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Redox reactions of an Mo(V) tetrasulfophthalocyanine

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Abstract

The preparation of an Mo(V) tetrasulfophthalocyanine and some of its thermal and photochemical reactions have been investigated in this work. Electrochemical processes have been followed by means of the UV–Vis spectral changes and compared with those observed in flash photolysis. Mo(IV) and Mo(V)-ligand-radical species are common intermediates of the electrochemical and photochemical reactions. In 254 nm irradiations of the Mo(V) tetrasulfophthalocyanine in aqueous solutions of 2-propanol, the macrocycle can be photohydrogenated and the product of the photolysis can be reoxidized with O_2 back to the parent complex.

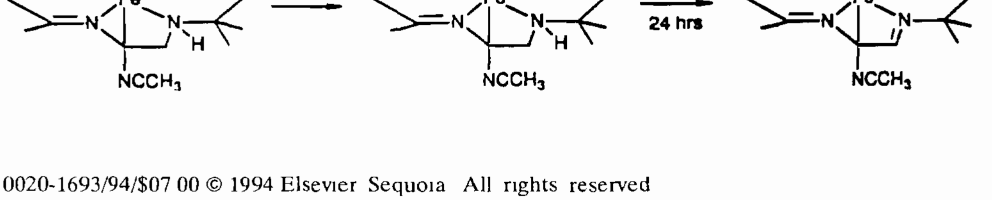
Key words Electrochemistry, Molybdenum complexes; Macrocyclic ligand complexes; Phthalocyanine complexes

Introduction

A number of examples of metal ion catalyzed hydrogenation and dehydrogenation reactions of macrocyclic ligands have been reported in the literature [1] Common to these processes, is the participation of coordination complexes with metal ions in unstable oxidation states. For example, $Me_6[14]4,11\text{-diene}N_4$ coordinated to Fe(II), eqn. (1), undergoes a dehydrogenation reaction which is mediated by an Fe(III) complex.

The same macrocycle coordinated to Ni(II) undergoes dehydrogenation, eqn. (2), or hydrogenation, eqn. (3), reactions under appropriate chemical conditions.

If such ligand hydrogenation/dehydrogenation processes are made labile and reversible by coordination of the macrocycle to a given metal ion, the complex may have a number of practical applications, e.g. as a catalyst of redox reactions and/or in cycles for the storage of solar energy [2]. The reversibility exhibited by some redox reactions involving phthalocyanine complexes is appealing from such a standpoint. Several literature reports about the preparation of molybdenum phthalocyanines have shown that compounds of Mo(IV) and Mo(V) exhibit sufficient thermal stability for their isolation as pure products [3–5]. There is little information, however, about the thermal and photochemical reactivity of the Mo macrocycles in general and phthalocyanines in particular [6]. In this work, we report experimental observations about the reversible thermal and photochemical hydrogenation of the Mo(V) macrocycle.



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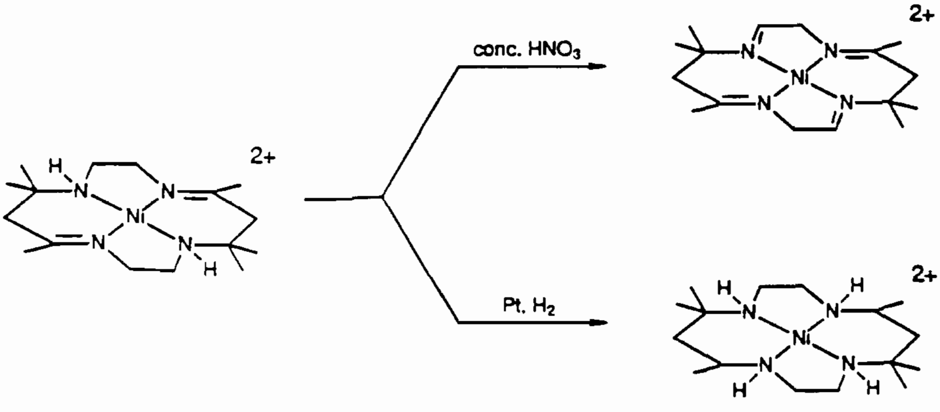

(2)

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Experimental

Photochemical procedures

The flash photolysis apparatus for the measurement of transient spectra and the investigation of reaction kinetics has been described elsewhere [7, 8]. A Quanta Ray Nd:YAG laser was used for the irradiation of samples at 265 nm in flash photolysis experiments requiring ns-time resolution. Two Xe flash lamps and appropriate cutoff filters were used for UV irradiations, $\lambda_{\text{excit}} > 240$ nm, in flash photolysis with μs–ms time resolutions Continuous photolyses at 254 nm were carried out with low pressure Hg lamps with intensities, $I_0 = 5.0 \times 10^{-6}$ Einstein dm^{-3} s^{-1} In all these experiments, solutions of the photolyte were deaerated with streams of ultrapure N_2 before and during the irradiation.

Electrochemical procedures

Cyclic voltammograms were run with 0.1 M tetrabutylammonium hexafluorophosphate in DMF on a PAR 175/173 using a Pt disk working electrode, an Ag wire auxiliary electrode and SCE reference in a standard H cell. Differential pulse polarography (DPP) was performed using a PAR 174A with the same solvent and electrodes. Controlled-potential electrolytes were carried out in a cell with two cylinders of Pt gauze as working and auxiliary electrodes and an Ag/AgCl-coated wire as a reference electrode The auxiliary electrode was separated from the compartment housing the other two by a glass frit. The solutions used in these electrochemical experiments were deaerated with streams of ultrapure Ar.

Materials

The pentahydrate of the Mo(V) tetrasulfophthalocyanine, abbreviated as $Na_4[Mo(O)(OH)TsPc] \cdot 5H_2O$, was prepared by a modification of the method reported by Weber and Busch [9] Molybdenum hexacarbonyl, 2 18 g, from Alfa was used as a reactant in the preparation. The compound was dispersed in a mixture containing 5.0 g of the monosodium salt of 4-sulfophthalic acid, 6.0 g of urea, 0.5 g of ammonium chloride and 0.05 g of ammonium molybdate. The solid mixture was added to 5 cc of nitrobenzene and refluxed for 5 h at 180–200 °C The crude product was washed with 200 cc of methanol and added to 100 cc of 1.0 M HCl saturated with NaCl The solution was brought to a rapid boiling, cooled to room temperature and filtered The solid material was dissolved in 90 cc of 0.1 M NaOH, heated to 80 °C and filtered hot. A pure compound was separated by centrifugation after the addition of 5–10 g of NaCl and 200 cc of 95% ethanol to the filtrate. The sulfophthalocyanine was recrystallized three times from aqueous solutions by adding 95% ethanol *Anal.* Found: C, 33.48; H, 2.18; N, 10.15; O, 25.85. Calc. for $MoC_{32}O_{23}N_9S_4H_{47}Na_4$: C, 33.71; H, 2 02; N, 9.83; O, 26.69%.

Tetraethylammonium (Et_4N) salts were prepared via cation exchange chromatography using Whatman C52 cation exchange resin that was pre-equilibrated with Et_4NCl, then washed with water. The crude material of the preparation (above) was dissolved in water and sorbed onto a 1.5×15 cm column of the resin. The sorbate was eluted with water and the solid recovered by evaporation of the solvent under reduced pressure. The desired oxy-hydroxy product was obtained by the gel-filtration procedure described next A 20 mg sample of the complex was dissolved in water and sorbed onto a 2×23 cm column of Sephadex G25 resin (swelled in water) and eluted with water. Two bands were observed, the first band was deep green, and the second was blue–green The delineation between the bands was not clear and only the first 75% of the front fraction was collected. This was run through another G25 column where it remained as a tight band. Solutions of colloidal Pt-catalyst were prepared according to a literature procedure [10].

Tetraethyl ammonium perchlorate was recrystallized twice from boiling ethanol. Spectrophotometric grade

DMF, DMSO and 2-propanol were used in electrochemical or photochemical experiments. Other materials were reagent grade and used without further purification

Results and discussion

The product prepared by the procedure described above has the stoichiometry expected for an Mo(V) complex of the ligand 4,4′,4″,4‴-tetrasulfophthalocyanine. In addition, the IR and ESR spectra of the solid Et_4N^+ or Na^+ salts, Fig. 1, are in accord with those already assigned to a phthalocyanine with a group, $O{=}Mo^V{-}OH^-$ [3, 4]. In these regards, the monomeric formula of the complex anion can be conveniently abbreviated as $Mo^V(O)(OH)TsPc^{4-}$. Thermal and photochemical properties of this Mo(V) complex investigated in this work are reported below.

Species in aqueous and non-aqueous solutions

The UV–Vis spectrum of the compound in aqueous or DMF solutions, respectively, exhibited absorption bands whose positions were close to those of equivalent bands in the spectra of transition metal ion phthalocyanines. The formation of aggregates was investigated by means of the UV–Vis spectra of $Mo(O)(OH)TsPc^{4-}$ solutions with concentrations of complex between 10^{-4} and 10^{-6} M. No aggregation was detected in DMF and DMSO where the Mo(V) compound exhibited the absorption spectra of the monomeric phthalocyanines. For example in DMSO solutions, $[Mo^V(O)(OH)TsPc^{4-}] \simeq 10^{-5}$ M, the lowest energy band, $\lambda_{max} = 696$ nm and $\epsilon \sim 1.4\ 10^4\ M^{-1}\ cm^{-1}$, is found at lower energies than the literature report [5], $\lambda_{max} = 630$ nm, and by its position and shape can be assigned to a monomeric species [6, 11].

Departures from Beer's law in the spectra of aqueous solutions were similar to those previously observed in the aggregation of Co(III) tetrasulfophthalocyanine [8]. The dependence of the 696 nm optical density on the complex concentration was in accordance with aggregation into dimeric species for the range of concentration indicated above. Indeed, the spectra in aqueous solutions, $[Mo^V(O)(OH)TsPc^{4-}] \leqslant 10^{-4}$ M, exhibits a broad NIR band, $\lambda_{max} = 680$ nm, which is typical of dimeric sulfophthalocyanine aggregates, e.g. $(Mo^V(O)(OH)TsPc^{4-})_2$ [6, 11]. It is possible that such aggregates have $Mo^V{-}O{-}Mo^V$ bonds similar to those of other related macrocyclic complexes [12–15].

Electrochemical reduction

Two major waves and two minor waves, i.e. at −0.108, −0.806 and −1.123, −1.370 V, were observed in DPP measurements, Fig. 2. By contrast, little electrochemical information could be derived from the rather featureless cyclic voltammograms in DMF. the poor solubility of the complex in such a solvent seems to be the reason hindering the experimental observations

Controlled potential electrolytes of monomeric $Mo^V(O)(OH)TsPc^{4-}$ in deaerated DMF, applied voltages −0.35 or −0.40 V versus SCE, were followed by means of the spectral changes, Fig 3(a). The reduction of the Mo(V) complex by one or less than one Faraday/mol generates an ESR mute molybdenum phthalocyanine with an intense absorption at $\lambda_{max} = 675$ nm (Q band) and absorptions at shorter wavelengths. These are expected properties for an Mo(IV) species

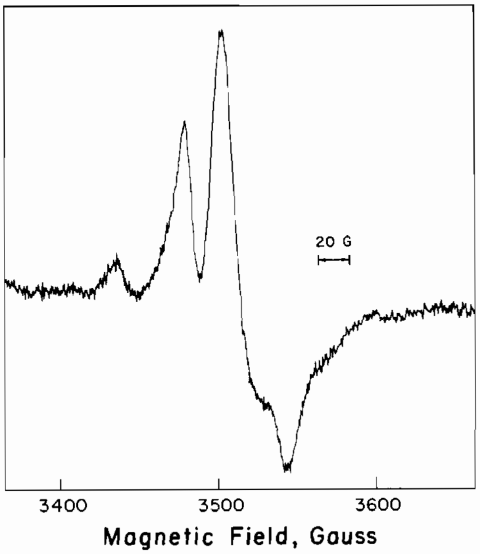

Fig. 1 ESR powder spectrum of $Na_4Mo(O)(OH)TsPc$ at room temperature

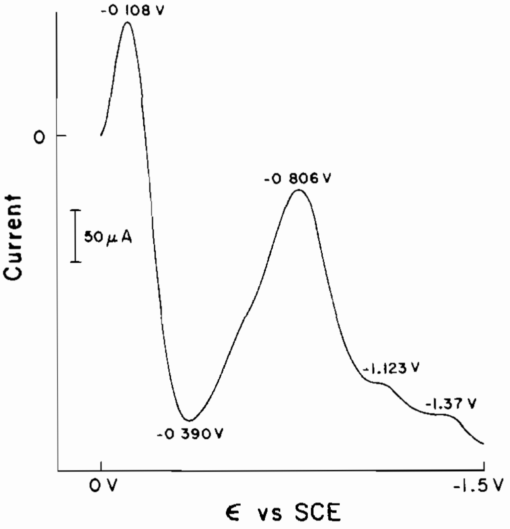

Fig 2 Trace from a DPP scan of deaerated $Mo^V(O)(OH)TsPc^{5-}$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate as a support electrolyte Scan rate of 10 mV/s and 25 mV PP

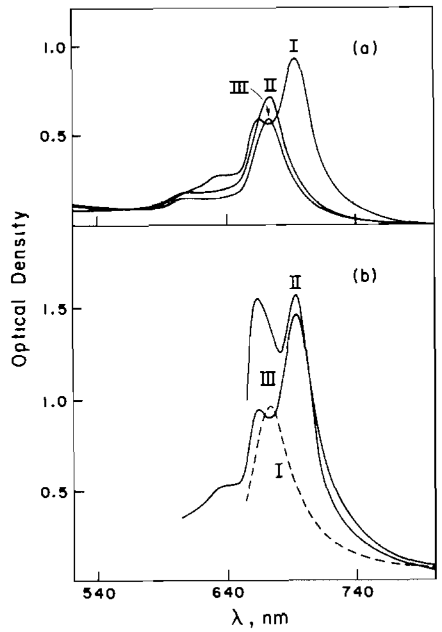

Fig 3. Spectral changes induced in the electrochemical reduction of $Mo^V(O)(OH)TsPc^{4-}$ (a) and in the air reoxidation of the reduction product (b) The spectrum I in (a) has been recorded with solutions of the Mo(V) complex in deaerated DMF before electrolysis, the spectra II and III have been respectively recorded after reductions with 1 0 Faraday/mol and 1 5 Faraday/mol. The aeration of the solution, (b), causes the spectrum to change from the one corresponding to the product of the $Mo^V(O)(OH)TsPc^{4-}$ reduction, I, to the spectrum of an intermediate, II, first and to the final product, III, later

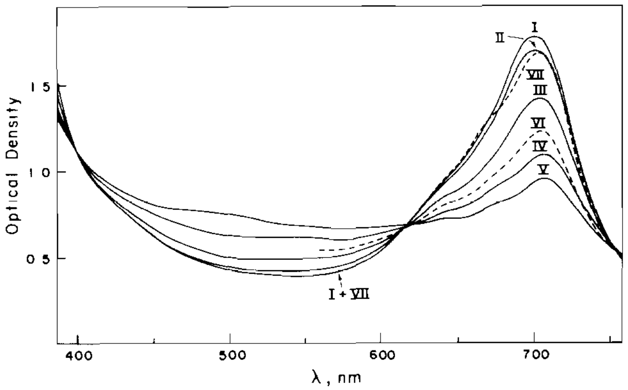

Fig. 4 Spectral changes induced in 253.7 nm photolyses of $(Mo^V(O)(OH)TsPc^{4-})_2$ in aqueous-deaerated 2 0 M 2-propanol. The irradiations are I, 0, II, 2, III, 7, IV, 12, V, 22 min The dashed lines, VI and VII, are spectra recorded 4 and 8 min, respectively, after V has been exposed to air

[3–5, 11]*. Such an electrochemically generated Mo(IV) sulfophthalocyanine was reoxidized with O_2 to an Mo(V) species with a spectrum similar to the one recorded with the parent $Mo^V(O)(OH)TsPc$. The reoxidation process is a complex one which involves reaction intermediates. Such intermediates were detected by means of the UV–Vis spectra recorded at various times following aeration of the solution from the electrochemical reduction, Fig. 3(b). Since Mo(V) porphyrins with coordinated peroxide are known to be stable in solution [16, 17], it is possible that the observed transient species have either peroxo or superoxo ligands. Such an assignment receives further support from the previously reported observation of peroxo and superoxo species in the oxidation of Co(II) sulfophthalocyanine by O_2 [7].

Photochemical reactions

No photochemical transformations were observed in 640 nm steady state photolyses of $Mo^V(O)(OH)TsPc^{4-}$ in DMF. Only fast fluorescence, $\tau < 10$ ns, with a low quantum yield, $\phi \sim 10^{-3}$, was detected in these experiments. Irradiations, $\lambda_{exc} = 254$ nm, of $(Mo^V(O)(OH)$-$TsPc^{4-})_2$ in deaerated 10% 2-propanol, pH 6, were followed by means of the spectral changes, Fig. 4. Bleach of the spectrum at wavelengths longer than 630 nm and the appearance of weaker absorptions between 400 and 650 nm signal the photochemical formation of a species with a reduced macrocycle, i.e. the result of a double bond hydrogenation and the disruption of the π-system conjugation*. When this product reacts with O_2, the spectrum of $(Mo^V(O)(OH)TsPc^{4-})_2$ is regenerated, curves VI and VII in Fig 4, and H_2O_2 is detected at the end of the oxidation**. Transient absorptions, seen as a shoulder, $\lambda \sim 670$ nm, on the absorption band at 703 nm, indicate that the reoxidation of the photochemical product involves metastable species, probably peroxo and/or superoxo complexes, similar to those reported above for the oxidation of the electrochemically generated Mo(IV). Moreover, the anaerobic mixing of a colloidal Pt solution with deaerated solutions of the photohydrogenated sulfophthalocyanine resulted in a spontaneous conversion of such a complex to $(Mo^V(O)(OH)TsPc^{4-})_2$ and liberation of H_2. The recovery of the parent complex in these oxidations reveals that the ligand remains a close macrocycle after the photochemical reduction and that it is able to transfer reduction equivalents to other substrates.

The results of the photochemical experiments can be rationalized in terms of a photoredox dissociation, eqn. (4), previously reported for other phthalocyanines [6, 8].

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*The small concentration of complex and small volumes of solution used in these experiments prevented us from isolating the reaction product.

**H_2O_2 was investigated by following the formation of I_2 when H_2O_2 reacted with I^-

$$(\mathrm{Mo^V(O)(OH)TsPc^{4-}})_2 \xrightarrow{h\nu} \mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{3-}} + \mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{5-}} \qquad (4)$$

$\lambda_{exc} = (250 \pm 10)$ nm

In flash photolysis, the photodissociation of the Mo(V) dimer, eqn. (4), was observed as a fast process, i.e. with a lifetime $\tau \leqslant 10$ ns, which leads to the products, $\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{3-}}$ and $\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{5-}}$, with oxidized and reduced macrocycles. The radical nature of these intermediates was assessed by comparing features of transient spectra recorded in less than 100 ns with those reported for radicals of other metallophthalocyanines [8, 18, 19]. The abstraction of H atoms from 2-propanol by sulfophthalocyanine radicals, eqn. (5), is a well characterized process which is faster than the radical recombination, eqn. (6), when 2-propanol concentrations exceed 0.1 M [8, 18, 19].

$$\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{3-}} + \mathrm{(CH_3)_2CHOH} \longrightarrow \mathrm{Mo^V(O)(OH)TsPcH^{3-}} + \mathrm{(CH_3)_2COH^{\bullet}} \qquad (5)$$

$$\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{3-}} + \mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{5-}} \longrightarrow (\mathrm{Mo^V(O)(OH)TsPc^{4-}})_2 \qquad (6)$$

The spectrum recorded with a 250 ns delay from the 266 nm flash irradiation of the Mo(V) complex in 2 M 2-propanol, Fig. 5(a), can be assigned, therefore, to $\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{3-}}$.

Some additional spectral changes, Fig. 5(a), were observed after the appearance of the sulfophthalocyanine radical. This optical transient lasts into the μs time domain, Fig. 5(b), and decay rate of the optical density is independent of the sulfophthalocyanine and 2-propanol concentrations. It is possible, therefore, that the low concentrations of Mo(V) used in flash photolysis experiments prevent a reaction between excess complex and $\mathrm{(CH_3)_2\dot{C}OH}$ and that hydroxylalkyl radicals undergo disproportionation, eqn. (7), in accordance with literature reports [20].

$$2\mathrm{(CH_3)_2COH^{\bullet}} \longrightarrow \mathrm{(CH_3)_2CHOH} + \mathrm{(CH_3)_2CO} \qquad (7)$$

The spectral changes in Fig. 5 have been associated with an intramolecular electron transfer conversion of $\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{5-}}$ to a more stable Mo(IV) complex, eqn. (8).

$$\mathrm{Mo^V(O)(OH)(TsPc^{\bullet})^{5-}} \longrightarrow \mathrm{Mo^{IV}(O)(OH)TsPc^{5-}} \qquad (\tau \sim 500 \text{ ns}) \qquad (8)$$

Intramolecular electron transfers of the kind indicated in eqn. (8) have been observed before with other phthalocyanine radicals, e.g. the conversion of $\mathrm{Co^{III}(TsPc^{\bullet})^{3-}}$ to $\mathrm{Co^{II}(TsPc)^{4-}}$ [8]. Electrochemical results (above) show that the driving force of such reactions must be the larger stability of the species with a reduced metal center versus the one having a reduced macrocycle. Optical density changes related to the formation of the continuous photolysis product with a hydrogenated macrocycle were observed in an ms to s time domain. They appear to be kinetically of a second order with respect to the concentration of Mo(IV) intermediate. The appearance of the reduced product can be described in terms of eqn. (9).

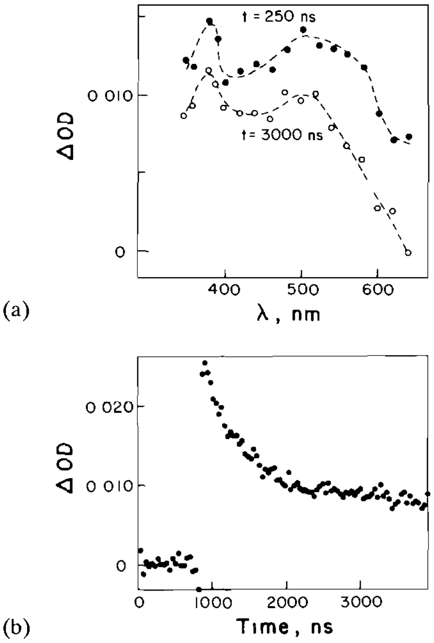

Fig. 5. Transient spectra (a) recorded in 266 nm laser flash irradiations of $(\mathrm{Mo(O)(OH)TsPc^{4-}})_2$ in aqueous-deaerated 2 0 M 2-propanol The time-resolved 580 nm optical density changes are shown in (b)

$$2\mathrm{Mo^{IV}(O)(OH)TsPc^{5-}} \xrightarrow{2\mathrm{H}^+} \mathrm{M^V(O)(OH)(TsPcH_2)^{4-}} + \mathrm{Mo^V(O)(OH)TsPc^{4-}} \qquad (9)$$

Conclusions

Mo(IV) is sufficiently stabilized in sulfophthalocyanine to be the product of an electrochemical reduction in DMF. In aqueous solutions, however, it mediates the reduction of the ligand. Since the reduced ligand remains a close macrocycle, it is able to transfer reduction equivalents to other substrates and regenerate the parent Mo(V) complex. It is possible that other Mo(V) macrocyclic complexes may undergo similar redox processes.

Acknowledgements

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