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Sulfur Site Iodine Adduct of a Nickel Thiolate Complex

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Introduction

The metal-bound thiolates of *N*,*N*′-bis(mercaptoethyl)-1,5-diazacyclooctanenickel(II), **Ni-1**, and N,N′-bis(2-mercaptomethylpropane)-1,5-diazacyclooctanenickel(II), **Ni-1***, exhibit sulfur-based nucleophilicity ranging from alkylation,[1] oxygenation,[2] and metalation[3] to small molecule adduct formation.[4] Adducts formed from SO$_2$ and the nickel thiolates precipitate out of methanol, forming highly stable crystalline lattices in the case of **Ni-1**·SO$_2$, Figure 1.[4] Whereas a purge of N$_2$ easily removes the SO$_2$ from **Ni-1**·SO$_2$, dissolved in CH$_3$CN, solid samples are stable to vacuum (~0.01 Torr) overnight. In contrast, SO$_2$ dissociates readily from solid and solution forms of the sterically hindered **Ni-1***·SO$_2$.

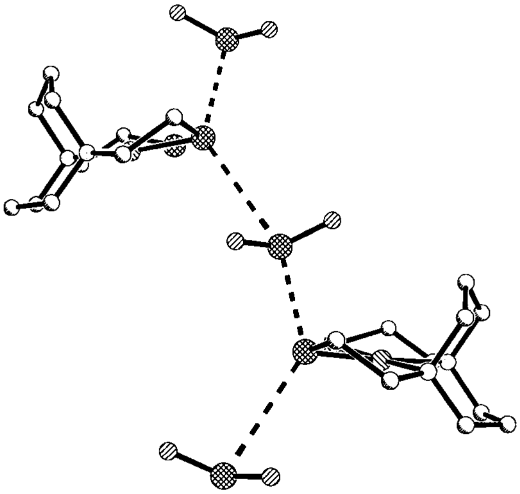
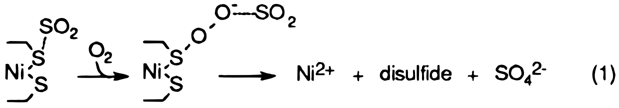


Figure 1. A portion of the packing diagram of the crystal structure of **Ni-1**·SO$_2$.[4] The shorter $S_{thiolate}-S_{SO_2}$ distance is 2.597 Å and the longer (intermolecular interaction) is 3.692 Å.

The reactivity of O$_2$ with **Ni-1** and **Ni-1*** is also well established. In fact, such an **Ni-1**·O$_2$ or **Ni-1***·O$_2$ adduct is a key proposed intermediate in thiolate-S oxygenation by molecular O$_2$ in either $^1\Delta O_2$ or $^3\Delta O_2$ form, a reaction that yields primarily S-bound sulfinates and sulfenates.[2] An interesting aspect of the SO$_2$ adducts is their reactivity with O$_2$; a rapid reaction of **Ni-1**·SO$_2$ with O$_2$ results in formation of SO$_4^{2-}$, using oxidation of the thiolates to disulfide as the electron source in the sulfate-forming reaction.[4] As implied in eq 1, and in analogy to a similar sulfate-forming reaction by Vaska's salt,[5] we have suggested that the SO$_2$ intercepts the sulfperoxy intermediate in the oxygenation process of Ni−SR. It is expected that such first-coordination sphere reactivity could be a hallmark of nickel thiolates, and therefore, adducts of other diatomics might lend veracity to the proposed intermediate. Herein we report on the interactions of I$_2$ with the nickel thiolates. The resulting adduct of the **Ni-1*** dithiolate may be regarded as a charge-transfer complex of diiodine, which further emphasizes that the donor ability of nickel thiolate sulfur is much like that of thioethers or triphenylphosphine.[6,7]



Experimental Section

General Methods. Reagent-grade solvents were dried and purified according to published procedures.[8] Where necessary, standard Schlenk and glovebox techniques were employed which used argon (passed through a drying column) as the inert gas.

Physical Measurements. UV−vis spectra were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer. Mass spectra were obtained using positive ion electrospray ionization (ESI) on a Vestec 201A quadrupole mass spectrometer. The mass spectra were recorded on a Technivent Vector One data system. Conductance measurements were performed using an Orion model 160 conductance meter equipped with an Orion two-electrode conductivity cell manufactured by Sybron Corp. The cell constant was determined to be 0.112 cm^{-1}.

X-ray crystallographic data were obtained on a Siemens R3m/V single-crystal X-ray diffractometer operating at 55 kV and 30 mA, Mo Kα ($\lambda = 0.710\,73$ Å) radiation equipped with a Siemens LT-2 cryostat. Diffractometer control software P3VAX 3.42 was supplied by Siemens Analytical Instruments, Inc. All crystallographic calculations were performed with use of the Siemens SHELXTL-PLUS program package.[9] The structures were solved by direct methods. Anisotropic

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Table 1. Crystal Parameters and X-ray Diffraction Data for **Ni-1***$\cdot I_2$

empirical formula	$C_{14}H_{28}N_2S_2I_2Ni$
fw	601.01
space group	$P2_1/c$
a, Å	7.826(3)
b, Å	22.292(8)
c, Å	12.430(5)
β, deg	108.01(3)
V, Å^3	2062.2(13)
ρ (calcd) g/cm^3	1.936
Z	4
temp, °C	25
radiation (λ, Å)	Mo Kα (0.710 73)
min/max transm	0.803/0.997
abs coeff, cm^{-1}	41.34
$R(F)$,[a] $R_w(F^2)$[b]	0.0652, 0.1300

[a] $R(F) = \sum|F_o - F_c|/\sum|F_o|$. $R_w(F^2) = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [b] $I > 2\sigma(I)$.

refinement for all non-hydrogen atoms was done by a full-matrix least-squares method. A single crystal was mounted on a glass fiber with epoxy cement either at room temperature or at 163 K in an N_2 cold stream.

Synthesis and Reactions. Complexes *N,N′*-bis(mercaptoethyl)-1,5-diazacyclooctanenickel(II), **Ni-1**, and *N,N′*-bis(2-mercaptomethylpropane)-1,5-diazacyclooctanenickel(II), **Ni-1***, were prepared according to published procedures.[10]

Ni-1 + I_2. In a 50-mL Schlenk flask, 50 mg (0.172 mmol) of **Ni-1** was degassed and dissolved in 3 mL of MeOH. To this solution, I_2 (44 mg, 0.173 mmol dissolved in 5 mL of MeOH) was added via cannula without stirring. After 3 min, a fine brown powder began to settle out. Within 10 minutes, the solution was almost colorless. The supernatant was removed from the brown solid by cannula, and the product was washed with MeOH (4 × 10-mL aliquots) to remove any unreacted starting materials. Mass spectroscopy indicated the formation of a previously characterized trimetallic product, $[(\mathbf{Ni\text{-}1})_2Ni]^{2+}(I^-)_2$,[11] obtained in ca. 75% yield.

Ni-1*$\cdot$**I_2**. A 50-mL round-bottomed flask containing 57.7 mg (0.166 mmol) of **Ni-1*** was degassed, and to it was added 15 mL of dry, degassed MeOH. In a separate flask, 42.8 mg (0.168 mmol) of I_2 was degassed briefly to expel most of the oxygen but not long enough to have significant loss of the I_2 as a vapor. The iodine was then dissolved in 10 mL of dry, degassed MeOH, and the solution was slowly transferred by cannula into the flask containing the purple **Ni-1*** solution. Without stirring, a fluffy microcrystalline brown precipitate settled out after 3−4 min. (Stirring affords a fine brown powder.) The supernatant was then removed via cannula, and the product was washed 4 times with 15-mL aliquots of MeOH to remove unreacted starting material. After being dried, the brown product was isolated in yields of approximately 70% and was found to be air stable for several days. This product is also stable under vacuum (∼0.01 Torr) for several days. Anal. Calcd (measured) for $C_{14}H_{28}N_2S_2NiI_2$: C, 28.0 (27.8); H, 4.70 (4.74); N, 4.66 (4.56).

Crystals were obtained using FeI_2 as the iodine source. The FeI_2 was weighed out in the glovebox (0.07 g/0.23 mmol) and dissolved in 40 mL of THF. The solution was stirred for 2 h and then filtered into a flask containing 0.0784 g of **Ni-1*** dissolved in a minimum of methanol (∼2−3 mL). Such solutions were transferred to double crystallization tubes, using ether in the outer tube for diffusion. Dark brown, air-stable crystals were selected (picked out of a mixture of brown powder and crystalline material) for X-ray crystallographic analysis and found to be in the monoclinic space group of $P2_1/c$. The cell parameters are contained in Table 1, and a full structure report is deposited as Supporting Information.

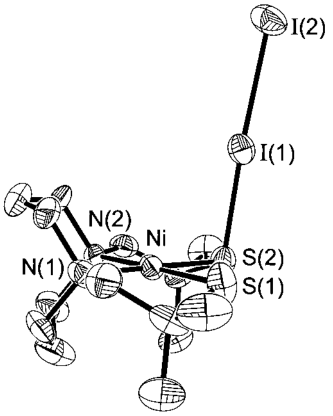
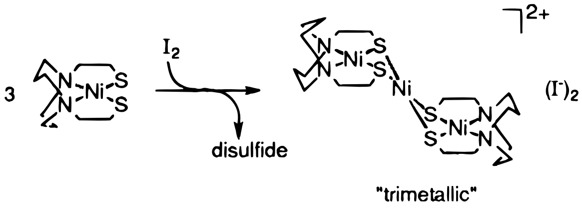


Figure 2. Molecular structure of **Ni-1***$\cdot I_2$ with hydrogens omitted; thermal ellipsoids represent 50% probability.

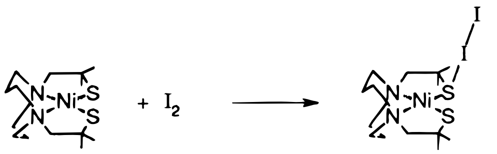
Results and Discussion

Iodine, I_2, reacts with **Ni-1** in methanol to yield the well-characterized trimetallic via a process attributable to electron transfer from thiolate, disulfide formation with Ni^{2+} loss, and subsequent attachment to two parent **Ni-1** complexes, eq 2.[11]



(2)

In contrast, similar exposure of the sterically hindered **Ni-1*** to iodine yields the brown **Ni-1***$\cdot I_2$ adduct, eq 3. While pure I_2



(3)

produced powders of the adduct which analyzed well for the 1:1 adduct, crystals suitable for X-ray analysis were obtained only when FeI_2 (presumably contaminated with excess I_2 as suggested by the purple vapor over the solid material) was used as the iodine source. Originally introduced to **Ni-1*** for the purpose of preparing thiolate-bridged NiFe heterometallics as models for the active site of [NiFe]H_2ase,[12] the "iodine rich" FeI_2 evidently serves as a slow release source of I_2. Such an observation of iodine adducts arising from metal iodides is not without precedence; for example, Cotton and Kibala observed products arising from $Ph_3P\cdot I_2$ interaction while examining the reactivity of Ph_3P with ZrI_4.[7] Subsequently the $Ph_3P\cdot I_2$ adduct was structurally characterized, vide infra.[13]

Figure 2 shows the molecular structure of **Ni-1***$\cdot$**I_2** and a portion of the packing diagram is given in Figure 3. The bond lengths and angles listed in Table 2 indicate the Ni coordination in **Ni-1***$\cdot I_2$ is little changed from the parent **Ni-1***. Similar results were observed for the SO_2 adduct of **Ni-1** in that the NiN_2S_2 plane is conserved.[4] The I_2 sits on a sulfur with

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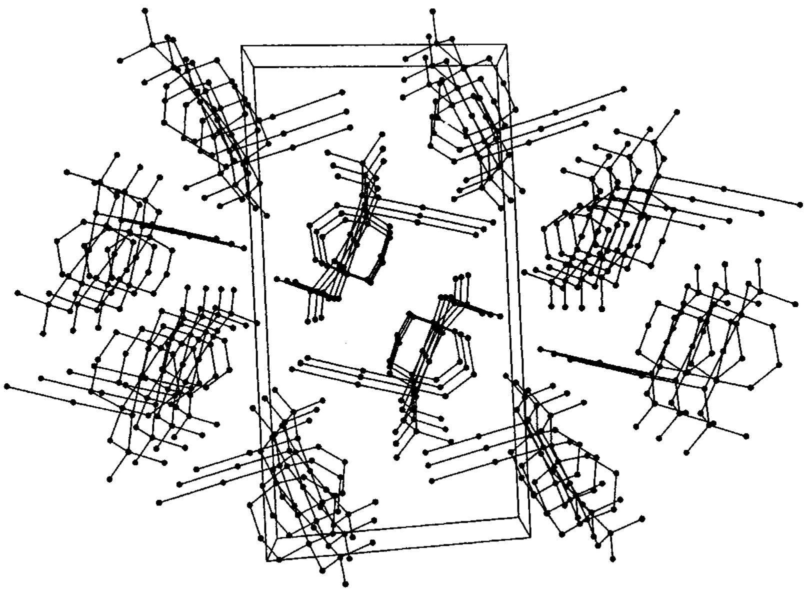


Figure 3. Packing diagram of **Ni-1***·I_2 displaying the orientation of I−I with respect to the next closest molecule.

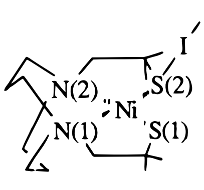
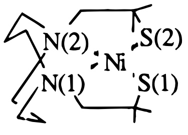
substantial linearity of the S−I−I bonds, 176.9 (1)°, as expected from previous examples of R_2S-I_2 adducts.[6] The ∠Ni−S(2)−I(1) of 101.02° suggests the involvement of a thiolate sulfur lone pair with tetrahedral character and is characterized by a relatively short S−I distance of 2.601(4) Å. This apparently strong S:→I bond gives rise to an I−I bond distance of 3.026(2) Å, which is significantly longer than the bond distances of free iodine in the gaseous state, 2.667(2) Å,[14] and in the solid state, 2.715(6) Å.[15]

The donor/acceptor bond distance data observed for **Ni-1***·I_2 is consistent with the inverse relationship of S−I and I−I distances found for a series of structurally characterized adducts of I_2 and thioethers/thiocrown ethers as analyzed by Shröder et al.[6] Thus the S−I bonding interaction results in donation of electron density into the I_2 σ^* orbital, i.e., antibonding with respect to the I−I bond.[16] Although elongated, the second iodine atom is still close enough to be considered bound and not a counterion.[7]

The extended structure or packing diagram of **Ni-1***·I_2, Figure 3, shows that the iodines are oriented such that they cannot interact with other sulfurs or iodines from neighboring complexes. This is unusual for iodine complexes which typically form chains through long-range interactions.[17] For example, only one of a series of thiacrown−I_2 adducts, [14]aneS_4·I_2, shows molecularly distinct R_2S·I_2 units similar to **Ni-1***·I_2.[6]

As a solid or in solution, **Ni-1***·I_2 is stable upon exposure to air. Thermal decomposition of the solid occurs at >200 °C, and there is no evidence of I_2 loss, even at the high temperatures preceding decomposition. Like the SO_2 adduct, the small-molecule adduct cannot be disrupted when the solid is placed under vacuum for extended periods of time. In contrast to the SO_2 adducts, **Ni-1**·SO_2 or **Ni-1***·SO_2, the iodine adduct is not disrupted or degraded when a CH_3CN solution of **Ni-1***·I_2 is purged with an inert gas. The adduct, **Ni-1***·I_2, is insoluble in most organic solvents. It is slightly soluble in CH_3CN (30 mg/100 mL) and also in the more polar solvent DMSO. However, on long standing in DMSO, the orange brown color of the solution fades to colorless with no observable precipitate.

Table 2. Comparison of **Ni-1***·I_2 metric data to the parent complex, **Ni-1***

	 **Ni-1*·I2**	 **Ni-1***
Ni-S(1)	2.162(4)Å	2.152(1)Å
Ni-S(2)	2.169(4)	2.152(1)
Ni-N(1)	1.954(11)	1.995(3)
Ni-N(2)	1.981(10)	1.995(3)
I(1)-S(2)	2.601(4)	
I(1)-I(2)	3.0163(18)	
N(1)-Ni-N(2)	91.3(5)°	90.4(2)°
S(1)-Ni-S(2)	87.73(15)	88.8(1)
Ni-S(2)-I(1)	101.02(14)	
S(2)-I(1)-I(2)	176.92(9)	
N(1)-Ni-S(1)	90.2(4)	90.4(1)
N(2)-Ni-S(2)	90.8(3)	90.4(2)

The Nature of "Ni-1*·I_2" in Polar Solvents. The solution injection technique of ESI mass spectroscopy shows two nickel-containing fragments, as established by isotopomer distribution, for **Ni-1***·I_2, *neither of which is the parent peak*. One signal has a *m*/*z* value of 346 which corresponds to the dithiolate, **Ni-1***. The other peak has a *m*/*z* value of 473 which corresponds to **Ni-1***·I^+, implying a heterolysis of the I_2 bond.

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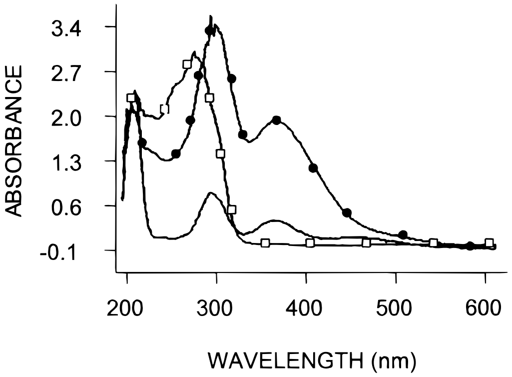

Figure 4. UV−vis of (—) I_2, (□) **Ni-1***, (●) **Ni-1***·I_2. All samples are 0.2 mM in CH_3CN and 22 °C.

The concentration dependence of solution conductivity of **Ni-1***·I_2 provides further evidence of heterolytic I_2 cleavage or ionization in solution. For both **Ni-1***·I_2 and pure I_2 in CH_3CN, plots of molar conductivity versus concentration follow the form of a higher-order polynomial instead of a straight line, suggesting ionization with ion-pairing occurs.[18] For both, the molar conductivities at a concentration of 1 mM are approximately 160, which corresponds to a uni−uni electrolyte in solution, attributable to **Ni-1***·I^+/I^- for the former and I^+/I_3^- for the latter.

Figure 4 presents the UV−vis spectrum (in CH_3CN) of the **Ni-1***·I_2 adduct with spectral overlays of pure I_2 and **Ni-1*** for comparison. All are at 0.2 mM concentration. Notably, the absorbances at 362 and 292 nm are observed for both I_2 and **Ni-1***·I_2, with a large gain in intensity for the latter. Since the conductivity and mass spectral data above suggest heterolytic cleavage of I_2, we assume the UV−vis spectrum indicates the presence of I_3^- and **Ni-1***·I^+ in the polar solvent. More I_3^- is produced in solution of the **Ni-1***·I_2 adduct than in pure I_2. The L → M charge-transfer band at 280 nm for **Ni-1*** appears to shift into and be overwhelmed by the 292-nm band of I_2 in the spectrum of the **Ni-1***·I_2 adduct. Since the **Ni-1***·I^+ species has not yet been isolated in the absence of the $I^-/I_2/I_3^-$ equilibria, the nature of the charge-transfer band is not clearly established.

While there are numerous examples of I_2 adducts of organic sulfides, $R_2S\cdots I_2$,[6,17,19] and thiones, $R_2C{=}S\cdots I_2$,[20] and a few cases of coordination complex inorganic sulfides using a bridging sulfide as the I_2 binding site,[21] two adducts appear to be most pertinent as analogues of **Ni-1***·I_2. The structure of the [14]aneS_4·I_2 tetrathiacrown ether adduct, vide supra,[6] is appropriate for comparison because of its lack of intermolecular interactions. It shows a longer S−I distance, 2.859(3) Å, and a shorter I−I distance, 2.8095(11) Å, as compared to the **Ni-1***·I_2 adduct, thus indicating the greater donor ability of the formally anionic thiolato sulfur as compared to the organic thioether. This result correlates with earlier studies as described below.

Earlier we assembled data for a comparison of the ability of the **Ni-1** dithiolate with thioethers, thiolates, and the classic ligand in organometallic chemistry, Ph_3P, to serve as a 2-electron donor ligand to $Fe(CO)_4$ using ν(CO) IR spectroscopy as a probe.[22] The ν(CO) values are listed in footnote 23[22,24,25] and indicate an order of donor ability: $SPh^- \geq$ **Ni·1** > $PPh_3 \cong$ MeSPh. Thus the S−I and I−I distances in I_2 adducts of **Ni-1*** and the thiacrowns are consistent with their donor abilities to the metal carbonyl. However, the interaction with PPh_3 is not so clear-cut. As indicated above, a report of I_2 reactions with PPh_3,[7] which included disproportionation of I_2 to yield $[PPh_3I]^+I_3^-$, predated a report of the simple adduct $Ph_3P{\cdot}I_2$ whose X-ray crystal structure finds a quite long I−I distance of 3.16 Å.[13] This apparent reversal of donor ability of PPh_3 and **Ni-1*** toward I_2 as contrasted to their donor ability toward $Fe(CO)_4$ must be attributed to the nature of the acceptors. Unlike I_2, the metal carbonyl $Fe(CO)_4$ has capability to back-donate electron density to π-accepting ligands. The metal thiolate has no possibility of π-accepting; PPh_3 has at least a limited capability.

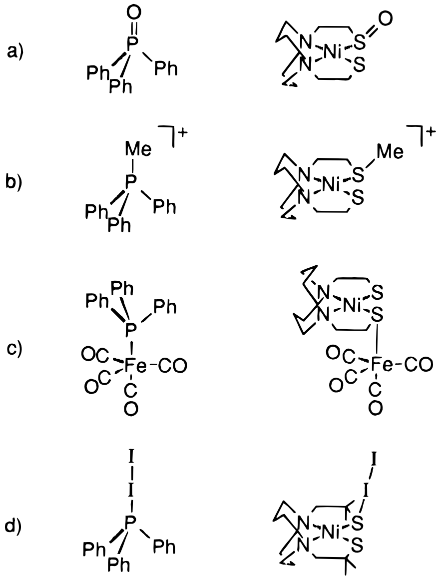

Figure 5. Comparison of nickel thiolate reactivity as nucleophile and analogous triphenylphosphine products.

Figure 5 outlines further analogies of the P-donor nucleophile PPh_3 to the S-donor of **Ni-1***, including oxygenation,[2] alkylation,[1] and ligation.[22] A conspicuous deviation in reaction possibilities of PPh_3 and **Ni-1** is the potential for redox activity in the latter. The sulfur-based electron transfer from **Ni-1** which oxidizes the thiolate to thiyl and hence to disulfide and reduces I_2 to I^- is obviously impossible for PPh_3. Since **Ni-1** and **Ni-1*** have similar and accessible E_{ox} values, a disparity is found in that electron transfer from **Ni-1** leads to the fully oxidized trimetallic complex, while this does not occur with the **Ni-1*** species. The cause of the discrepancy in **Ni-1** and **Ni-1*** reactivity, eqs 2 and 3, must lie in the relative stability of the products. The trimetallic of **Ni-1** is a ubiquitous product of oxidation, whereas the steric hindrance in **Ni-1*** greatly impedes formation of aggregates.

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(23) Solution ν(CO) IR (cm^{-1}) for $LFe(CO)_4$: L = **Ni-1** (THF) 2030 (s), 1945 (m), 1926 (vs), 1907 (vs);[22] PPh_3 (hexane): 2052 (m), 1980 (m), 1947 (vs);[24] MeSPh (hexane): 2057 (m), 1979 (s), 1956 (vs), 1946 (vs);[25] SPh^- (acetone), 2016 (m), 1910 (vs).[25]

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Supporting Information Available: Diagrams and tables of crystallographic data collection parameters, atomic coordinates, and a complete listing of bond lengths and bond angles for **Ni-1***·I_2 (6 pages). Ordering information is given on any current masthead page.

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