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ARTICLE

A hexanuclear manganese(II) complex: Synthesis, characterization and catalytic activity toward organic sulfide oxidation†

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Herein we report on the synthesis and characterization of a hexanuclear [Mn^{II}₆] wheel-like assembly with naphthalene-1,8-dicarboxylate and 1,10-phenanthroline as ligands. Overall antiferromagnetic behavior of the magnetic properties is observed. The complex is a catalyst toward organic sulfide oxidation in the presence of H₂O₂ with good selectivity (98-100%).

Introduction

Oxidation reactions to produce useful chemicals are among important reactions in both small and industrial scales.¹ The application of transition metal complexes as catalysts in organic synthesis is an exciting field of research, and they are extensively employed in a wide range of areas of preparative organic chemistry.²

Among those reactions, the selective oxidation of sulfides is an important transformation in organic synthesis, leading to sulfoxides, playing the role of essential intermediates.³

Sulfur-containing compounds play an important role in the pharmaceutical industry and particularly as antibacterial agents with sulfur at an elevated oxidation state.⁴ To obtain many of these agents, oxidation of a sulfide is often required. Among different sulfide oxidation reactions, the oxidation of a sulfide to a sulfoxide is especially important. The oxidation reaction performances with a very wide variety of reagents and catalysts.⁵ Hydrogen peroxide is a commonly used oxidant due to its low-cost and that it is environmentally friendly. In recent years, some transition-metal catalysts such as vanadium,⁶ rhenium,⁷ iron,⁸ manganese⁹ and titanium¹⁰ have been widely used to catalyze the selective oxidation of sulfides to sulfoxides, in the presence of hydrogen peroxide.

Manganese compounds are not only low cost and environmentally friendly, but also used by Nature in a variety of metalloenzymes specially to oxidation reactions.¹¹ Thus, manganese complexes with different ligands were used as catalysts to promote oxidation reactions.¹²

In this paper we present a new hexanuclear Mn(II) complex (**1**) active as a catalyst towards oxidation reactions, in particular of sulfides.

Experimental

Synthesis

A mixture of MnCl₂·4H₂O (395.82 mg, 2 mmol), naphthalene-1,8-dicarboxylic anhydride (396.36 mg, 2 mmol), NaOH (80.4 mg, 2 mmol) and phenanthroline (396.48 mg, 2 mmol) in acetonitrile-water (30 ml, V/V, 1:2) was sealed in a 100 ml stainless steel reactor with a Teflon liner and heated at 393 K for 24 h. Then, the reactor was cooled slowly to room temperature and the mixture was filtered, yielding yellow block-shaped single crystals of **1** suitable for X-ray analysis after one week (yield 24%).

Structure 1

X-ray diffraction experiment: Single crystal of **1** in form of a yellow polyhedron was mounted on a Stoe IPDS2 diffractometer equipped with MoK_α radiation source and an image plate detector (see Table 1 for basic crystallographic data).

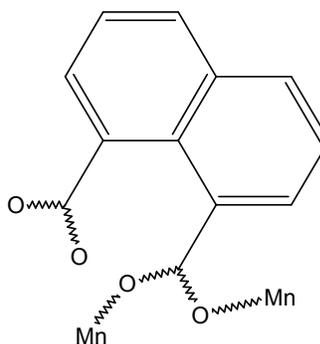
Details on structure refinement: The crystal structure **1** was solved by direct methods with SHELXS97 software and refined in SHELXL97.¹³

Table 1. Selected X-ray data for **1**.

Formula	$\text{Mn}_6\text{C}_{144}\text{H}_{108}\text{N}_{12}\text{O}_{36} \cdot 18.12(\text{H}_2\text{O})$
Formula weight	3220.25
Temperature [K]	100(2)
λ [Å]	0.71073
Crystal system	trigonal
Space group	$\bar{R}3$
a [Å]	19.708 (3)
c [Å]	30.193 (4)
V [Å ³]	10156 (3)
Z , ρ_{calc} [g cm ⁻³]	3, 1.580
μ [mm ⁻¹]	0.65
$F(000)$	4971
Crystal size [mm]	0.19 × 0.19 × 0.18
θ range [°]	1.37–24.99
reflins: total/unique	62327/3977
$R(\text{int})$	0.075
Abs. corr.	numerical
Min., max. transmission factors	0.985, 0.990
Data/restraints/params	3977/0/335
GOF on F^2	1.00
$R1$ [$I > 2\sigma(I)$]	0.029
wR_2 (all data)	0.041
Max., min. $\Delta\rho_{\text{elect}}$ [e Å ⁻³]	0.35, -0.30

Disordered water molecules of solvation were localized. O2W/O22W are cooperatively disordered with the refined occupancy factors of 0.72(1)/0.28(1), respectively. The occupancies of O3W/O33W/O23W/O4W were refined and subsequently fixed at the refined values of 0.38(1), 0.19(1), 0.17(1) and 0.28(1), respectively. O11W lies in special position on a three-fold symmetry axis with symmetry-induced disorder of H atoms, taken into account by setting the corresponding occupancies. All H atoms, excluding these bonded to most of the disordered water molecules, were found on difference Fourier maps. In case of water H atoms a DFIX restraint was used to set the O-H bond length at 0.82 Å. Subsequently the H atoms parameters were constrained with $U_{\text{eq}} = 1.5/1.2U_{\text{eq}}$ (parent atom) for water/aromatic C-bonded H atoms, respectively. On the final difference Fourier map the highest rest peak of 0.35 e/Å³ is located at 0.04 Å from Mn1.

CCDC-1004129 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Scheme 1.** Coordination mode of the naphthalene-1,8-dicarboxylate ligand in **1**.

Other measurements

MIR spectra of the samples prepared in form of KBr pellets were recorded on a Genesis FT-Spectrometer (ATI Mattson) in the range between 400 and 4000 cm⁻¹. Measurements of magnetic properties were carried out with a Quantum Design SQUID magnetometer for the sample of **1** (6.83 mg) in scotch tape holder within a temperature range of 2–300 K applying external fields of 500 and 1000 Gs. Diamagnetic corrections were introduced using Pascal constants.¹⁴

General procedure for sulfide oxidation

To a solution of sulfide (0.2 mmol, see Table 2), chlorobenzene (0.2 mmol) as internal standard and **1** (0.005 mmol) in a 1:1 mixture of CH₃OH/CH₂Cl₂ (1 mL) was added 0.2 mmol H₂O₂ as an oxidant. For the analysis of products, after stirring at room temperature for 2 h, the solution was subjected to ether extraction (3 × 10 mL), and the extract was also concentrated down to 1.0 mL by distillation in a rotary evaporator at room temperature. Then, a sample (2 µL) was taken from the solution and analyzed by gas chromatography (GC). The retention times of the peaks were compared with those of commercial standards, and chlorobenzene was used as an internal standard for the GC yield calculation.

Results and discussion

1 was synthesized by a simple method, and by the reaction of MnCl₂·4H₂O (2 mmol), naphthalene-1,8-dicarboxylic anhydride (2 mmol), NaOH (2 mmol) and phenantroline (2 mmol) in acetonitrile/water and in a steel reactor with a Teflon liner at 393 K for 24 h. **1** is a hexanuclear [Mn^{II}₆] wheel-like assembly of ~ 22.8 Å outer diameter with naphthalene-1,8-dicarboxylate and 1,10-phenanthroline acting as bridging and terminal ligands, respectively (Fig. 1). Chen reported on an analogous tetranuclear assembly with 2,2'-bipyridyl acting as terminal ligand and naphthalene-1,8-dicarboxylate forming carboxylate bridges between the Mn²⁺ ions.^{15a} In the reported literature six structures of Mn complexes with naphthalene-1,8-dicarboxylate ligand are known.¹⁵ Complexes with this ligand have also been reported for other transition metals: Cd, Cu, Zn and Ag.¹⁶

The complex molecule lies in special position on a three-fold inverse axis, so that only one Mn²⁺ ion, two water ligands, one terminal 1,10-phenanthroline ligand and one bridging naphthalene-1,8-dicarboxylate ligand are symmetry-independent (Fig. 1a).

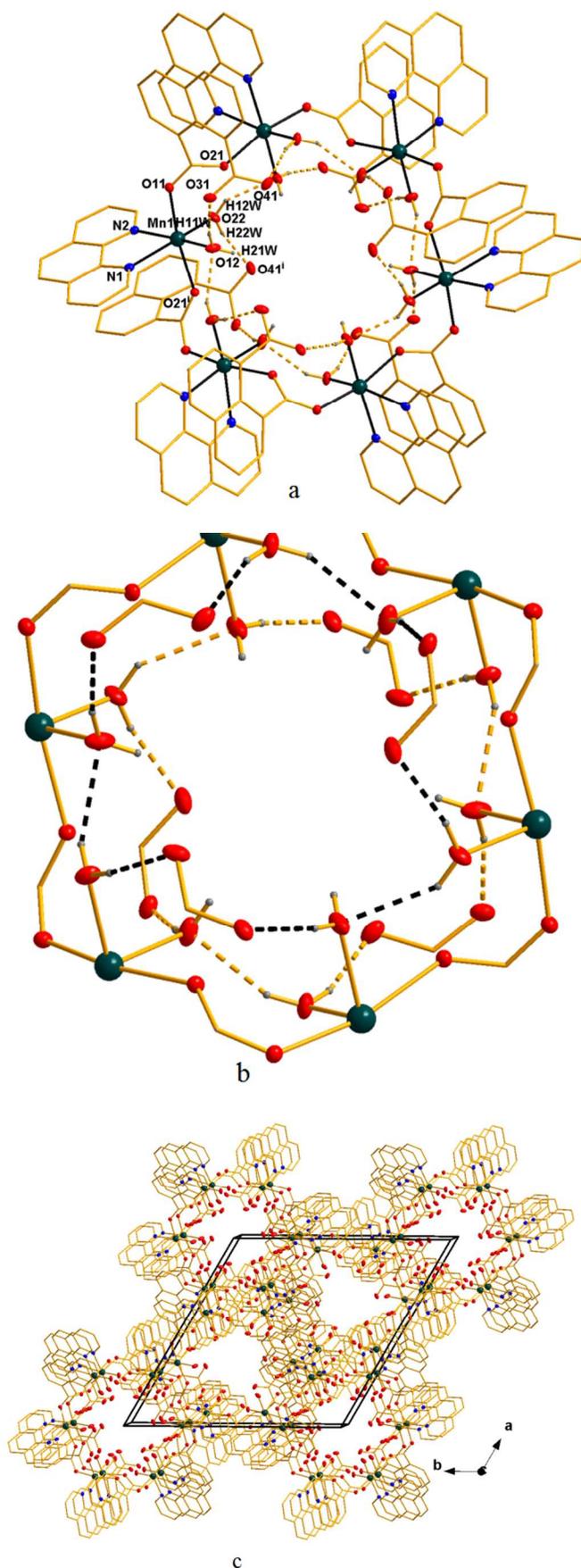


Fig. 1. (a) Structure of the compound **1** with atom labeling scheme and bonds to Mn²⁺ ions highlighted in black. The non-labeled part is generated by the symmetry operation $x, -y, z$. Thermal ellipsoids are plotted at 30% probability level. C-bonded H atoms are omitted, C atoms are shown as sticks for clarity. (b) Hydrogen-bonded core with two S₉(24) graph-set motifs, one of which is denoted in black. Hydrogen bonds are shown as dashed lines. (c) Overlapped columns of complex molecules extending along [001]. H atoms are omitted, C atoms are shown as sticks.

Coordination sphere of each Mn²⁺ ion includes two phenanthroline (N atoms), two carboxylate, O atoms from two different naphthalene-1,8-dicarboxylate ligands, and two water ligands. The corresponding geometric parameters are listed in Table S1 (ESI†). The analysis of the bond lengths, including BVS calculations (Table S2, ESI†) and charge balance considerations confirms the Mn(II) oxidation state. Coordination mode of the bridging ligand is illustrated in Scheme 1. The Mn-coordinated/non-coordinated carboxylate groups are twisted with respect to the plane of the naphthyl ring by 48.2(2)/49.0(2)°, respectively.

It is interesting to note that only one carboxylate group is involved in Mn–O coordination bonds (*syn/anti* arrangement), whereas the second carboxylate group participates solely in the formation of intramolecular O–H...O hydrogen bonds (Table S3, ESI†). In these hydrogen bonds the O12–water ligand acts as donor to the neighbouring carboxylate group and as acceptor to the neighbouring water ligand. The O22–water ligand is an O–H...O hydrogen bond donor to the neighbouring carboxylate and water ligand. Thus two stacked puckered S₉(24) graph-set motifs¹⁷ are formed (Fig. 1b). On the other hand, in all reported transition metal complexes with the naphthalene-1,8-dicarboxylate ligand^{15,16} both carboxylate groups participate in the formation of coordination bonds.

Within the molecular wheel structure the shortest Mn...Mn distance is of 5.267(1) Å. The neighbouring 1,10-phenanthroline and naphthalene-1,8-dicarboxylate rings are involved in a weak stacking interaction with *centroid...centroid* distance of ~3.7 Å.

The complex molecules in **1** form overlapped columns extending along [001] (Fig. 1c). Voids between the columns are occupied by disordered water molecules. Inside each molecular wheel heavily disordered water molecules form “droplets” of ~3.7 Å diameter, interacting with the hydrophilic interior through O–H...O hydrogen bonds.

The IR spectrum of **1** indicates peaks at 3400–3500 cm⁻¹ (OH groups), 3100–2900 cm⁻¹ (aromatic C–H stretching vibrations), 1600–1550 cm⁻¹ (ν(C=N), ν(C=O) and ν(C=C) stretches), 1470–1020 cm⁻¹ (ν(C–C) + ν(C–N) vibrations), and 810–710 cm⁻¹ (aromatic C–H deformation vibrations) (Fig S1, ESI†).

Magnetic properties of **1** were studied at broad temperature range at the fields of 500 and 1000 Gs, respectively. Fig. 2 shows the temperature dependence of the χT product at 1000 Gs. The χT values are essentially not dependent on the field value. A dominating antiferromagnetic behavior is confirmed by the χT value at 1000 Gs at ~295 K of 20.78 cm³mol⁻¹K, which is lower than theoretically expected for the presence of six non-interacting Mn²⁺ ions (26.25 cm³mol⁻¹K, S = 5/2). These values are constant until ~50 K and then rapidly decrease to ~7 cm³mol⁻¹K at 2 K. The Mn²⁺ ions in **1** interact through carboxylate bridges, displaying *syn-anti* coordination modes, which can lead to only weak magnetic interactions.¹⁸ Additional magnetic exchange pathways may involve hydrogen bonds. Westerhausen *et al.* also investigated a wheel-like [Mn₆] complex with bis(8-amidoquinoline) ligand showing antiferromagnetic coupling of the Mn²⁺ ions, consistent with results of DFT calculations.¹⁹ On the other hand, an analogous [Fe^{III}₆] complex was reported to display close-lying ferromagnetically and antiferromagnetically coupled states.

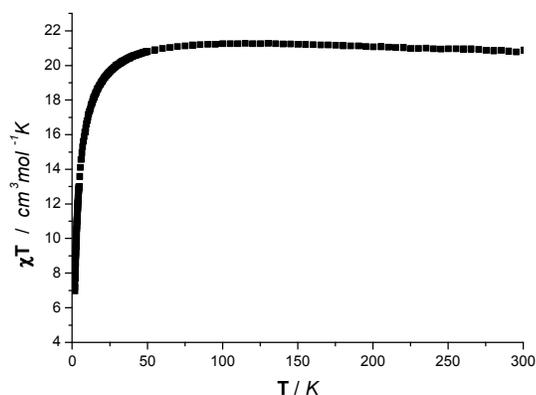


Fig. 2 χT vs. T dependence at 1000 Gs for **1**.

Initially, oxidation processes of methylphenylsulfide (MPS) were examined without catalyst and with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ or **1** to study the effects of different catalysts on the oxidation of **MPS**. As reported in Table 2, the maximum activity has been observed with **1** and oxidation of **MPS** without a catalyst gives very low conversion. Further screening with 0.03 mmol of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was also carried out, but none of them provided the product in a yield as high as that obtained in the presence of **1**.

The compound **1** was found to be a catalyst for oxidation of various sulfides. Without catalyst, low sulfide oxidation was observed (Table 2, entries 1). However, $\text{Mn}(\text{II})$ acetate shows catalytic activity for sulfide oxidation (Table 2, entries 2,3). *bpy* improves conversion and selectivity of $\text{Mn}(\text{II})$ acetate (Table 2, entries 4). A series of various types of structurally diverse sulfides were subjected to the oxidation reaction using **1** complex as a catalyst and H_2O_2 as an oxidant. Arylalkyl (Table 2, entries 5,6), arylbenzyl (Table 2, entry 7), dibenzyl (Table 2, entry 8), diaryl (Table 2, entry 9) and dialkyl (Table 2, entries 10-12) sulfides underwent clean and selective oxidation to the corresponding sulfoxides under air, with impressive selectivities (98-100%). In a few cases, minor amounts of byproducts resulting from overoxidation to sulfone were found (Entries 1-5). It was observed that aromatic sulfides undergo oxidation reactions more easily than aliphatic substrates. Moreover, in the case of dialkyl sulfides (Table 2, entries 10-12), no overoxidation to sulfone was observed. As shown in Table 2, the catalytic oxidation of sulfides showed moderate efficiency in yield but excellent in selectivity. The highest and the lowest conversions were obtained for ethylphenylsulfide (65%) and dioctyl sulfide (39%), respectively (Table 2, entries 5 and 12). After sulfide-oxidation reaction, FTIR spectra (Fig S1, ESI[†]) shows that all organic functions are still present but XRD patterns (Fig S2, ESI[†]) cannot give a definitive clue that structure is maintained. The results show that although **1** indicates good activity toward sulfide oxidation, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}/\text{bpy}$ show very similar activity for sulfide oxidation. We cannot relate the activity of **1** to leaking of a few $\text{Mn}(\text{II})$ ions to solution, because even equal mol of $\text{Mn}(\text{II})$ shows higher activity for **1** in the organic sulfide-oxidation reaction (Entry 3 and 5, 0.005 mmol from **1** have similar mol $\text{Mn}(\text{II})$ ions in 0.03 mmol $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$).

Table 2. Oxidation of sulfides catalyzed by **1** / H_2O_2 .^a

Entry	Catalyst (amount of catalyst)	Substrate	Conversion (%) ^b (TON) ^c	Selectivity (%) ^d
1	-	Ph-S-CH ₃	12	87
2	$\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.005 mmol)	Ph-S-CH ₃	33	93
3	$\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.03 mmol)	Ph-S-CH ₃	45	89
4	$\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.03 mmol + 0.03 mmol <i>bpy</i>)	Ph-S-CH ₃	51	93
5	1 (0.005 mmol)	Ph-S-CH ₃	63 (25)	99
6	1 (0.005 mmol)	Ph-S-C ₂ H ₅	65 (26)	99
7	1 (0.005 mmol)	Ph-S-CH ₂ Ph	61 (24)	99
8	1 (0.005 mmol)	PhCH ₂ -S-CH ₂ Ph	63 (25)	98
9	1 (0.005 mmol)	Ph-S-Ph	54 (22)	100
10	1 (0.005 mmol)	C ₂ H ₅ -S-C ₂ H ₅	49 (20)	100
11	1 (0.005 mmol)	C ₈ H ₉ -S-C ₈ H ₉	43 (17)	100
12	1 (0.005 mmol)	C ₈ H ₁₇ -S-C ₈ H ₁₇	39 (16)	100

^a The molar ratios for **1**:substrate:oxidant are 1:40:40. The reactions were performed in (1:1) mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (1 mL) under air at room temperature. ^b The GC yields (%) are measured relative to the starting sulfide. ^c TON = (mmol of sulfoxide + mmol of sulfone)/mmol of catalyst. ^d Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

Fu's group reported that hexadentate 8-quinolinolato manganese(III) complexes in the presence of NH_4OAc , HOAc and aqueous solution of hydrogen peroxide were found to efficiently catalyze the mild oxidation of thioanisole in environmentally benign acetone–water media. The achieved conversion was from 21 to 93% and the corresponding selectivities were 34-86%.²⁰ Bagherzade's Group showed that efficient catalytic systems for the oxidation of sulfides with urea hydrogen peroxide (UHP) with short reaction times (5 min) and under mild conditions are manganese(III) oxazoline complexes. The conversion was from 65 to 90% and the selectivities were 45-85%.²¹ The Group also investigated a polymeric manganese(II) complex with iminodiacetate. This complex exhibited an excellent catalytic activity and selectivity for oxidation of various sulfides to the corresponding sulfoxides using UHP as oxidant under air at room temperature.²² Najafpour *et al.* reported that a dimanganese complex with "back-to-back" 1,4-bis(2,2':6,2''-terpyridin-4'-yl) benzene ligand catalyzes oxidation of various sulfides to the corresponding sulfoxides with conversion 30-72% and selectivity of 100% in the presence of H_2O_2 .²³ The Group also reported on sulfides to sulfoxides oxidation by mononuclear manganese(II) complexes with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*). The achieved conversion and selectivities were of 26-57% and 94-100, respectively.

For **1** the obtained conversion and selectivity were 33-51% and 96-100%. Conversion of 39-63%, and selectivity of 98-100% places **1** among most selective catalysts toward sulfide oxidation.

Conclusions

The new hexanuclear $[\text{Mn}^{\text{II}}_6]$ wheel-like assembly with naphthalene-1,8-dicarboxylate and 1,10-phenanthroline has been synthesized and characterized. The solid state studies further evidenced that coordination sphere of each Mn^{2+} ion includes two phenanthroline N atoms, two carboxylate O atoms from two different naphthalene-1,8-dicarboxylate ligands and two water ligands. We demonstrated the effectiveness of this complex as a catalyst for the oxidation of sulfides to the corresponding sulfoxides. Conversion of 39-63%, and selectivity of 98-100% is observed for the compound as a catalyst. Although we found that $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ shows activity toward organic sulfide oxidation but both conversion

and selectivity are lower than **1** under these conditions. An easy preparation method, mild reaction conditions, high yields of the products, short reaction times and high selectivities make this catalytic system very useful for oxidation reactions.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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