Molecular Complexes of Metallo Tetraphenyl Porphyrins with 2,4,5,7-Tetranitro Fluorenone

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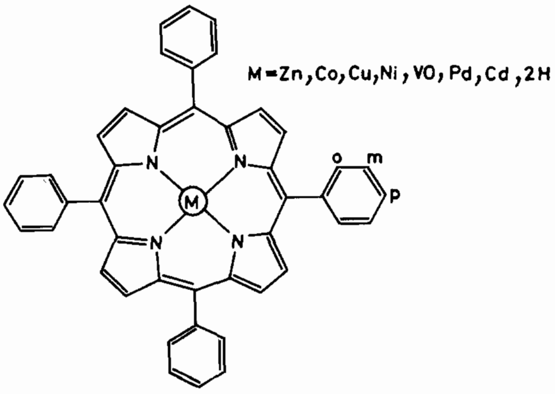
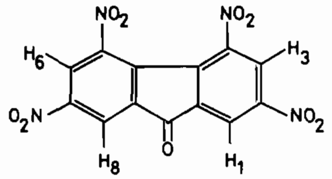
The interactions of mesotetraphenyl porphyrin and its metallo derivatives with 2,4,5,7-tetra nitrofluorenone have been studied using spectroscopic methods. The association constants (K) for 1:1 complexes in CH_2Cl_2 *follow the order* $Pd^{+2} > Co^{+2} > Cu^{+2} > VO^{+2} > Ni^{+2} > Zn^{+2}$*. The values of K are accounted in terms of stereochemistry of MTPPs and the electronic configuration of the metal ions. The magnitude and direction of the proton NMR shifts of the acceptor and donor in the complexes and their ESR parameters furnish information as to the possible structures of these complexes in solution.*

Introduction

Molecular complexation of porphyrins and their metal derivatives with diverse organic molecules has been the subject of numerous studies because of their presence and participation in many reactions of chemical and biochemical interest [1–4]. The porphyrins essentially function as donors in most of these reactions [5]. Amongst the possible interactions that lead to ground state stabilisation in such complexes, a significant contribution has been that of π–π interactions [6]. The important factors favouring maximum π–π interactions are the planarity and compatibility in sizes of the participating molecules. Amongst the π-acceptors, nitrofluorenones offer a good choice since the carbon skeleton of the fluorenones span a distance of 1.2 nm, comparable to that of tetraphenyl porphyrin (TPP) ~ (1.5 nm). The free base porphyrin is essentially planar and introduction of metal ions into the porphyrin cavity results in the deviation of planarity. The departure from planarity depends on the ionic size, spin state and coordination number of the metal ions. The interactions that define overlap criteria as outlined above would in effect be reflected in the magnitude of binding constants and thermodynamic factors. Thus a study of metalloporphyrins as donors is important and interesting from the point of view of the functional role of metal ions in governing the overall stabilities.



TETRAPHENYL PORPHYRIN



TETRA NITRO FLUORENONE

Fig. 1. Structure of metallo-tetraphenyl porphyrins and 2,4,5,7-tetranitrofluorenone.

In the present study, 2,4,5,7-tetranitrofluorenone (TENF) was chosen as an acceptor and TPP along with the metallo derivatives (VO^{2+}, Mn^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+} and Cd^{2+}) were employed as donors (Fig. 1). A perusal of literature reveals limited study on the employ of TENF as an acceptor

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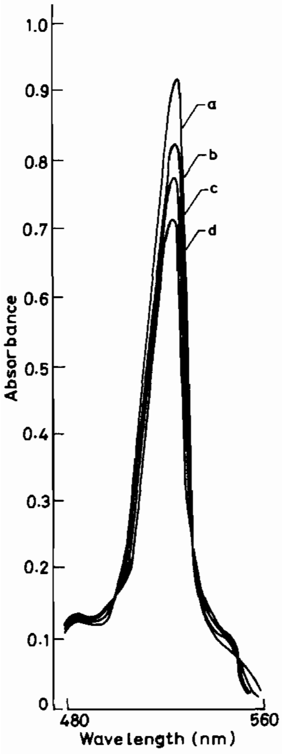

Fig. 2. Visible absorption spectra of (a) PdTPP 3.90 × 10^{-5} *M*) containing the following concentrations of TENF at 25 °C, (b) 4.89 × 10^{-4} *M* (c) 1.63 × 10^{-3} *M*, (d) 7.33 × 10^{-3} *M*.

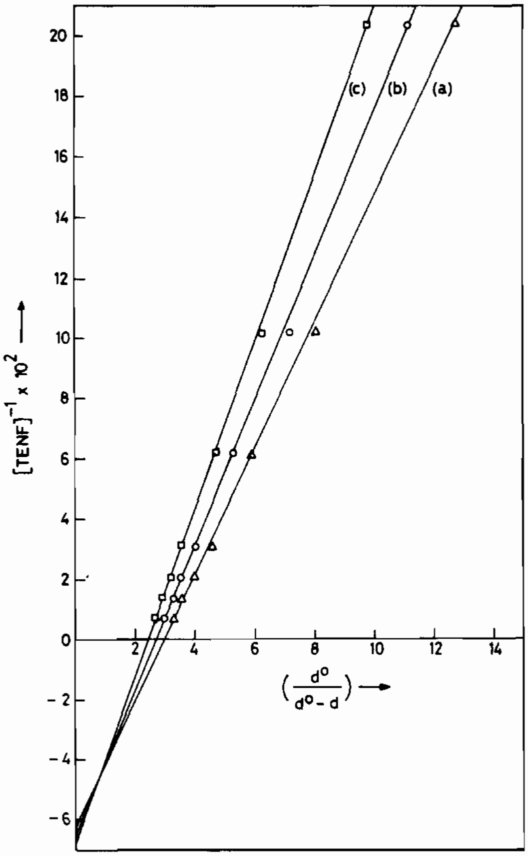

Fig. 3. Plot of $1/C_A$ *vs.* (d^o/d^o – d) for PdTPP interaction with TENF at different temperatures (a) 25 °C, (b) 13 °C and (c) 5 °C.

with the porphyrins. A preliminary structural report [7] on the Ni-etioporphyrin TENF (1:2) complex is worthy of mention here and this points out the essential planarity of the donor and acceptor molecules and the Ni atom is situated 0.36 nm away from the acceptor. The present investigation is directed towards the determination of the stoichiometry of the complexes in solution, the binding constants, thermodynamic parameters and spectral (^{1}H NMR and ESR) data that are important to derive information regarding the relative orientation of the donor and acceptor in the complexes in solution.

Experimental

The TPP and the metal derivatives were synthesised and purified as described in the literature [8]. TENF was obtained from Aldrich chemicals (U.S.A.) and recrystallised from hot acetic acid. CH_2Cl_2 was purified and distilled prior to use. The spectrometers used in the present study are essentially the same as described elsewhere [9].

Optical absorption spectral method was used to evaluate association constants and other thermodynamic parameters. The visible spectra were recorded on a series of solutions containing a fixed concentration of TPP/MTPP ($\sim 10^{-5}$ *M*) and varying concentrations of TENF (0.001 to 0.01 *M*) satisfying the condition (donor) $\ll$ (acceptor). Duplicate sets of experiments were carried out to check the reproducibility of the data points.

Results and Discussion

The visible absorption bands (Q bands) of MTPTs are characteristic of the nature of the metal ions in the porphyrin cavity. On addition of TENF, a decrease in intensity of the bands was observed in addition to the presence of isosbestic points (Fig. 2). These are in accord with the formation of molecular complexes between the MTPP and TENF in solution. The relative lowering of the absorbance on increasing addition of TENF was analysed using the expression developed by Nash [10]. The linearity of the plots reveal that the predominant species that exists in solution is the 1:1 complex (Fig. 3). The data treatment is essentially the same as reported in our earlier work [9]. The values of absorbance for each

TABLE I. Stability and Thermodynamic Parameters of MTPP Interaction with TENF.

Complex	Temp. °C	K dm^{-3} mol^{-1}	$-\Delta H$ kJ mol^{-1}	ΔS J deg^{-1} mol^{-1}
CoTPP–TENF	25.0	571 ± 100	2.8 ± 0.70	43.2 ± 1.5
	14.5	593 ± 110		
	5.0	620 ± 130		
CuTPP–TENF	25.0	448 ± 80	5.3 ± 0.70	33.0 ± 1.6
	14.5	508 ± 100		
	4.0	528 ± 120		
NiTPP–TENF	25.0	178 ± 60	5.5 ± 0.50	24.7 ± 1.0
	10.0	204 ± 70		
	4.0	209 ± 75		
ZnTPP–TENF	25.0	77 ± 25	9.4 ± 0.50	4.5 ± 0.6
	14.0	95 ± 30		
	5.0	101 ± 30		
PdTPP–TENF	25.0	627 ± 100	2.6 ± 0.60	44.8 ± 1.0
	13.0	651 ± 110		
	5.0	676 ± 125		
VOTPP–TENF	25.0	283 ± 60	5.1 ± 0.60	29.8 ± 0.6
	14.0	310 ± 65		
	5.0	328 ± 70		
MnTPPCl–TENF	25.0	64 ± 20	11.2 ± 0.50	2.6 ± 0.5
	16.0	78 ± 22		
	5.0	89 ± 25		
TPP–TENF	25.0	116 ± 30	12.7 ± 0.5	−31.8 ± 0.5
	13.0	140 ± 35		
	5.0	170 ± 40		
CdTPP–TENF (Ether)	25.0	665 ± 160	3.9 ± 0.5	40.7 ± 0.7
	12.0	729 ± 180		
	3.0	754 ± 210		

addition of TENF is monitored at different wavelengths in the absorption profile and the K value obtained remained constant at different wave lengths. The possible existence of complexes of 1:2 (MTPP: TENF) stoichiometry in solution was then analysed using the method of Bent and French [11]. The slopes of the logarithmic plots [11] yield valued in the range 0.8 to 1.6, indicating the existence of higher order complexes. We are unable to quantify the stability constants of such complexes, because of their presence only in very low concentrations. However, the presence of these complexes do not essentially alter the magnitudes of K values calculated for 1:1 complexes. The reliability of these values were once again checked using the saturation factor criteria [12]. The values of K and thermodynamic parameters are given in Table I.

An examination of the K-values for different divalent first row transition (MTPPs) association with TENF reveal the following decreasing order of stability Co^{+2} > Cu^{+2} > VO^{+2} > Ni^{+2} > 2H > Zn^{+2}. The binding constant for trivalent metal ion (Mn^{+3}) is generally less than those observed for divalent metal ions. The stability sequence is similar to that observed for TNB complexes [9]. This order of stabilities of molecular association is different from those observed for ligand binding where coordinative forces form the source of stabilisation. Further, the observation that the binding constants of second row transition metal ions is greater than first row divalent metal ion (Cd^{+2} > Zn^{+2} and Pd^{2+} > Ni^{2+}) implies the importance of ionic size and spread of electron distribution in governing the overall formation constants of molecular complexes.

The thermodynamic parameters, ΔH and ΔS values, are not found to be significantly different among the divalent MTPPs with the exception of ZnTPP. The relatively higher ΔH value and decreased

TABLE II. ESR Parameters of MTPP–TENF Complexes in Toluene Glasses.

Complex	$g_\parallel$	$g_\perp$	$A_\parallel^M\ 10^4$ cm^{-1}	$A_\perp^M\ 10^4$ cm^{-1}	$A_\parallel^N\ 10^4$ cm^{-1}	$A_\perp^N\ 10^4$ cm^{-1}
CuTPP	2.185	2.047	208.10	31.55	14.70	15.70
CuTPP–TENF	2.176	2.042	207.30	32.45	15.25	16.20
VOTPP	1.968	1.997	164.30	57.60		
VOTPP–TENF	1.961	1.990	160.80	58.80		
CoTPP[a]	1.970	2.80	141.00	210.00		
CoTPP–TENF	2.085	2.960	243.40[b]	287.9[c]		

[a] Values for CoTPP in Toluene are taken from B. B. Wayland and P. Mohajer, *J. Am. Chem. Soc.*, *93*, 5295 (1971). [b] Average of 3 high field lines (250 G). [c] Average of 4 lines (208.33 G).

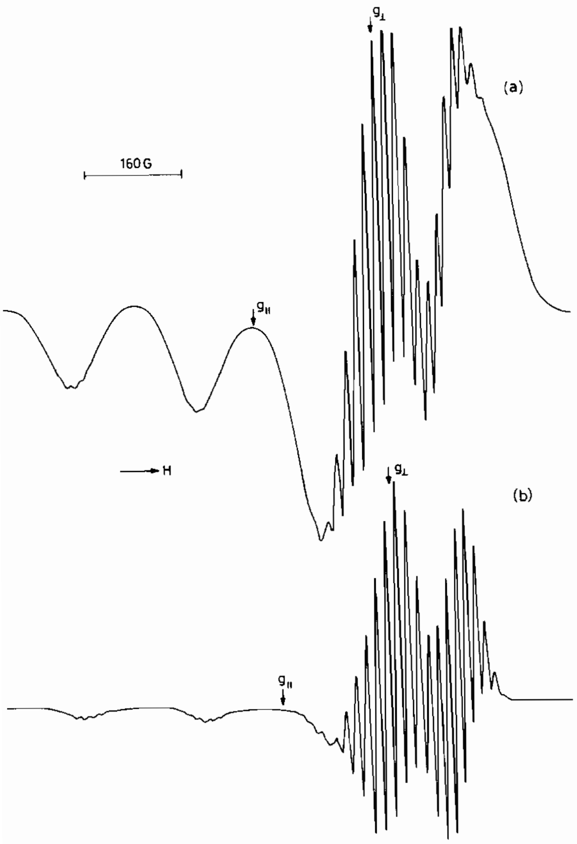

Fig. 4. ESR spectra of (a) CuTPP and (b) CuTPP–TENF in toluene glass at 100 K.

ΔS value resemble closely those observed for the corresponding complex with TNB, indicating that packing considerations are important in governing the stability [9]. It is difficult to rationalise the different stereochemistries of MTPPs with the ΔH or ΔS values. However, the ΔH and ΔS values for trivalent Mn are different from those observed for divalent MTPPs. This seems to suggest that the binding in TPP arise from a possible axial ligation of the carbonyl group to Mn(III).

The ESR spectra of MTPPs, (M = VO^{2+}, Co^{2+} and Cu^{2+}) and their complexes in toluene at 100 K display characteristic features in parallel and perpendicular regions (Fig. 4), thereby permitting evaluation of ESR parameters (Table II). The slight decrease in $g_\parallel$ and $A_\parallel^M$ values with accompanying increase in $A_\perp^N$ and $A_\parallel^N$ values relative to the free MTPPs in the case of CuTPP and VOTPP complexes are in agreement with the formation of molecular complexes [13]. The manifestation of such effects arise from the relatively small change in the distribution of π-electron levels of the porphyrin π-system as a consequence of donation to the acceptor. The slight decrease in the value of α^2 (the covalency factor) in the complex relative to free CuTPP slightly increases the charge on the central copper atom, which results in lowering of the copper $d_{x^2-y^2}$ orbital facilitating easy mixing with the ligand σ-orbitals. On the other hand, in CoTPP the unpaired electron resides in d_{z^2} orbital and the acceptor molecule will essentially sense the axially oriented d_{z^2} orbital. Such interaction will be reflected in the magnetic isotropic values, ($g_\parallel^2 - g_\perp^2$), the magnitude of which depends on the energy difference $\Delta E(a_1 - e)$ [3b]. The observed increase in ($g_\parallel^2 - g_\perp^2$) values for the CoTPP complex reflects a decrease in $\Delta E(a_1 - e)$, thereby indicating that the π-donation by the porphyrin is transmitted through the bonding framework. The decrease in the $\Delta E(a_1 - e)$ value essentially implies lowering of the d_{z^2} orbital on complexation, such that the π-complexation with the acceptor affects the nitrogen basicity altering the Co–N σ-bond. Alternately, if the coordinative interaction prevails, this would raise the d_{z^2} orbital thereby increasing the separation $\Delta E(a_1 - e)$. The present results indicate that the π–π interactions are dominant and this influences the electronic levels of the central metal ions.

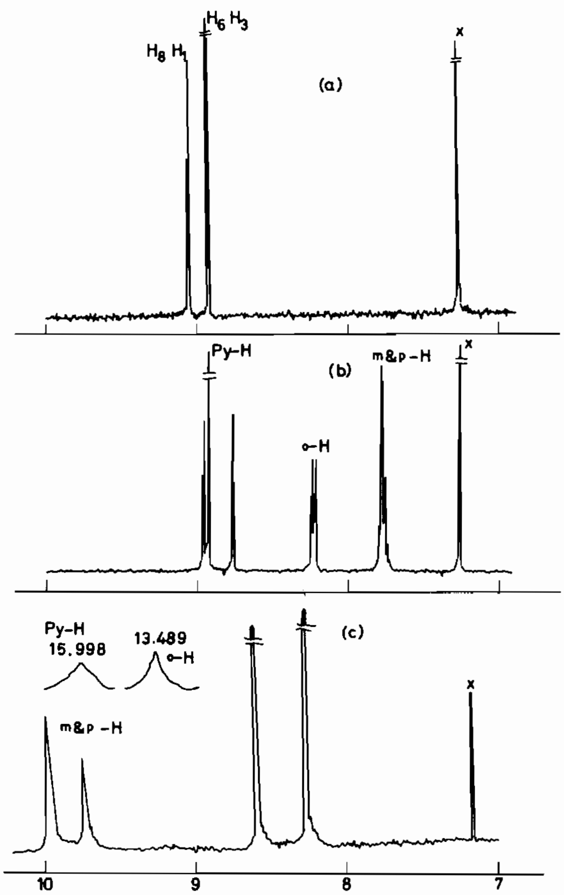

Fig. 5. ^{1}H NMR spectra of (a) TENF (b) 1:1 complex of ZnTPP–TENF and (c) 1:1 complex of CoTPP–TENF.

In view of the observations that the interactions are essentially localised in the π-system of porphyrins, the ^{1}H NMR spectral studies were undertaken to arrive at the relative orientations of the molecules in solution. We examined the effect of complexation from the proton resonance shifts experienced both by acceptor and donor MTPPs (M = VO, Mn, Co, Ni, Zn and Pd). The data obtained in the spin free complexes are used to distinguish the dipolar and ring current contributions to the proton resonance shifts. The ^{1}H NMR resonances of TENF were assigned earlier [14]. In all the complexes the proton resonances of the acceptor are shielded and the extent of shielding is dependent on the nature of the metal ions (Fig. 5). The multiplet structure of the acceptor proton resonances is retained in all the complexes, except for TPP and paramagnetic MTPP complexes. Amongst the acceptor protons, H_3 and H_6 resonances are relatively more shielded than others, implying that they are situated closer to the porphyrin periphery. The H_1 and H_8 resonances also experience shielding though the magnitudes of these are smaller than H_3 and H_6. The sensitivity of these resonances to complexation is brought about in the plot of shifts of these protons *versus* the magnitude of K in the diamagnetic MTPP complexes (Fig. 6). As anticipated, these proton resonances are broadened (~30 H_z) in spin-free MTPP complexes owing to dipolar effects.

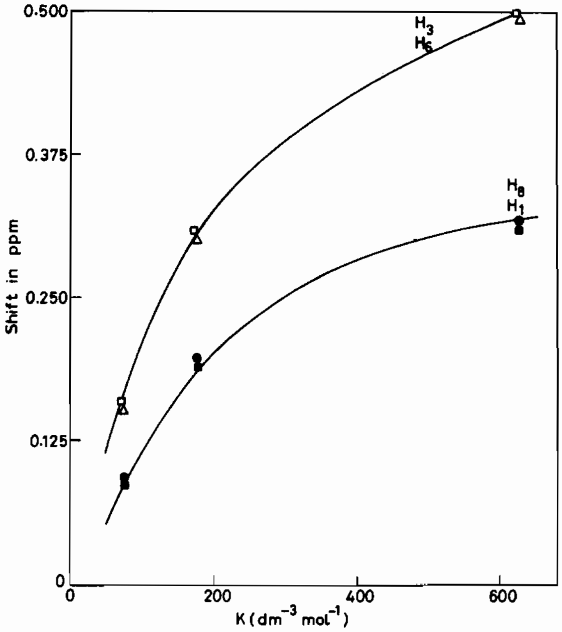

Fig. 6. Plot of K *vs.* the shift in different proton resonances of TENF on complexation.

The complexation effect on the donor protons of pyrrole and ortho, meta and para of the meso aryl group is more pronounced in the paramagnetic complexes. A down-field shift of 0.036 δ of the pyrrole protons and the decreased line width of both pyrrole and ortho hydrogens (shortened T_{1e}) in CoTPP complexes are significant. Though the pyrrole proton resonance of VOTPP could not be located, this resonance in MnTPPCl at −23.018δ is shielded, reduced in intensity and broadened. The meta and para protons in VOTPP and MnTPPCl are broadened after complexation. On the other hand, in the case of diamagnetic complexes although the pyrrole proton resonances experiences shielding, the ortho, meta and para proton resonances of the aryl ring experience both deshielding and shielding effects depending on the metal ion. However, the magnitudes of these shifts are very small.

An attempt has been made to rationalise the direction and magnitude of shifts experienced by the acceptor and the donor protons in the complexes in terms of overlap pictures, using CPK models (Fig. 7). Three situations are realised: (a) the acceptor is placed over the porphyrin plane such that the axis passing through the five membered ring of the fluorenone is coincident with the C_4 axis of the porphyrin.

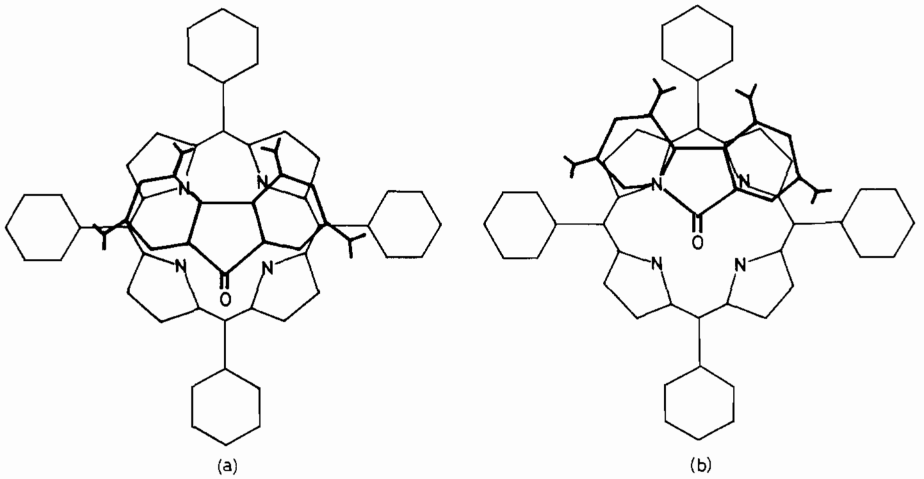

Fig. 7. Possible overlap pictures of the donor and acceptor in solution: (a) the C_4 axis of the porphyrin is coincident with the C_5 axis of the fluorenone skeleton and (b) the keto carbonyl group of the fluorenone is above the metal ion (see text).

This plane-to-plane overlap would essentially dispose the TENF protons over the porphyrin core such that the NO_2 groups lie between the aryl groups of TPP. In this case the protons of TENF would experience uniform shielding. (b) The acceptor can be displaced over the porphyrin core such that the keto carbonyl group is tilted towards the metal, in order to promote keto carbonyl interaction with the central metal ion. This would position the H_1 and H_8 protons nearer to the porphyrin core whereas H_3 and H_6 lie away from it. (c) Alternatively, the keto group can be tilted away from the metal centre which would bring the H_3 and H_6 protons near to the porphyrin core. We believe that an overlap described in (c) is more likely since the ν(CO) in the IR region is not perturbed in the complexes, if the situation described in (b) were to be true. Further, the observed larger magnitude of shielding of H_3 and H_6 proton of TENF require that these are positioned near to the porphyrin core. The overlap structure proposed here differs from that of the reported by X-ray crystallographic study in many ways. We are able to quantify the parameters only for 1:1 complexes while the crystal structure data is for a 1:2 complex. Secondly, the choice of the porphyrin is different from that reported in the structural study. It is likely in the meso aryl TPP, the situations can be different since the aryl substituents themselves are good donors. Thirdly, the tilting of the keto carbonyl group away from the central metal ion is found in the crystal structure of the 1:2 complex. We believe that the solution structure described here faithfully represent the data obtained; however, a detailed picture must await the X-ray structural work on these complexes.

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