Gentisate-1,2-dioxygenase activity by an iron(II)-phenanthroline complex

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Abstract. In this work, we have synthesised and crystallographically characterized a mononuclear iron(II) complex, $[\text{Fe}(\text{phen})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**1**) (phen = 1,10-phenanthroline). Single crystal X-ray diffraction (SXR) analysis revealed that **1** crystallizes in monoclinic system with $P 1^-$ space group. The lattice water molecules in **1** form a water-nitrate cluster, $(\text{H}_2\text{O})_2 \cdots (\text{NO}_3)_2$ through strong H-bonding interaction mediated *via* iron(II) complex in a unique binding motif and provide additional stability to the compound in the solid state. This iron(II) complex is able to catalyze the cleavage of aromatic C-C linkage of 2,5-dihydroxybenzoic acid (Gentisic acid, GA) in oxygen environment. The iron(II) complex in the presence of two equivalent of triethylamine (Et_3N) binds with GA stoichiometrically in acetonitrile medium at 25 °C. Observation of GA-to-iron LMCT optical bands at 521 and 609 nm supports *in situ* generated iron-GA adduct in solution. This *in situ* generated iron-GA adduct reacts with molecular oxygen at the rate, $k_{\text{obs}} = 6.58 \times 10^{-3} \text{ min}^{-1}$ in acetonitrile and affords exclusively 2-oxo-4-hydroxy-hepta-3,5-dienedioic acid. The incorporation of both the oxygen atoms of molecular oxygen in the bio-mimicking activity of gentisate-1,2-dioxygenase by this iron(II)-phenanthroline complex remain a rare example in scientific literature.

Keywords. Iron(II); phenanthroline; X-ray structure; gentisate-1,2-dioxygenase activity; bio-mimicking chemistry.

1. Introduction

Iron(II) complexes containing N-donor ligands not only help to enrich molecular library but also bring a new source of light to unveil different mechanistic fate related to organic transformations in chemical and biological sciences.^{1–3} Investigation of physico-chemical properties of these iron(II) complexes leads to important information to develop the science of living world. Among the different organic transformations in chemical and biological sciences, aerobic degradation of aromatic compounds by iron complexes remains a very difficult challenge to the chemists.^{4–6} Especially, iron-based bio-models relevant to important microorganisms in biochemistry provide significant insights towards aromatic ring-fission of substrates like catechol,

protocatechuate, homoprotocatechuate, hydroquinone, gentisate or homogentisate (or their substituted derivatives).^{7–9} 2,5-dihydroxybenzoic acid, which is commonly known as Gentisic acid is a key intermediate in aerobic bacterial pathways for the metabolism of a large number of aromatic compounds, including anthranilate, β -naphthol, 4-hydroxy benzoates, flavonones, salicylate, *etc.*¹⁰ Among these aromatic ring cleavage enzymes, gentisate 1,2-dioxygenase from *Pseudaminobacter salicylatoxidans* BN12 (*P. salicylatoxidans*) appears to be most versatile since it is able to convert a wide range of substituted salicylates with the highest order of enzymatic activities.^{11,12} The cell using gentisate derives carbon and energy from direct or indirect conversion of maleylpyruvate to metabolites.¹³ During the investigation of oxygen activation

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of 2,5-dihydroxybenzoic acid using iron complexes as catalysts, the aromatic ring-cleavage occurs generally in 1,2-position¹⁴ with the formation of dicarboxylic acids and the presence of hydroxyl/amino groups in the substrate assist to activate the aromatic ring for the electrophilic attack of the dioxygen molecule during such dioxygenase activities. Further, it is commonly seen that catalytic iron(III) complexes lead to intra-diol cleaving products while iron(II) complexes lead to the production of extra-diol cleaving products.^{15–19}

In many $[\text{FeN}_6]^{2+}$ systems, the cationic low spin $[\text{Fe}(2, 2'\text{-bipyridine})_3]^{2+}$ or $[\text{Fe}(2, 2', 2', 6'\text{-terpyridine})_2]^{2+}$ ions,²⁰ remain important examples for the spin cross over systems, tris(6-methyl-2,2'-bipyridine) iron(II) and bis(2,4-bis(pyridin-2-yl)thiazole)iron(II) ions.²¹ In our recent work, we have synthesized and structurally characterized similar iron(II)-phenanthroline complex, $[\text{Fe}(1,10\text{-phenanthroline})_3]\text{Cl}_2$ and explored its catalytic activity towards catechol dioxygenase functionality.^{6b} Herein, we report the synthesis and structural characterization of a new ferroin analogue, $[\text{Fe}(1,10\text{-phenanthroline})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**1**). The lattice water molecules showed unique binding motifs in forming a novel water-nitrate cluster mediated *via* metal complex which provide additional stability to the solid. This iron(II) complex has been evaluated as a functional model to mimic the catalytic cycles of gentisate-1,2-dioxygenase enzyme in acetonitrile medium and it is found that iron(II) catalyst exclusively produced 2-oxo-4-hydroxy-hepta-3,5-dienedioic acid at the rate, $k_{\text{obs}} = 6.58 \times 10^{-3} \text{ min}^{-1}$.

2. Experimental

2.1 Materials

High purity 1,10-phenanthroline (E Merck, India), ferric nitrate nonahydrate (Alfa-Aesar, UK), 2,5-dihydroxy benzoic acid (Sigma Aldrich, USA) were used as purchased. All other chemicals and solvents were of analytical grade and were used as received without further purification.

2.2 Synthesis of $[\text{Fe}(\text{phen})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**1**)

An aqueous solution of phenanthroline (0.540 g, 3 mM in 15 mL) was added dropwise to an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.404 g, 1 mM in 10 mL) and stirred the solution for 30 min. The dark blue coloured solution was kept in air for slow evaporation to obtain the crystalline product.

Yield: $\sim 0.750 \text{ g}$ ($\sim 66\%$ based on metal salt). Anal. Calc. for $\text{C}_{36}\text{H}_{28}\text{N}_8\text{O}_8\text{Fe}$ (**1**): C, 57.16; H, 3.73; N, 14.81%. Found: C, 57.06; H, 3.66; N, 14.78%. IR (KBr, cm^{-1}): 1621, 1606 ($\nu_{\text{C}=\text{N}}$), 1384, ($\nu_{\text{NO}_3^-}$), 3541 & 3487 ($\nu_{\text{O}-\text{H}}$); UV-Vis (λ_{max} ,

nm, 10^{-4} M , 1 cm optical pathlength, Abs, MeCN): 269 (1.27), 293 (0.83), 319 (0.37), 515 (0.51); EI-MS (MeCN): m/z , 597.41 $[\text{1}+\text{H}^+]^+$.

2.3 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Fourier Transform Infrared (FT IR) spectra (KBr discs, $4000\text{--}300 \text{ cm}^{-1}$) were recorded using an FTIR-8400S SHIMADZU spectrophotometer in the range $400\text{--}3600 \text{ cm}^{-1}$. Ground-state absorption measurements were made with a JASCO model V-730 UV-Vis spectrophotometer. The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-500 MHz spectrometer. The Electron Paramagnetic Resonance (EPR) spectrum was recorded on a Bruker EMX-X band spectrometer. Electrospray ionization (EI) mass spectrum was recorded using a Q-tof-micro quadrupole mass spectrometer. Molar conductivity was recorded using a Mettler conductivity meter. A Gouy balance was used to determine the magnetic moments of the powdered samples, employing $\text{Hg}(\text{II})$ tetrathiocyanatocobaltate(II) as a calibrant. Diamagnetic corrections were made from Pascal's constants. Thermal analysis was carried out on a PerkinElmer Diamond TG/DTA system up to 700°C in a static nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$.

2.4 Crystal structure determination and refinement

Single crystal X-ray diffraction data of the iron(II) complex were collected using a Bruker SMART APEX II diffractometer equipped with Mercury CCD detector. The data were collected with graphite monochromated Mo – $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K using ω scans. The data were reduced using Crystal Clear suite 2.0.²² and the space group determination was done using Olex2. The structure was resolved by direct method and refined by full-matrix least-squares procedures using the SHELXL-2014/7²³ software package through OLEX2 suite.²⁴

2.5 Gentisate-1,2-dioxygenase activity of the iron(II)-phenanthroline complex

To investigate the gentisate dioxygenase activity of the complex, a 10^{-3} M solution of **1** in acetonitrile (MeCN) was treated with a 10^{-3} M solution of Gentisic acid (GA) in oxygen saturated MeCN with two equivalents of triethylamine at room temperature. Absorbance vs. wavelength (wavelength scans) of the solution was recorded at regular time intervals for 3 h in the wavelength range of 200–900 nm. It may be noted here that a blank experiment without iron(II)-phenanthroline complex (catalyst) did not show any decrement of optical bands and hence, didn't form any cleavage products up to 6 h in MeCN. The solvent was equilibrated at the atmospheric pressure of O_2 at 25°C using a known procedure with modifications.²⁵ Investigation of dioxygen

reactivity of the *in situ* generated Fe-gentisate adduct was carried out in oxygen saturated MeCN medium at 25 °C. Kinetic analyses²⁶ of the gentisate cleavage reactions were carried out by time-dependent measurement of the disappearance of the lower energy GA-to-iron LMCT band at ambient temperature (25 °C) by exposing to molecular oxygen.

2.6 Determination of salicylate cleavage products

0.756 g (0.1 mM) of the iron(II) complex **1** was reacted with 0.0310 g (0.02 mM) of GA in an oxygen saturated MeCN (100 mL) at ambient condition and then allowed to slow stir for 18 h. The residue was then treated with 15 mL of 2M HCl and the gentisate cleavage products were extracted with diethylether (3 × 10 mL) and dried over anhydrous sodium sulfate. After the removal of solvent, the gentisate cleavage product was quantified and analyzed by HPLC and ¹H NMR spectroscopy. ¹H NMR data for 2,5-dihydroxybenzoic acid cleavage products (500 MHz, CDCl₃): δ = 2-oxo-4-hydroxy-hepta-3,5-dienedioic acid: 6.65 (d, 1H), 10.81 (s, 1H); 6.37 (dd, 1H), 6.43 (d, 1H).

3. Results and Discussion

3.1 Synthesis and structural characterization of the Fe(II) complex (**1**)

The tris(phenanthroline)iron(II) nitrate dihydrate complex was synthesized by simple mixing of iron nitrate with phenanthroline ligand in an aqueous medium under stirring condition. The structural formulation was determined through different spectroscopic methods & analytical techniques. The geometry of the iron(II) complex (**1**) was determined and confirmed by single crystal X-ray diffraction study.

The IR spectrum of **1** (Figure S1 in Supplementary Information) shows the characteristic patterns for the presence of phenanthroline ligand, nitrate anions and water molecules. Strong characteristic peaks at ~1621 and 1606 cm⁻¹ corroborate the presence of diimine ligands in **1**,²⁷ while the very strong peak at 1384 cm⁻¹ indicates the existence of nitrate ion. Two splitting peaks at 3541 and 3487 at cm⁻¹ reveal the presence of water molecules in **1**. Room temperature magnetic susceptibility analysis reveals the diamagnetic nature of the iron centre as disclosed by $\mu_{\text{eff}} = \sim 0.3$ BM.

The absorption spectrum of **1** for 1 × 10⁻⁴ M acetonitrile solution shows characteristic electronic transitions at 269, 293 and 515 nm. The high energy bands at 269 and 293 nm are assignable to n-π* and π-π* transitions of the C=N chromophore in phenanthroline ligand. Presence of a low-intensity broad band in the

visible region at 515 nm (Figure S2, Abs vs wavelength, 1 cm optical path length) suggests the existence of octahedral geometry around the iron centre in solution.²⁸ The structural integrity in solution state for the iron(II) complex was further confirmed by ESI mass spectral analysis. The ESI mass spectrum of **1** in MeCN medium exhibits the molecular ion peak, at m/z 597.41 as [Fe(phen)₃]²⁺-H⁺ (Figure S3 in Supplementary Information). The absorption bands for the iron(II) complex in solution also remain unaffected over a period of 72 h which support in favour of stable molecular ion in solution. We have also recorded EPR spectrum of **1** in the MeCN medium at room temperature. The EPR spectrum of **1** is silent and inactive. This nature of EPR spectrum justifies the low spin state of the iron(II) complex in MeCN and indicates its diamagnetic nature.

To investigate the electrolytic nature of the complex in 1.0 × 10⁻³ M MeCN solution, we have also determined the molar conductance value at room temperature. The value of molar conductivity is found as 197 μS/cm which suggests about 1:2 electrolytic ratio in solution.²⁹ This molar conductance value is smaller than that for a normal 1:2 type electrolyte in MeCN. Probably, the existence of water-nitrate cluster in solution lowers the molar conductivity value and accounts for the smaller value.

3.2 Description of the crystal structure

We have carried out single crystal X-ray diffraction study to determine the molecular structure of iron(II) complex. The ORTEP diagram of the iron(II) complex is shown in Figure 1. The X-ray crystallographic data and refinement parameters for **1** are presented in Table 1. Important bond lengths and angles are summarized in Table 2.

Figure 1. An ORTEP diagram of iron(II)-phenanthroline complex (30% ellipsoid probability).

Table 1. Crystallographic refinement parameters of [Fe(phen)₃](NO₃)₂·2H₂O (**1**).

Parameters	Fe(II) compound
Empirical formula	C ₃₆ H ₂₈ N ₈ O ₈ Fe
Formula weight	756.52
Temperature (K)	293
Crystal system	Triclinic
Space group	<i>P</i> 1 [−]
<i>a</i> (Å)	8.7902(15)
<i>b</i> (Å)	12.518(2)
<i>c</i> (Å)	14.929(3)
Volume (Å ³)	1629.5(5)
<i>Z</i>	2
ρ (gcm ^{−3})	1.542
μ (mm ^{−1})	0.532
<i>F</i> (000)	780
θ ranges (°)	3.0°–27.50°
<i>R</i> _{int}	0.083
<i>R</i> (reflections)	17846
<i>wR</i> ₂ (reflections)	7451
Final <i>R</i> indices	0.0873, 0.2387
Largest peak and hole (eÅ ^{−3})	0.55, − 0.38

X-ray structure of iron(II) complex reveals that the compound crystallizes in a triclinic system with *P*1[−] space group. Fe(II) ion exists in an octahedral geometry and the hexacoordination is satisfied by six N atoms of three phen ligands. The Fe1–N5 bond length, 1.978(4) Å, is slightly longer than other Fe–N bonds; the average Fe–N bond length is 1.966 Å in agreement with previously reported results for analogous compounds.³⁰ The bond angles, N–Fe–N and bond lengths of C–N, and C–C in the phenanthroline, all fall within the range of the literature values.³¹

3.3 Water-nitrate cluster

Investigation of the crystal packing for the iron(II) complex reveals that layers of the [Fe(phen)₃]²⁺ cations are separated by the layers of tetrameric water-nitrate clusters (Figure S4 in SI). Both the layers are associated with intermolecular C – H ··· O hydrogen bonding interactions. But, we had a special interest in water-nitrate cluster since this type of association may lead to important insights in the living world.³² The intermolecular hydrogen bonding association along *b*-axis among the lattice aqua molecules and counter anionic nitrate ions [(H1B ··· O7, 2.08; H1A ··· O3, 1.90; H2A ··· O3, 2.39; H2B ··· O5, 2.53) Figure 2, Table S1 in SI]. We have also made a comparison between our iron(II) complex with a few structurally related complexes.³³ To the best of our knowledge, this binding mode among the solvent molecules and counter-anions remains a novel one that was not previously observed. The small NO₃ ··· H₂O ··· NO₃ ··· H₂O cluster grows along *b* axis mediated *via* cationic Fe(II)-phenanthroline units and looks like a zigzag 1D chain.

We have considered FTIR spectrum to reveal the nature of water-nitrate clusters present in **1**. The vibrational stretching frequencies for O–H bonds of the water-nitrate cluster have been characterized by FT-IR analysis of **1**. A weak broad splitting peaks appear at 3541 cm^{−1} in the spectrum followed by a broad band centered around 3487 cm^{−1} (Figure S1 in SI). In our previous work, we observed a 1D water-nitrate cluster mediated *via* cobalt(III)-bipyridine complex^{33a} and the vibration frequencies for O–H bond in water-nitrate cluster in cobalt(III)-bipyridine complex resembles well with the O–H bond in this water-nitrate cluster in tris(phenanthroline)iron(II) complex. In this

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Bond distances			
N1–Fe1	1.966(4)	N4–Fe1	1.964(4)
N2–Fe1	1.958(4)	N5–Fe1	1.978(4)
N3–Fe1	1.968(4)	N6–Fe1	1.967(4)
Bond angles			
N1–Fe1–N2	82.59(17)	N2–Fe1–N6	92.74(17)
N1–Fe1–N3	95.55(18)	N3–Fe1–N4	82.83(18)
N1–Fe1–N4	174.97(17)	N3–Fe1–N5	91.59(17)
N1–Fe1–N5	95.12(17)	N3–Fe1–N6	173.55(17)
N1–Fe1–N6	88.52(16)	N4–Fe1–N5	89.70(16)
N2–Fe1–N3	92.75(17)	N4–Fe1–N6	93.52(17)
N2–Fe1–N4	92.71(17)	N5–Fe1–N6	83.04(17)
N2–Fe1–N5	175.27(17)

Figure 2. Formation of $[(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2]$ clusters in the structure of **1**.

Scheme 1. Aromatic ring fission products of GA using Fe(II) complex in oxygenated MeCN.

case, the slight difference in the stretching vibration with the reported work arises from a different mode of self-assembly between lattice water and aqua molecules.^{33a,b,c}

4. Thermogravimetric analysis

The thermal properties of **1** in nitrogen atmosphere were studied by TG analysis in order to determine its stability. The complex is decomposed in three clearly defined steps with the final residue corresponding to iron oxide. The first step corresponds to the loss of two water molecules at $\sim 103^\circ\text{C}$ (Figure S4 in SI) while in the second step anionic nitrate ion decomposes at $\sim 300^\circ\text{C}$. In the final step, phenanthroline decomposes and the main architecture around metal coordination is lost. This result resembles very well with reported results.^{33a,b}

4.1 Gentisate dioxygenase activity of the iron(II) phenanthroline complex

The oxygenation reactions for the iron(II) complex was carried out using 2,5-dihydroxybenzoic acid (GA) as the convenient substrate in acetonitrile (Scheme 1).

The gentisate adducts of iron(II) complex were generated *in situ* in MeCN, and O_2 activation in presence of triethylamine was studied by monitoring the decay of low energy band of GA to Fe LMCT (Figure 3). The *in situ* generated iron-gentisate adduct in presence of triethylamine reacts with molecular oxygen in the MeCN medium at ambient conditions over a period of 3 h and two new visible bands with absorption maximum

Figure 3. Absorption spectral changes during the reaction of the *in situ* generated GA-Fe(III) adduct (1×10^{-3} M of **1** and 1×10^{-3} M of GA, 1 cm optical path length) with O_2 (The spectra were recorded after every 15 min); Inset: Plot of Abs vs Time.

at 521 and 609 nm (Figure 3), were observed for the catechol adduct of complex **1**. The lower energy bands with decreasing absorbance are attributed to GA^{2-} -to-iron LMCT transitions involving two different gentisate ligand orbitals.^{5,6,34–36c} As reported in many cases, the energy of the LMCT transitions strongly depends on the nature of the ligands, and it reflects the Lewis acidity of the iron center in the complex.^{37,38} The disappearance of the lower-energy GA-to-iron LMCT band (Figure 4) on oxygenation exhibits pseudo-first-order kinetics, as judged from the linearity of the plot $[1 + \log(\text{Abs})]$ versus time⁶ (Figure 4), and the value of k_{obs} was obtained

Figure 4. Plot of $[1 + \log(\text{Abs})]$ vs time for the reaction of *in situ* generated GA-Fe(III) adduct with O_2 at 25°C in MeCN solution.

from the slope of the plot. The pseudo-first order rate constant was determined as $k_{\text{obs}} = 6.58 \times 10^{-3} \text{ min}^{-1}$.

The purified product was dissolved in CDCl_3 and ^1H NMR spectrum was recorded. The ^1H NMR spectrum produced a set of the characteristic signal for four olefinic protons (Figure S5 in SI). The ^1H NMR data thus confirmed the oxidative cleavage of gentisate to 2-oxo-4-hydroxy-hepta-3,5-dienedioic acid. The amount of organic product from oxidative cleavage of GA accounts for $\sim 73\%$ and the remaining 27% is accounted as inactivated substrate.

In order to evaluate the mechanistic route for the catalytic cycle of gentisate activity by **1** (Scheme 2), we have carried out ESI mass spectral analysis of the reaction mixture in acetonitrile medium. The mass spectrum of the reaction mixture in MeCN solution (Figure S6 in SI) exhibits mainly the characteristic peaks

Scheme 2. Proposed mechanistic pathway for gentisate activity by **1**.

at m/z 569.07 and 601.13 with isotope distribution patterns. These characteristic peaks further corroborated the cationic species, $[(\text{Fe}(\text{phen})_2\text{-GA}) + \text{H}^+]$ and $[(\text{Fe}(\text{phen})_2\text{-GA-O}_2) + \text{H}^+]$, respectively. Further, the characteristic peak at $m/z \sim 569.07$ indicates the presence of coordinated gentisate to iron centre.

Although the iron(II) complex is inert in MeCN solution, in the presence of GA, one of the three phenanthroline ligands decomposes from the coordination zone of iron(II) centre. The iron-gentisate adduct in the presence of molecular oxygen form a peroxo-iron-gentisate intermediate through substrate activation pathway^{34–38}. In our case, probably the facial mode of coordination by gentisate facilitates the formation of peroxo intermediate adopting a pseudo-axial arrangement at iron centre and subsequently, heterolytic O–O bond cleavage following Criegee rearrangement affords exclusive production of cleavage product (Scheme 2). Although, extensive experimental studies have to be carried out in order to find mechanistic insights to this gentisate-1,2-dioxygenase bio-mimicking activity. Further, scientific reports are limited for such gentisate-1,2-dioxygenase activity by iron(II) complexes and hence, we are not in a position to highlight this activity with recently reported work.

5. Conclusions

Herein, we report the synthesis and structural characterization of a new ferriin analogue, $[\text{Fe}(1,10\text{-phenanthroline})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**1**). The lattice water molecules showed unique binding motifs in forming a novel water-nitrate cluster, which provides additional stability to the solid. This iron(II) complex has been evaluated as a functional model to mimic the catalytic cycle of gentisate-1,2-dioxygenase enzyme in acetonitrile medium. The iron(II) catalyst exhibits catalytic efficacy in the presence of triethylamine towards gentisic acid and produced exclusively 2-oxohepta-3,5-dienedioic acid at the rate, $k_{\text{obs}} = 6.58 \times 10^{-3} \text{ min}^{-1}$ by the involvement of molecular oxygen. This tris(phenanthroline)-iron(II) nitrate is an addition to the class of gentisate-1,2-dioxygenase with good catalytic activity and functional bio-mimicking efficacy. Further, experiments would be helpful to enlighten the gentisate mimicking activity.

Supplementary Information (SI)

CCDC 1581209 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or

e-mail: deposit@ccdc.cam.ac.uk. Experimental information such as FT-IR spectrum, UV-Vis spectrum, ESI mass spectra, TGA plot, ¹H NMR of cleavage products, and H-bonded interaction parameters are available at www.ias.ac.in/chemsci.

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