line at −14.3 ppm can be assigned to the overlap of the other methyl and the ring II α methylene. By analogy with the manganese(III) porphyrin nmr spectra, the protons on carbons that are not directly attached to the conjugated system of the chlorophyll macrocycle should show resonances within the diamagnetic region. The nmr spectra of zinc(II) methyl pheophorbide *a*[7] and metal-free methyl pheophorbide *a* in $CDCl_3$[8] have been previously reported. For these materials, the ring IV methyl line is at −1.82 ppm while the methylene line of the propionic acid side chain is at −2.45 ppm, the ring IV protons are at −4.40 and −4.13 ppm, and the ring V proton is at −6.22 ppm. Reasonable assignments for the Mn(III) complex would be that the ring IV methylene and ring II β-methyl proton resonances are assigned to the line at −2.6 ppm, the ring IV protons (overlapped with the ester methyl and β methylene) to the line at −3.7 ppm, and the ring IV methyl to the line at −1.3 ppm. In the upfield region two lines are seen which can be assigned to the meso protons (2:1). The vinyl protons show a broad hump at +8.6 ppm. The downfield portion of the vinyl resonances and the ring V protons are not seen even in $CDCl_3$-TMS solution.

The assignments made above are straightforward in the case of etioporphyrin I. Further, for the other porphyrins the assignment of lines to groups of protons is reasonable and consistent with those made for high- and low-spin iron(III) porphyrins.[3,9,10] On the other hand, designation of the proton resonances for the complicated methyl pheophorbide *a* complex is a good deal less certain and only the extreme downfield and extreme upfield lines can be assigned with any confidence. A study of other chloro-

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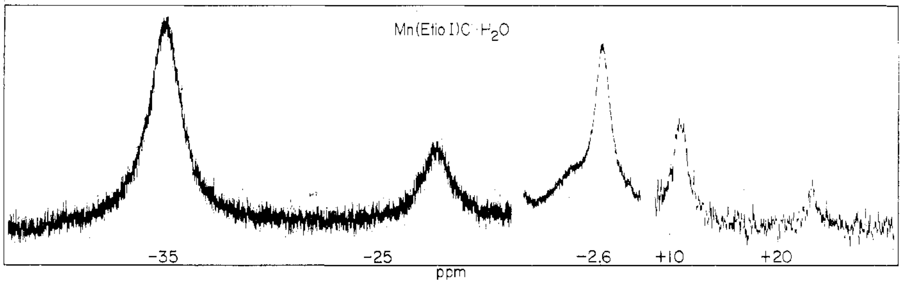

Figure 2. The complete nmr spectrum of Mn[Etio I]Cl·H$_2$O. The upfield region (10–20 ppm) is the result of 256 time-averaged scans. The remaining sections are single scans.

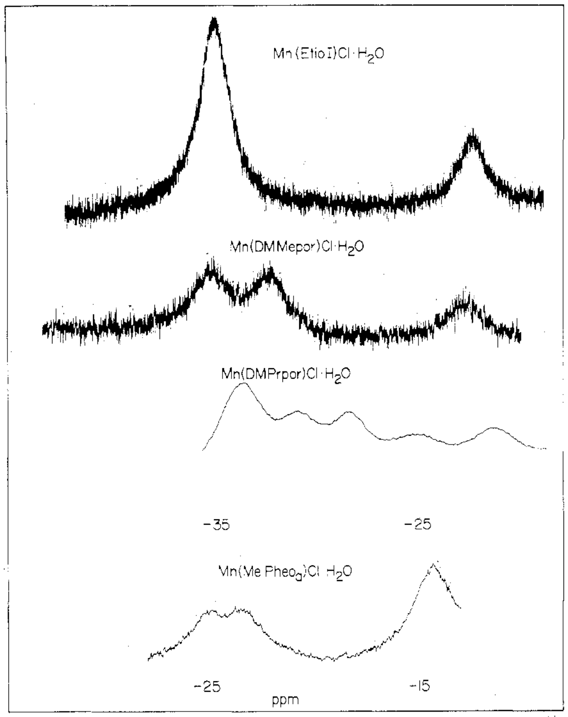

Figure 3. A comparison of the low-field portion of the nmr spectra of several manganese porphyrins. The low-field portions of Mn[Etio I]Cl·H$_2$O and Mn[DMMepor]Cl·H$_2$O are single scans. The low-field portion for Mn[DMPrpor]Cl·H$_2$O is the result of 512 time-averaged scans and that of Mn[MePheo *a*]Cl·H$_2$O the result of 56 time-averaged scans.

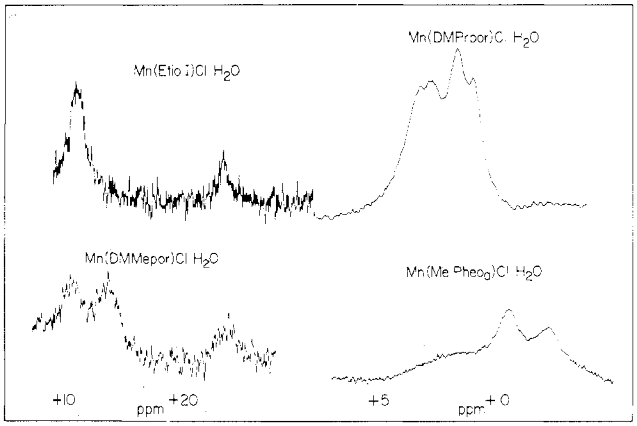

Figure 4. A comparison of the high-field portion of the nmr spectra of several manganese porphyrins. These partial spectra are the result of 256 time-averaged scans for Mn[Etio I]Cl·H$_2$O, 512 scans for Mn[DMMepor]Cl·H$_2$O, 512 scans for Mn[DMPrPor]Cl·H$_2$O, and 110 scans for Mn[MePheo *a*]Cl·H$_2$O.

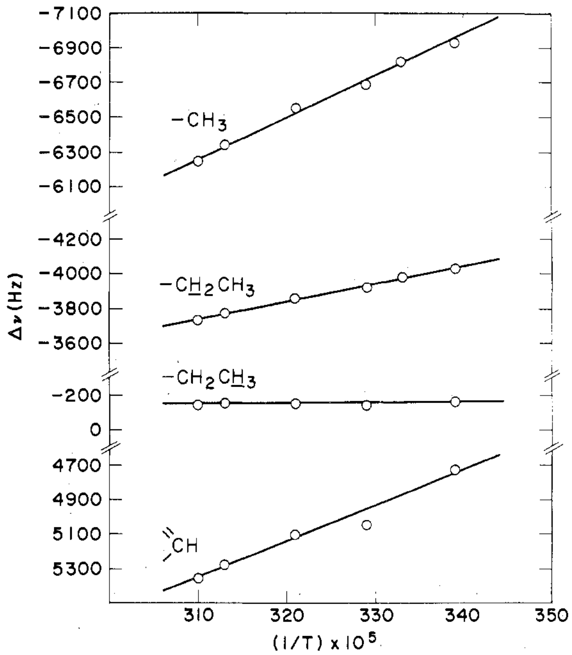

Figure 5. A plot of Δν *vs.* 1/*T* for four of the proton species in Mn[Etio I]Cl·H$_2$O.

phyll derivatives would aid in assigning the individual resonances. A line at +24 ppm is also seen in the spectra of the etioporphyrin I and mesoporphyrin IX dimethyl ester complexes. The relative area of this line is consistent with that expected for the two protons of a water molecule indicated in the empirical formula for the complexes. However, attempts to remove the line by treating the solid complexes with D$_2$O were unsuccessful. Further, axially bound solvent molecules like methanol on manganese(III) porphyrins[11] or dimethyl sulfoxide on the high-spin iron(III) porphyrin[9] show resonances that are broadened and shifted downfield from the free solvent molecule. Examination of the spectra even in the -6 to -10 ppm region with CDCl$_3$-TMS solutions does not reveal any additional lines. Assignment of the extreme upfield line to an impurity is unlikely since the line appears in a region of the spectrum far removed from the diamagnetic region.

Examination of the limited temperature dependence of the proton resonances for the etioporphyrin complex, shown in Figure 5, indicates that the methyl and methylene protons show the expected Curie law dependence. Extrapolation to $T^{-1} = 0$ gives chemical shift values of -4.5 and -6.2 ppm, respectively. Although these values are within the diamagnetic range, the infinite temperature shifts are 0.6 and 1.8 ppm to low field of the corresponding metal-free etioporphyrin I lines.[6] It has been suggested that this effect may arise from a small temperature dependence of the scalar coupling constant. It must be admitted, however, that the

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temperature range studied is quite short so that a curvature may not be evident and also that the long extrapolation to $T^{-1} = 0$ may give rise to small errors of 1-2 ppm. A more serious anomaly is the temperature dependence of the meso proton resonance. The figure shows non-Curie dependence with an extrapolated chemical shift value of +47 ppm and not −10 ppm as expected.

Discussion

Resonances assignable to protons of the methyl and methylene groups attached directly to the porphyrin ring are shifted downfield. Conversely, resonances assignable to protons one carbon removed from the unsaturated ring experience little or no shift from the expected diamagnetic position.[6] Finally, methine protons which are directly attached to the unsaturated porphyrin macrocycle give resonances at high field. Taking the mesoporphyrin IX dimethyl ester as an example, the ring methyl and methylene protons are shifted ~32 and ~19 ppm to low field in the paramagnetic Mn(III) complexes when compared to diamagnetic metal-free porphyrins[6] or metalloporphyrins. Conversely, meso protons give lines shifted upfield by some 20 ppm. The α-methylene shift is only about two-thirds of that of the methyl group shift even though both carbon atoms are directly attached to the porphyrin ring. It has been suggested that this diminution in shift arises from the strongly hindered rotation of the α-methylene group.[7] For the series of compounds the methyl and α-methylene resonances shift to low field in the order Etio I $\geqslant$ DMMesopor $>$ DMPrpor $>$ MePheo *a*. This is in the order of decreasing σ-donor strength of the porphyrin. Surprisingly, the meso proton resonances do not show any regular dependence on ligand basicity.

The high-spin iron(III) porphyrins show paramagnetic shifts of −72 ppm for methyl and +66 ppm for meso protons of [Fe(DMDepor)Cl] in $CDCl_3$ at 35°.[10] The values for the similar complex [Mn(DMMesopor)Cl·H_2O] are −32 and +20 ppm. Similarly, comparing [Fe(Et_8por)Cl] in $CDCl_3$ at 29°, the Fe(III) complex shows the α-methylene proton at −37 ppm and the meso proton at +65 ppm[3b] while for the corresponding manganese(III) etioporphyrin complex the shifts are −19 and +20 ppm. Thus, for the ring methyl and methylene, the manganese shifts are half as large while for the meso protons the shifts are only one-third as large as the iron shifts. The change in spin in going from Mn, $S = 2$, to Fe, $S = {}^5/_2$, should give rise to a shift roughly scaled to $S(S + 1)$. This leads to an expected shift for Mn(III) of 69% of that of Fe(III), all other things being equal. Thus, the reduction in shift in going from Fe to Mn is somewhat greater than would be expected just on the basis of spin-state changes.

The observed chemical shifts of the protons in the paramagnetic manganese porphyrins can be considered as the sum of the chemical shift for a corresponding diamagnetic porphyrin material plus a shift due to the contact term and one due to a pseudocontact term. The contact term arises from the presence of unpaired electron spin density on the ligand and as such is related to the details of bonding in the complex. The pseudocontact term arises from a dipolar interaction between the electronic magnetic moment and the nuclear spin. The problem is to divide the observed shifts between contact and dipolar shifts. The magnitude of the dipolar shifts can be estimated if the molecular structure, zero-field splitting, and *g*-value anisotropy are known.[12]

The mechanism that gives rise to the contact interaction may involve the π-electron system or the σ-electron system or a combination of both. The contact mechanism in low-spin iron(III) porphyrins has been shown to be a π delocalization.[13] In this case, the sign of the chemical shift is opposite for the methyl and α-methylene protons as compared to the meso protons; *i.e.*, the former are shifted downfield while the latter are shifted upfield. In the case of the high-spin iron complexes the methyl and α-methylene protons are all shifted downfield while the meso protons are shifted upfield. The contact shifts have thus been interpreted as arising from a combination of σ and π delocalization of spin.[3b,9] The nmr spectra of the manganese(III) porphyrins clearly show that the sign of the shift for the methyl and α-methylene protons is opposite to that of the meso protons. Further, recent observations on chloro(tetraphenylporphyrin)manganese(III) indicate that the ring protons appear at ~+35 ppm.[3b] The data would seem to support the notion that a π delocalization is occurring here. The difference in mechanism of spin delocalization in going from high-spin Fe(III) to Mn(III) can be rationalized by considering the electronic distribution in the two complexes. In the Fe(III) complex the d-orbital population is $(d_{xy})^1 (d_{xz}, d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$ while for Mn(III) it is $(d_{xy})^1(d_{xz}, d_y)^2(d_{z^2})^1$. It is readily seen that in the iron complex the orbital that is predominantly involved in σ bonding with the porphyrin, $d_{x^2-y^2}$, is occupied by an unpaired electron. On the other hand, this orbital is empty in the Mn(III) complex. Therefore, while spin delocalization can occur *via* the σ orbitals of Fe(III) similar delocalization for Mn(III) is unlikely. In both cases, however, the metal π-bonding orbitals d_{xz},d_{yz} contain unpaired electron spin density so that a delocalization mechanism is possible for manganese(III) porphyrins.

Registry No. [Mn(DMDePor)Cl·H_2O], 29160-42-7; [Mn(DMMesoPor)Cl·H_2O], 29160-43-8; [Mn(DMPrPor)Cl·H_2O], 22357-85-3; [Mn(Etio I)Cl·H_2O], 29356-47-6; [Mn(MePheo *a*)Cl·H_2O], 29356-49-8.

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