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Article

Cu₄₂Ge₂₄Na₄—A Giant Trimetallic Sesquioxane Cage: Synthesis, Structure, and Catalytic Activity

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Abstract: Unprecedented germanium-based sesquioxane exhibits an extremely high nuclearity (Cu₄₂Ge₂₄Na₄) and unusual encapsulation features. The compound demonstrated a high catalytic activity in the oxidative amidation of alcohols, with cost-effective catalyst loading down to 400 ppm of copper, and in the oxidation of cyclohexane and other alkanes with H₂O₂ in acetonitrile in the presence of nitric acid. Selectivity parameters and the mode of dependence of initial cyclohexane oxidation rate on initial concentration of the hydrocarbon indicate that the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary product. Alcohols have been transformed into the corresponding ketones by the catalytic oxidation with *tert*-butyl hydroperoxide.

Keywords: alkanes; amides; hydrogen peroxide; multinuclear complexes; iron complexes; metallasiloxanes

1. Introduction

The interest to cagelike compounds—which find many unique applications [1–4]—is determined by the kaleidoscopic multiplicity of their molecular topologies as well as flexibility in the preparation of either metal-free [5–8] or metal-based [9–12] complexes (with an opportunity to combine several different metal atoms within one molecule). A proper choice of the ligand is of obvious significance for the synthesis of metallacages. For example, heterochained ligands based on (R)Si-O-(R)Si fragments have proven promising for the synthesis of numerous metallacomplexes [4,13–16]. It is the quantity of organic groups at the silicon atoms that are mainly responsible for the resultant complex's molecular topology. Notably, the majority of cage-like metalladerivatives are enabled by branched

monosubstituted ($\text{RSiO}_{1.5}$) silsesquioxane ligands [17–19]. It is ultimately surprising but to the best of our knowledge germanium sesquioxane ligands that are the closest analogues of silsesquioxanes, have been scarcely studied in the context of a possible molecular design of metallacomplexes so far. We could mention here only the use of (i) bis(carboxyethyl)germanium sesquioxide [20–27] in hydrothermal reactions and (ii) $\text{PhGe}(\text{OMe})_3$ [28,29] in the self-assembly synthesis.

Here we present an alternative convenient and versatile approach to cage-like metallagermaniums sesquioxanes starting from oligomeric $[\text{PhGeO}_{1.5}]_n$ that is easily accessible via the hydrolytic polycondensation of PhGeCl_3 (Figure 1). The second step of the synthetic procedure consists in the generation of highly reactive $\text{PhGeO}^-\text{Na}^+$ fragments through the interaction of $[\text{PhGeO}_{1.5}]_n$ with sodium hydroxide. It has been revealed that the resulting mixture remained heterogeneous at a 1/1 reactant ratio ($\text{Na}/\text{Ge} = 1$). By increasing this ratio to 3/1 ($\text{Na}/\text{Ge} = 3$), a homogeneous solution is obtained, which is prone to exchange reactions with diverse sources of transition metal ions. A high concentration of sodium centers in the resultant sodium germanolate intermediate (formally, the latter could be regarded as $\text{PhGe}(\text{ONa})_3$) enables the uptake of a significant amount of transition metal ions by a simple and convenient reaction with a transition metal halide. Taking in mind the fact that Cu-based germsesquioxanes remain exclusively rare [24,30], we chose CuCl_2 as a source of transition metal ions for the very first trial of this reaction (Figure 1). This reaction accomplished in a DMF/CHCl_3 solvent system (also used for the crystallization) afforded a totally unexpected title product **1** in a 20% yield.

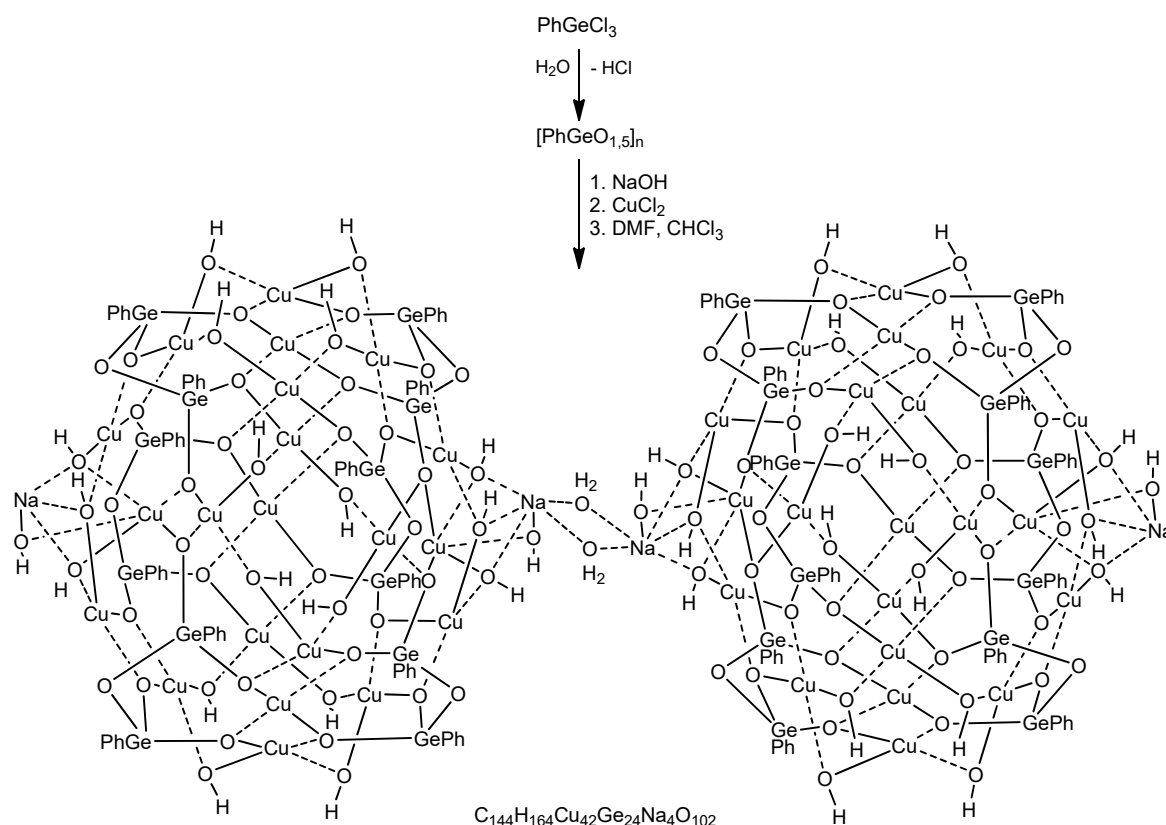


Figure 1. General scheme of synthesis and structure of coppersodiumgermsesquioxane **1**.

The structure of **1**, which is the first observation of a $\text{Cu}(\text{II}),\text{Na}$ -germsesquioxane cage, is unique both as compared to previously reported Cu-containing germsesquioxanes [24,30] and to the best of our knowledge, to any type of oxametalloclusters. Indeed, the whole complex of **1** is built up of two similar cage units of unprecedented $\text{Cu}_{21}\text{Ge}_{12}$ -nuclearity. An isolation of such metal-rich (the M/Ge ratio exceeds 1/1) product has never been reported for any metallagermaniums sesquioxanes [20–30]. In terms of topology, the spherical shape of cage-like components of product **1** could be compared

only to non-dimeric Cu(I)-based silsesquioxane reported by the team of Prof. Zhu and Prof. Roesky [31]. An intriguing feature of the spherical cage of **1** is its composition that could be described as a coordination complex of three identical units corresponding to the Cu₇ nuclearity (Figure 2, central panel).

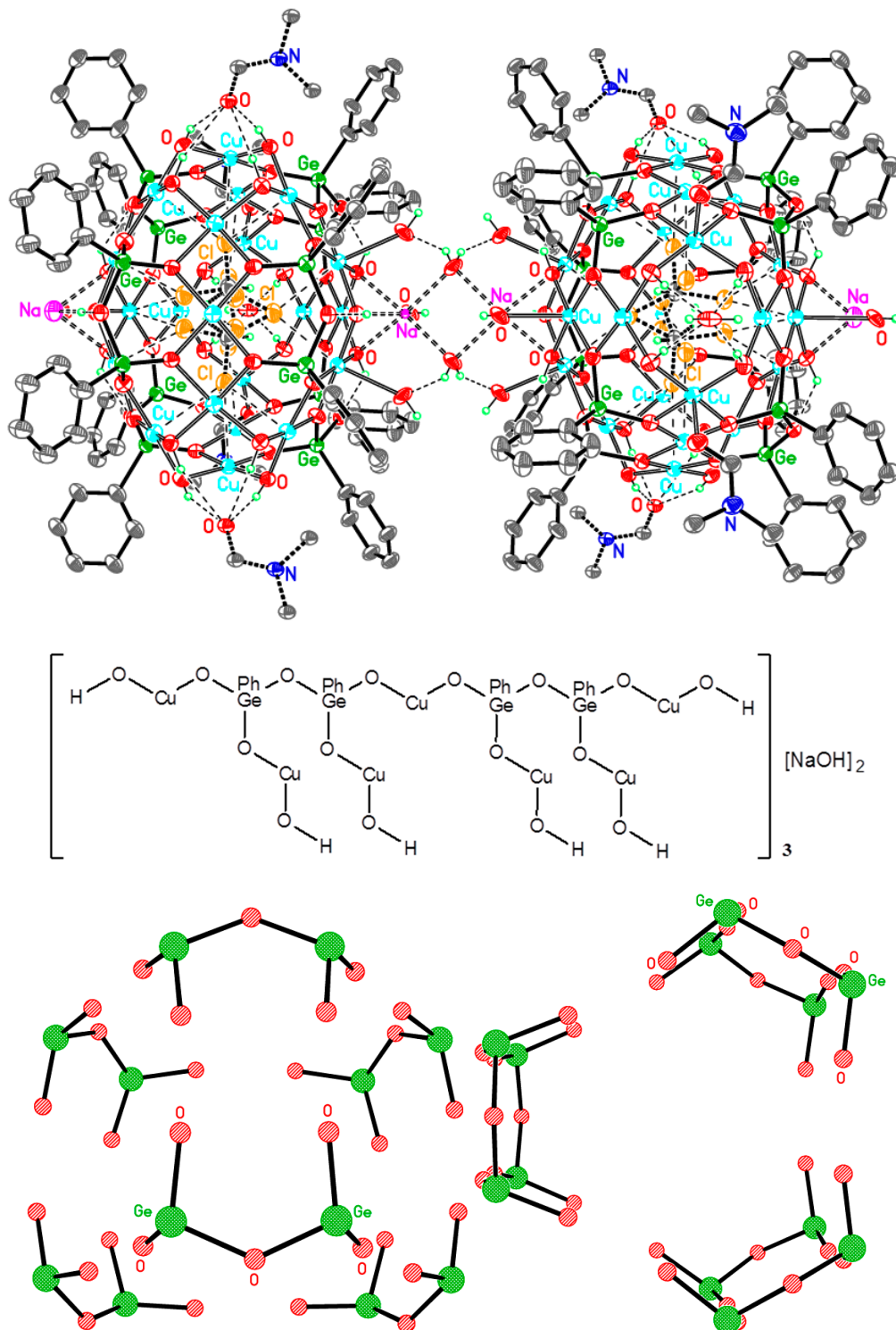


Figure 2. Top panel. The molecular structure of **1**. Central panel. A sketch of the cage's building block in **1**. Bottom panel. The structure of acyclic germoxane ligands in **1**.

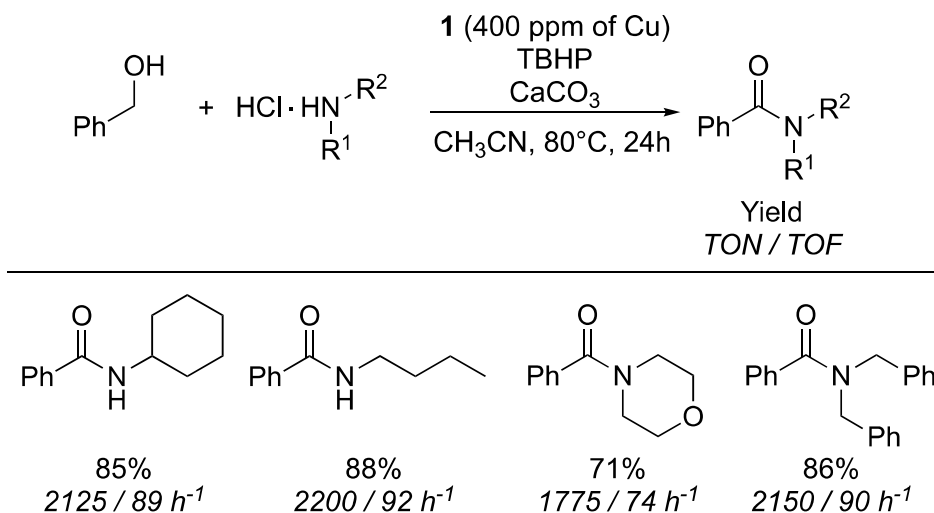
Keeping in mind the extraordinary type of nuclearity manifested by complex **1** a concise survey on related high-nuclearity clusters would be appropriate. A series of 3D open frameworks based on copper-germanium chalcogenides with such building blocks as $[\text{Cu}_8\text{Ge}_6\text{S}_{18}]^{4-}$, $[\text{Cu}_8\text{Ge}_6\text{Se}_{19}]^{4-}$, $[\text{Cu}_8\text{Ge}_6\text{Se}_{19}]^{6-}$, and $[\text{Cu}_{16}\text{Ge}_6\text{Se}_{31}]^{10-}$ have been reported [32,33]. Prof. Fenske and co-authors synthesized and characterized numerous copper-based high-nuclearity selenide and phosphide clusters stabilized by organophosphine ligands [34–36] among which $\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}$ reported back in 1993 still seems to be record-holding. Germanium is prone to the formation of zeolite-like microporous framework structures built up of structural units Ge_n with nuclearities n ranging from 7 to 10 [37–39]. Among polynuclear clusters retaining intrinsically molecular character, a remarkable series of germanium–tin selenides $[\text{Ge}_x\text{Sn}_{60-x}\text{Se}_{132}]^{24-}$ is worth noting, which was called by the authors “Zeoball” due to the combination of a spherical shape with zeolite-related composition [40,41].

Despite the high content of copper centers, the dimerization of two cage components in the structure of **1** is realized exclusively through sodium ions located at external positions and coordinated by oxygen centers of (i) four hydroxyl groups and (ii) two bridging water molecules. In turn, copper centers in **1** demonstrate several types of ligation. All copper ions are coordinated by oxa-ligands: (i) hydroxyl groups, (ii) solvating DMF molecule, and (iii) germesquioxane ligands. Noteworthy, all six germanium-containing fragments in compound **1** are bridging acyclic ones corresponding to the $\text{Ph}_2\text{Ge}_2\text{O}_5$ composition (Figure 2, bottom panel). Thus, **1** becomes the first example of a cage metallagermesquioxane bearing no cyclic germoxane ligands. Second, 21 copper ions in each cage of **1** form three Cu_3O_8 and six Cu_2O_6 nearly planar fragments, in which the metal atoms are tetra-coordinated in a square-planar fashion. Moreover, six copper atoms are additionally coordinated by two DMF and four OH external ligands, whereas thirteen copper atoms are additionally coordinated by chlorine atoms from the encapsulated chloroform molecule. Only two sterically shielded copper atoms preserve the four-coordinated geometry. The fact of chloroform’s encapsulation by itself is not unusual for the chemistry of cage compounds (more than 10 examples are described in [42]). Nevertheless, no examples of such an encapsulation have been reported so far for metallagermesquioxanes. Furthermore, this feature of product **1** as well as the additional coordination of chlorine atoms to the copper ions point to a possible template effect exerted by CHCl_3 during the assembly of cage metallagermesquioxanes, which was not emphasized in previous reports [20–30].

Compound **1** possesses a good solubility in most polar and non-polar aromatic organic solvents. Complex **1** was tested as a catalyst in the homogeneous oxidation. First, **1** was evaluated in the oxidative amidation of benzyl alcohol (Scheme 1). This reaction represents a promising alternative to classical amide bond formation that involves carboxylic acid, amine, and stoichiometric quantities of a coupling agent that could either be toxic or generate stoichiometric quantities of toxic side-products [43]. Herein, benzyl alcohol reacts in the presence of an ammonium chloride, calcium carbonate, *tert*-butyl hydroperoxide (TBHP), and a catalytic quantity of **1**. Corresponding amides could be obtained through a double oxidation of benzyl alcohol into benzaldehyde and then of corresponding hemiaminal into amide. Thanks to the good solubility of **1** in acetonitrile, stock solutions could be prepared and catalyst loading decreased down to 400 ppm of copper for this reaction. Hydrochloride salts of cyclohexyl amine and butyl amine could be converted efficiently with the isolation of corresponding amides in 85% and 88% yields, respectively. Similarly, tertiary amides featuring morpholine and dibenzylamine could be obtained in yields up to 86%. Turnover numbers (TON) and frequencies (TOF) were calculated [44] giving values up to 2200 and 92 h^{-1} . This represents a significant improvement compared to our seminal report on copper-catalyzed oxidative amidation (TON = 44, TOF = 11 h^{-1}) [45].

Complex **1** exhibited a high catalytic activity in the oxidation of cyclohexane and other alkanes with H_2O_2 in acetonitrile in the presence of nitric acid (Figure 3 and See Supplementary Materials). At lower temperatures, the oxidation is less efficient (See Supplementary Materials). The following selectivity parameters were obtained for the oxidation of *n*-heptane: C(1):C(2):C(3):C(4) = 1.0:7.4:7.2:7.9. These data as well as the character of dependence of the initial cyclohexane oxidation rate on the initial hydrocarbon concentration (approaching a plateau at $[\text{cyclohexane}]_0 > 0.3 \text{ M}$) indicate that

the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary products (Figure 4) [46–48]. The oxygenation of *cis*-1,2-dimethylcyclohexane with H₂O₂ catalyzed by complex **1** gave corresponding isomeric tertiary alcohols in a *trans/cis* ratio of 0.8. The oxidation with *m*-CPBA gave *trans/cis* = 0.5. Alcohols have been efficiently transformed into corresponding ketones by the catalytic oxidation with *tert*-butyl hydroperoxide (See Supplementary Materials).



Scheme 1. Catalytic properties of **1** in the oxidative amidation. Reaction conditions: ammonium chloride (0.5 mmol), benzyl alcohol (1.0 mmol), CaCO₃ (0.25 mmol), TBHP (5.5 M, 2.5 mmol), **1** (0.04 mol% of Cu), CH₃CN (1 mL), 80 °C, 24 h.

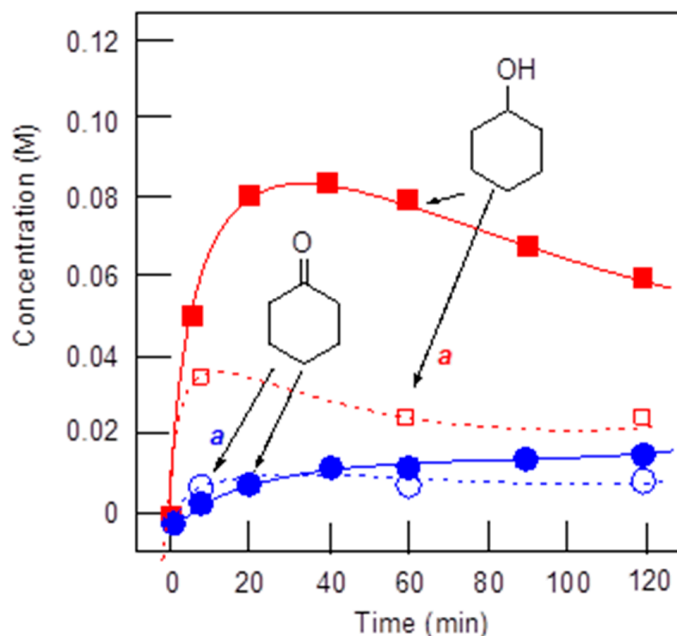


Figure 3. Accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with H₂O₂ (0.5 M containing 0.94 M H₂O) catalyzed by complex **1** (2.5×10^{-4} M) in the presence of HNO₃ (0.05 M) at 40 °C. Concentrations of products were measured by GC after the reduction of the reaction sample with solid PPh₃. The yield of oxygenates after 60 min was 22% (TON 400). Curves *a*: the same in the absence of HNO₃.

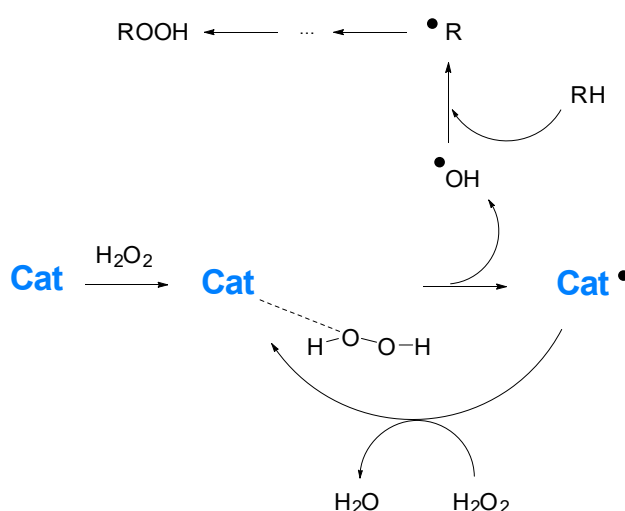


Figure 4. The tentatively proposed catalytic cycle for alkane oxygenation with hydrogen peroxide.

2. Conclusions

In conclusion, these studies demonstrate that simple PhGeCl₃ adduct could be converted via “hydrolytic polycondensation—NaOH cleavage—exchange interaction with CuCl₂” approach into a unique mixed-metal (Cu,Na) germanium-based phenylsesquioxane **1**. This three-stage method allowed to isolate product with an unprecedented high nuclearity (Cu₄₂Ge₂₄Na₄) and unusual encapsulation features. Complex **1** exhibited a high catalytic activity in the oxidative amidation of alcohols, with cost-effective catalyst loading down to 400 ppm of copper, and in the oxidation of cyclohexane and other alkanes with H₂O₂ in acetonitrile in the presence of nitric acid. Selectivity parameters and the mode of dependence of initial cyclohexane oxidation rate on initial concentration of the hydrocarbon indicate that the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary product. Alcohols have been transformed into the corresponding ketones by the catalytic oxidation with *tert*-butyl hydroperoxide. The current study advances our basic knowledge of cage metallacomplexes’ self-assembly principles and their application in homogeneous catalysis.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/10/484/s1>, Experimental and General procedure for the formation of amides.

Author Contributions: A.N.B., F.L., and G.B.S. conceived and designed the experiments; A.N.K., P.V.D., V.N.K., Y.V.Z., X.B., and L.S.S. performed the experiments; A.N.B., F.L., E.S.S., M.M.L., V.N.K., and G.B.S. analyzed the data; E.S.S., and Y.V.Z. contributed reagents/materials/analysis tools; A.N.B., Y.V.Z., F.L., and G.B.S. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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