

of the axial ligands increases. Ripan suggested the 250-nm band to be due to the  $\text{Co}(\text{DMG})_2$  moiety only; we feel this to be an insufficient explanation. Instead, we suggest that the charge-transfer band involves a transition from the  $^1A_1$  ground state of cobalt(III) to some higher state of the molecule involving considerable mixing of DMG orbitals. This state is probably at a rather constant energy (with respect to cobalt's field-free atomic term) throughout all the compounds.

As the field strength increases, lowering the  $^1A_1$  ground state of cobalt(III), the separation between ground and charge-transfer state increases. Thus, an increase in strength of axial ligands results in the charge-transfer band appearing at higher energy.

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## Magnetic Studies on Amino Acid Complexes of Copper(II). II. Novel Interactions in Tetrakis(L-tyrosinato)dicopper(II)<sup>1</sup>

By JUAN F. VILLA AND WILLIAM E. HATFIELD\*

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Tetrakis(L-tyrosinato)dicopper(II) is shown to exhibit spin-spin interactions yielding a triplet ground state with the singlet state at  $19.1 \text{ cm}^{-1}$  above the ground state. The epr spectrum of the half-field region also demonstrates the existence of spin-spin coupling. A value of  $D = 0.0213 \text{ cm}^{-1}$  is calculated from the half-field line. The observed spin interactions are shown to be of a strictly localized fashion within the dimers, but at very low temperatures ( $<17^\circ\text{K}$ ) a weak cooperative phenomenon becomes perceptible. A best fitting procedure of the magnetic susceptibility data yields the following values for the magnetic parameters:  $2J = +19.1 \text{ cm}^{-1}$ ,  $g = 2.17$ , and  $\theta = -2.06^\circ\text{K}$ . A model which accounts for the observed data is proposed. It involves a  $\sigma$ -orbital mechanism *via* the out-of-plane bonds. The carboxyl oxygens of the ligands act as bridges in the mechanism.

### Introduction

Recently we reported<sup>2-5</sup> the possibility of the existence of triplet ground states in coordination compounds of copper(II) where there are spin interactions between isolated pairs of copper ions.

In order to determine the frequency of this relatively rare phenomenon and the properties of the compounds that exhibit it, we have now studied tetrakis(L-tyrosinato)dicopper(II),  $[\text{Cu}(\text{tyr})_2]_2$ , which has been shown<sup>6</sup> to have the copper ions arranged in distinct dimeric units, as depicted in Figure 1. The coordination of the copper ions is made up by the nitrogen and carboxyl oxygen atoms of two tyrosine molecules. The fifth position of coordination is occupied by the oxygen atom of the adjacent half of the molecule while the sixth position is open. Some pertinent distances are given in Figure 1. The out-of-plane bonds (dotted in Figure 1) are longer than the in-plane bonds by about  $0.4 \text{ \AA}$  but still offer a possible pathway for electron delocalization and spin coupling between the copper ions.

Here we report the observation of spin interactions by means of electron paramagnetic resonance measurements and the characterization of the magnetic properties of  $[\text{Cu}(\text{tyr})_2]_2$  by measuring the susceptibility in the temperature range  $2.5\text{--}93^\circ\text{K}$ .

### Experimental Section

Tetrakis(L-tyrosinato)dicopper(II) was synthesized by a method similar to Laurie's,<sup>7</sup> by preparing an equimolar ( $0.125 \text{ M}$ ) aqueous solution of tyrosine and NaOH, warming to  $60^\circ$ , and adding dropwise an aqueous solution of  $\text{CuSO}_4$ . The final volume was about 250 ml. The precipitate which formed immediately was filtered and washed with water and ether. The mauve solid was dried over  $\text{P}_2\text{O}_5$ ; mp  $248\text{--}250^\circ \text{ dec}$ . *Anal.* Calcd for  $\text{Cu}(\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6)_2$ : Cu, 51.00; H, 4.76; N, 6.81. Found: Cu, 51.09; H, 4.76; N, 6.58. The analyses were carried out by Galbraith Laboratories, Inc.

All the physical measurements were carried out using polycrystalline samples of the pure compound. The epr spectra were obtained at room and liquid nitrogen temperatures with a Varian E-3 spectrometer, at a frequency of 9.191 GHz. Diphenylpicrylhydrazyl was used as an internal standard<sup>8</sup> ( $\langle g \rangle = 2.0036$ ). The magnetic susceptibility was measured in the temperature range from 300 to  $77^\circ\text{K}$  using a Faraday balance which has been described previously.<sup>9</sup> For the temperature range from 2.5 to  $77^\circ\text{K}$  a vibrating-sample magnetometer from Princeton Applied Research was used. The sample weight was about 0.1 g. The magnetic field was maintained constant at 10,000 G with a Ventron Instrument Corp. power supply equipped with a field control unit. A high-sensitivity, precalibrated germanium resistance thermometer from Scientific Instruments, Inc., was used to monitor the temperature. Appropriate corrections for the diamagnetism of the sample rod and sample container were applied, as well as corrections for the diamagnetism of the sample<sup>10</sup> ( $213 \times 10^{-1} \text{ cgsu}$ ) and for temperature-independent paramagnetism ( $100 \times 10^{-1} \text{ cgsu}$ ). The calculations were carried out using Fortran IV programs written for a Raytheon 706 computer with an SDT input-output system.

(1) Tyrosine is  $\beta$ -(4-hydroxyphenyl)- $\alpha$ -aminopropionic acid.

(2) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, *J. Amer. Chem. Soc.*, **92**, 4982 (1970).

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(8) D. J. E. Ingram, "Free Radicals, as Studied by Electron Spin Resonance," Butterworths, London, 1958, p 136.

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(10) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 403.

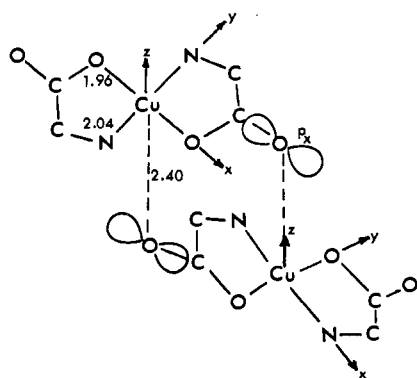


Figure 1.—Schematic representation of the structure of tetrakis(L-tyrosinato)dycopper(II).

### Results

The room-temperature<sup>11</sup> epr spectrum of tetrakis(L-tyrosinato)dycopper(II) from 0 to 5000 G shows a broad but definable axial spectrum near 3000 G, Figure 2, from which the parameters  $g_{||} = 2.21$ ,  $g_{\perp} = 2.10$ , and

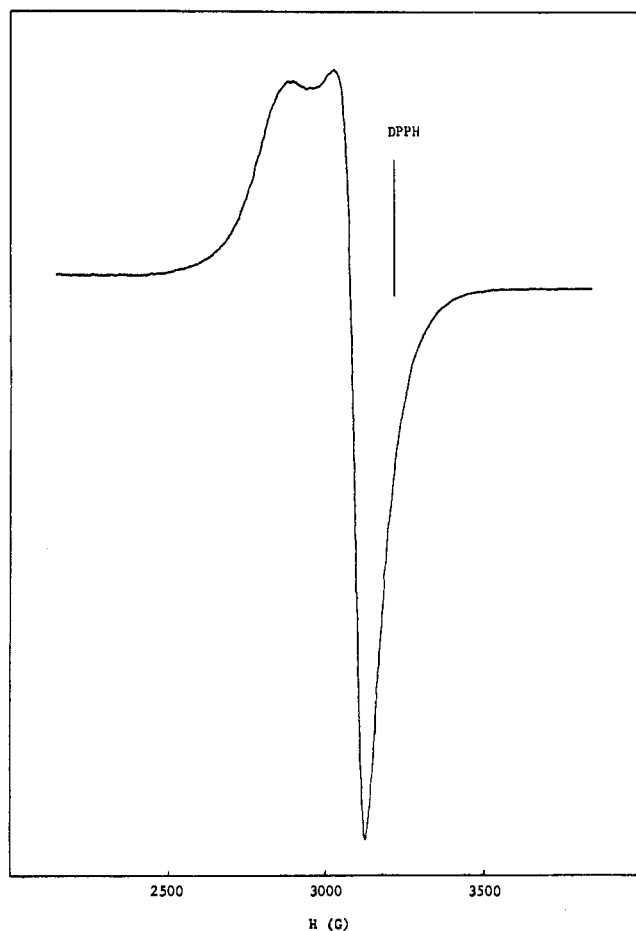


Figure 2.—The epr spectrum of tetrakis(L-tyrosinato)dycopper(II) in the range 0–5000 G.

$\langle g \rangle = 2.14$  can be calculated. Here  $\langle g \rangle = (g_{||} + 2g_{\perp})/3$ . The half-field region<sup>12,13</sup> displays an absorption band at 1525 G, Figure 3, which can be assigned to  $H_{\min}$ , the

(11) Another set of spectra was obtained at 77°K but only minor changes were observed.

(12) P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **41**, 379 (1964).

(13) J. F. Villa, J. M. Flowers, and W. E. Hatfield, *Spectrosc. Lett.*, **3**, 201 (1970).

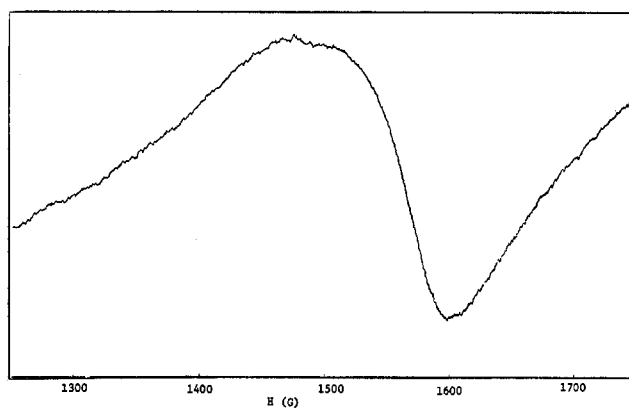


Figure 3.—The  $\Delta m_s = \pm 2$  transition in the epr spectrum of tetrakis(L-tyrosinato)dycopper(II).

minimum position of absorption of the  $\Delta m_s = \pm 2$  transitions. The large band to the right is part of the  $\Delta m_s = \pm 1$  spectra. Equation 1 can be used<sup>14</sup> in order

$$D = \frac{3}{4}[\omega_0^2 - (2\langle g \rangle \beta H_{\min})^2]^{1/2} \quad (1)$$

to obtain the zero-field splitting parameter  $D$ . Here  $\omega_0$  is the quantum of energy  $h\nu$ ,  $\nu$  is 9.191 GHz,  $\beta$  is the Bohr magneton, and  $\langle g \rangle$  is the average  $g$  value. The  $D$  value obtained is  $0.0213 \text{ cm}^{-1}$  which is of the same order of magnitude as that of some other copper(II) systems studied in our laboratory.<sup>15,16</sup>

In addition to the bands already discussed, there are some positions of absorption in the 2400-G region which could be due to the low-field parallel band of the triplet state. However, the intensity of the bands at higher fields has precluded an accurate positioning of the bands and thus does not permit their use to determine other triplet-state parameters.

The inverse magnetic susceptibility for this system is shown in Figure 4 from 2.5 to 292.5°K. The solid

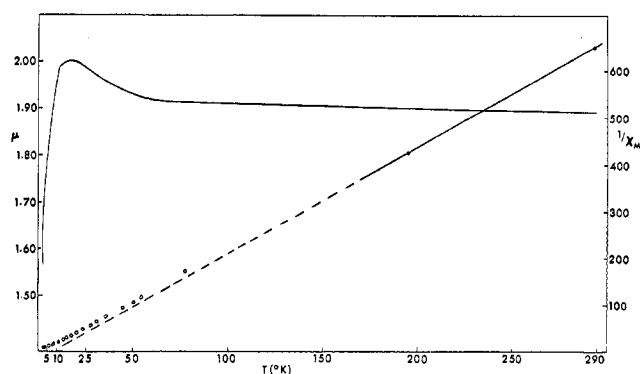


Figure 4.—The inverse magnetic susceptibility and magnetic moment of tetrakis(L-tyrosinato)dycopper(II) in the temperature range 2.5–292.5°K.

line constitutes the Curie–Weiss law with  $C = 0.411$  cgsu/deg and a Weiss constant of  $-5^\circ$ . Figure 5 contains the magnetic susceptibility and inverse magnetic susceptibility in the temperature range 2.5–54°K. The solid lines represent the theoretical values ob-

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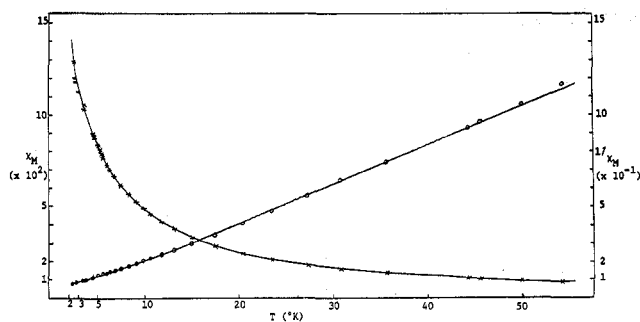


Figure 5.—Comparison of the calculated and observed magnetic susceptibilities of tetrakis(L-tyrosinato)dicopper(II). See text for parameters.

tained using<sup>17</sup> the modified Langevin equation

$$\chi_M = \frac{Ng^2\beta^2}{3k(T - \theta)} [1 + (1/3)e^{-2J/kT}]^{-1} \quad (2)$$

and the following values for the magnetic parameters:  $g = 2.17$ ,  $2J = +19.1$ , and  $\theta = -2.06^\circ\text{K}$ . Here  $2J$  is the energy of interaction between the spins within isolated dimers (defined by the Hamiltonian  $\mathcal{H} = -2J_{12}S_1 \cdot S_2$ ) and  $\theta$  is a parameter indicative of interaction among spins throughout the lattice. The values for the magnetic parameters were obtained by a computerized best fitting procedure where  $2J$  and  $g$  were allowed to vary to their best fitting values while keeping  $\theta$  constant. Then, a new  $\theta$  was chosen and so on until the overall best fitting  $2J$ ,  $g$ , and  $\theta$  parameters were obtained. The parameter  $A_{\text{BF}}$ , defined in eq 3, was used

$$A_{\text{BF}} = \sum_i [(\chi(\text{exptl})_i - \chi(\text{calcd})_i)T_i]^2 \quad (3)$$

as the criterion for the best fit. It is necessary to take the product of  $\Delta\chi$  and temperature at each point because the susceptibility increases as the temperature is decreased, and these large susceptibilities produce an undesirable effect on the fitting procedure.

Three-dimensional contour maps of the magnetic parameters<sup>4,15,18</sup> were built, in which points of equal value of the parameter  $A_{\text{BF}}$  were connected. The magnetic parameters converged to the values used to calculate the theoretical magnetic properties plotted as solid lines in Figure 5. Other values of  $\theta$  produced worse values for the fitting parameter  $A_{\text{BF}}$ . In addition, there is very good agreement between the experimental and calculated values (using the same magnetic parameters as above) for the effective magnetic moments of  $[\text{Cu}(\text{tyr})_2]_2$ . For positive  $J$  values the accuracy is probably no better than  $\pm 10\%$ , for it is usually beyond this range in  $J$  that the fitting parameter begins to increase significantly.

### Discussion

It is interesting to note that the spin-spin coupling present in this copper dimer yields an  $S = 1$  value. This is indicative that the spins of two copper ions within each dimer are coupled producing a magnetic triplet state and a singlet nonmagnetic state. This conclusion is based on the deviation from Curie-Weiss behavior of the magnetic susceptibility data (Figure 4) and on the very good fit of the magnetic data (Figure

5) by the use of the modified Langevin equation (eq 2) which applies to interacting dimers. The triplet state is the ground state and the singlet state lies  $19.1 \text{ cm}^{-1}$  above it. This is the first case where an amino acid-metal system has been shown to possess a triplet ground state and the results open up a whole new range of possibilities to consider when studying the larger metal-protein or metal-enzyme systems.

Apparently, dipolar and exchange interactions in the pure material make the triplet-state epr spectrum coalesce to a simple axial spectrum, as shown in Figure 2. This makes the observation of the low- and high-field triplet-state bands very difficult. The value of  $\theta = -2.06^\circ\text{K}$  deserves additional comment. It seems that, when the temperature is low enough, there is a weak-lattice antiferromagnetic effect which results in a diminution of the magnetism. Effectively, the spins tend to line in an antiparallel fashion among dimers or among groups of dimers. This fact is well exemplified by the observed decrease in the effective magnetic moments for this compound below  $17^\circ\text{K}$ .

We can now discuss the mechanism by which the electronic spins interact with each other. The copper-copper distance is too large to allow for localized dipolar coupling.<sup>19</sup> Direct superexchange would produce a singlet ground state in contrast with triplet ground state observed here. Therefore, it is expected that superexchange<sup>20,21</sup> via the bridging oxygen atoms is responsible for the observed interactions.

The mechanism for the spin-spin coupling which leads to the triplet ground state can be understood by references to Figure 1. Electron delocalization from the  $p_x$  oxygen orbital into the  $d_{x^2-y^2}$  orbital of copper 1 deposits some unpaired spin density of the same net orientation as that in copper 1 on the bridging oxygen atom. Then, coupling of the unpaired spins in orthogonal orbitals ( $p_x$  and  $d_{x^2-y^2}$  of copper 2) produces the triplet ground state. Also, a polarization effect<sup>19</sup> running from the  $p_x$  orbital to the  $d_{z^2}$  orbital of copper 2 deposits like spin density in the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals of copper 2 with the same magnetic result.

Comparison of these results with our previous results<sup>18</sup> on the tetrakis(diethylthiocarbamato)dicopper(II) system indicates that there is a difference in changing the bridging group from oxygen to sulfur, as measured by the  $2J$  values of  $19.1$  and  $24.0 \text{ cm}^{-1}$ , respectively. This difference amounts to about 20% of the magnitude of  $2J$  and is in the expected direction since the oxygen orbitals would be expected to be somewhat less available to copper for delocalization than the sulfur orbitals, making the spin coupling through delocalization weaker.

### Conclusions

Epr and magnetic studies on tetrakis(L-tyrosinato)-dicopper(II) have shown that the spins of the two copper(II) ions in the dimeric molecule interact with each other, producing two spin states, of which the triplet is of lowest energy.

Comparison of the magnetic parameters to those of previously studied systems indicate that sulfur is a

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better atom for promoting the type of spin coupling studied here than oxygen. We are presently engaged<sup>22</sup> in the study of a nitrogen-bridged species.

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(22) J. F. Villa and W. E. Hatfield, to be submitted for publication.

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## Lewis Basicity of a Free-Radical Base. II

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Calorimetric measurements of the interaction of the free-radical base 2,2,6,6-tetramethylpiperidine-*N*-oxyl with the Lewis acids boron trifluoride and bis(hexafluoroacetylacetonato)copper(II) are reported. Using data previously reported,<sup>2</sup> the *C* and *E* numbers of the base were determined to be 6.21 and 0.915. The *C/E* ratio is much larger than other typical diamagnetic oxygen donor molecules, *e.g.*, ethyl acetate, dimethyl sulfoxide, and pyridine *N*-oxide, etc. The 1:1 adduct of Cu(hfac)<sub>2</sub> with the free-radical base was isolated and its magnetic properties were investigated. It was found that the adduct exhibited large intramolecular antiferromagnetic coupling. Various mechanisms of spin-spin interaction are proposed to explain its magnetic behavior. By comparing the enthalpy predicted for the formation of this adduct from the *E* and *C* correlation with that measured experimentally, the contribution to the stability of this adduct from spin-spin interaction can be estimated. The implication of these results to the bonding in systems involving coordinated O<sub>2</sub> are discussed.

### Introduction

In a previous article from this laboratory,<sup>2</sup> it was demonstrated on the basis of epr spectral studies that in adduct formation with the stable free-radical base 2,2,6,6-tetramethylpiperidine-*N*-oxyl (hereafter designated as TMPNO) the donor MO is largely a lone-pair oxygen orbital. In order to understand better the chemistry of this new class of donors, we have extended the calorimetric investigation of the Lewis basicity of TMPNO with a series of Lewis acids, including bis(hexafluoroacetylacetonato)copper(II). The copper complex has one unpaired electron (in the  $d_{x^2-y^2}$  orbital) which would be expected to undergo spin-spin exchange with the unpaired electron of TMPNO on adduct formation. The exchange of the two spins with each other is of interest, from the standpoint of the theory of both spin exchange and oxygen coordination.

An additional objective of the present study was to investigate the deviation of the enthalpy of adduct formation in a system in which spin pairing occurred from the enthalpy predicted from our *E* and *C* equation.<sup>3</sup> This equation has been successfully applied to many donor-acceptor systems where steric effects are absent<sup>4</sup> and where there is no possibility of spin pairing between the donor and the acceptor.

### Experimental Section

(a) **Solvents.**—Reagent grade cyclohexane was stored over Linde 4A Molecular Sieves for several days prior to use. 1,2-Dichloroethane (Fischer Certified ACS grade) was stored over

Linde 4A Molecular Sieves for at least 24 hr and used without further purification. The sieves were discarded and replaced with a fresh portion after several days due to the discoloration of the sieves.

(b) **Preparation and Purification of Acids and Bases.**—The free-radical base was prepared and purified as previously described.<sup>2</sup> The hydrated bis(hexafluoroacetylacetonato)copper(II) was prepared as described previously.<sup>5</sup> The anhydrous form obtained by sublimation under reduced pressure could be stored over P<sub>2</sub>O<sub>5</sub> (*in vacuo*) for several days.

*Anal.* Calcd for CuC<sub>10</sub>H<sub>2</sub>O<sub>4</sub>F<sub>12</sub>: C, 25.13; H, 0.42; Cu, 13.31. Found: C, 24.97; H, 0.42; Cu, 13.12.

The boron trifluoride-diethyl ether adduct was purified as previously described.<sup>6</sup>

(c) **Preparation of the 1:1 Adduct of Cu(hfac)<sub>2</sub> with TMPNO.**—Stoichiometric amounts of Cu(hfac)<sub>2</sub> were mixed with the free radical in methylene chloride in a drybag and the solvent was removed by filtration. The resulting complex is not hygroscopic and the crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> by cooling the solution to Dry Ice temperature. The product was immediately filtered and stored over anhydrous P<sub>2</sub>O<sub>5</sub>.

*Anal.* Calcd for CuC<sub>19</sub>H<sub>20</sub>NO<sub>5</sub>F<sub>12</sub>: Cu, 10.03; C, 35.99; H, 3.16. Found: Cu, 9.99; C, 36.28; H, 3.24. The melting point was found to be 79–80° (uncorrected).

The nmr spectrum of the 1:1 adduct of Cu(hfac)<sub>2</sub> with TMPNO in CCl<sub>4</sub> was measured with the HR-220 nmr spectrometer by the staff of the Molecular Spectroscopy Laboratory of the University of Illinois. The probe temperature was 23°, and benzene was used as the internal reference.

The solution magnetic susceptibility was measured by the Evans method,<sup>7</sup> using the Jeol-C-60H. Several samples were run to check the reproducibility of the result. Great care was taken to differentiate the side-band signals from the signal due to the presence of the 1:1 adduct. TMS was used as the reference signal.

The magnetic susceptibility in the solid state (powder form) was measured by Faraday's method, using HgCo(SCN)<sub>4</sub> as the calibration standard. Because of the need for temperature studies, the magnetic study was also carried out on a vibrating-

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