

# Realgar as a Building Block for Lanthanide Clusters: Encapsulation of a Copper Cluster by a Lanthanide Cluster

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**S** Supporting Information

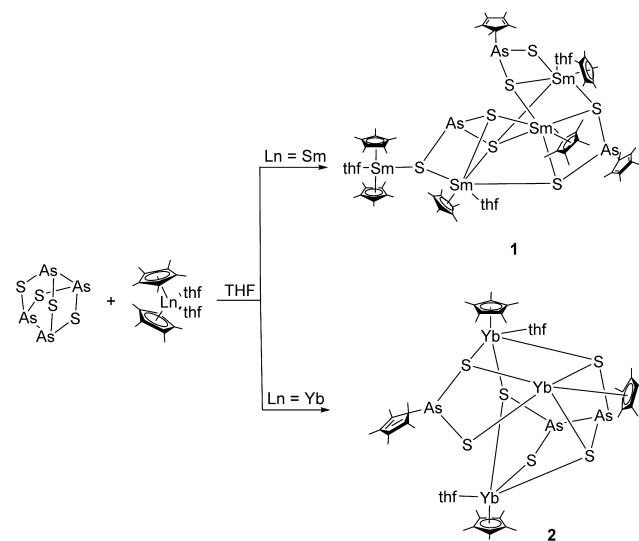
**ABSTRACT:** The reactions of the divalent lanthanide metallocenes  $[\text{Cp}^*_2\text{Ln}(\text{thf})_2]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{Ln} = \text{Sm}, \text{Yb}$ ) with realgar ( $\text{As}_4\text{S}_4$ ) gave the open cage tetrametallic complex  $[(\text{Cp}^*_2\text{Sm})(\text{Cp}^*\text{Sm})_3\text{AsS}_3(\text{Cp}^*\text{AsS}_2)_2(\text{thf})_3]$  (**1**) or the trimetallic cage compound  $[(\text{Cp}^*\text{Yb})_3\text{As}_2\text{S}_4(\text{Cp}^*\text{AsS}_2)(\text{thf})_2]$  (**2**), respectively, by reductive cleavage of the inorganic cage. As result of a  $\text{Cp}^*$  transfer, the novel  $\text{Cp}^*\text{AsS}_2^{2-}$  anion is formed. Moreover, the  $\text{As}_2\text{S}_4^{4-}$  anion, which is bound in **2**, is observed for the first time in coordination chemistry. Closed cage compounds are formed by either using bulkier ligands or a different As/S cage. The reaction of  $[\text{Cp}^*''_2\text{Sm}]$  ( $\text{Cp}^*'' = (1,2,4\text{-}t\text{-Bu})_3\text{C}_5\text{H}_2$ ) with  $\text{As}_4\text{S}_4$  and the reaction of  $[\text{Cp}^*_2\text{Yb}(\text{thf})_2]$  with dimorphite ( $\text{As}_4\text{S}_3$ ) gave the closed 11-vertex cage clusters  $[(\text{Cp}^*''\text{Sm})_3(\text{AsS}_3)_2]$  (**3**) and  $[(\text{Cp}^*\text{Yb})_3(\text{AsS}_3)_2]$  (**4**), respectively. The reaction of **3** with  $[\text{CuMes}]$  resulted in the formation of the Sm/S/Cu cluster  $[(\text{Cp}^*''\text{Sm}(\text{thf}))_4\text{Cu}_4\text{S}_6]$  (**5**), in which the Sm atoms encapsulate a classical  $\text{Cu}_4\text{S}_6^{8-}$  cluster core. This is the first transition metal chalcogenide cluster encapsulated by f-elements. Alternatively, the endohedral cluster can thus be described as  $[\text{Cu}_4@(\text{Cp}^*''\text{Sm}(\text{thf}))_4\text{S}_6]$ , in which a  $\text{Cu}_4$  tetrahedron is encapsulated by the samarium sulfido cluster  $\{(\text{Cp}^*''\text{Sm}(\text{thf}))_4\text{S}_6\}$ .

Transition metal sulfido clusters were synthesized over the last decades to study their structural and physical properties.<sup>1–3</sup> In this context, binary coinage metal chalcogenide clusters were investigated in detail because they feature relatively high ionic and even higher electric conductivity in the solid state, leading to properties that are positioned between those of semiconducting material and metallic phases.<sup>3</sup> In contrast to these investigations, lanthanide sulfido clusters are considerably less developed<sup>4–8</sup> and almost no significant research activity has been observed in this area for the last 10 years. Herein, we present the first synthesis of a copper sulfide cluster encapsulated by lanthanide atoms.

Our approach starts with the synthesis of mixed molecular pnictogenide/sulfur metal clusters. These compounds are well-established in transition metal chemistry,<sup>9–12</sup> but they are almost unknown for the lanthanides.<sup>13–15</sup> Since thioarsenate solid-state materials have been investigated for their applications in nonlinear optics and as semiconductors,<sup>16,17</sup> they are also potentially interesting for the lanthanides.

It is well-known that the mineral realgar ( $\text{As}_4\text{S}_4$ ) can be cleaved to give As/S building blocks.<sup>10,11,18–20</sup> Therefore,  $\text{As}_4\text{S}_4$  was treated with the lanthanide metallocenes  $[\text{Cp}^*_2\text{Ln}(\text{thf})_2]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{Ln} = \text{Sm}, \text{Yb}$ )<sup>21–24</sup> in a reductive approach to give the open cage tetrametallic complex  $[(\text{Cp}^*_2\text{Sm})(\text{Cp}^*\text{Sm})_3\text{AsS}_3(\text{Cp}^*\text{AsS}_2)_2(\text{thf})_3]$  (**1**) and the trimetallic compound  $[(\text{Cp}^*\text{Yb})_3\text{As}_2\text{S}_4(\text{Cp}^*\text{AsS}_2)(\text{thf})_2]$  (**2**), respectively (Scheme 1). As a result of the oxidation of the lanthanide atoms ( $\text{Ln}(\text{II}) \rightarrow \text{Ln}(\text{III})$ ), the  $\text{As}_4\text{S}_4$  cage is reduced and cleaved into fragments, which can be found in **1** and **2**.

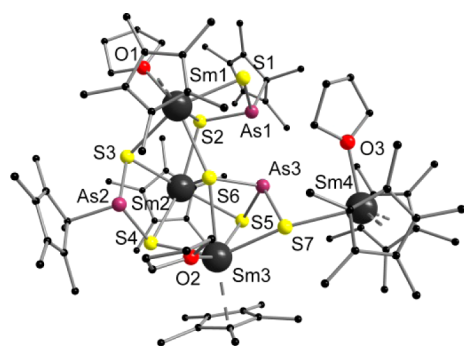
**Scheme 1. Synthesis of Compounds 1 and 2 from  $[\text{Cp}^*_2\text{Ln}(\text{thf})_2]$  ( $\text{Ln} = \text{Sm}, \text{Yb}$ ) and  $\text{As}_4\text{S}_4$**



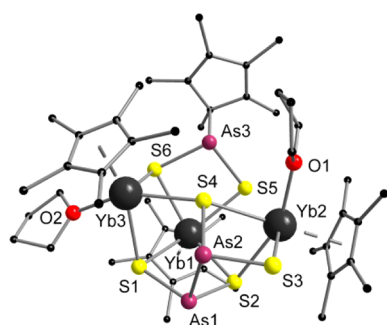
Compound **1** crystallized in two modifications (**1** and **1'**) with different amounts of lattice solvent. In both modifications, the bonding parameters do not differ significantly (Figure 1). After reduction, one thioarsenate anion ( $\text{AsS}_3^{3-}$ ;  $\text{As}_3$ ) is formed, which coordinates to all four Sm atoms through the sulfur atoms. Furthermore, two  $\text{Cp}^*$  anions were transferred to form the unprecedented  $\text{Cp}^*\text{AsS}_2^{2-}$  anion. As result of the transfer of the  $\text{Cp}^*$  ligand, there are, besides one  $\text{Cp}^*_2\text{Sm}$  fragment (Sm4), three  $\text{Cp}^*\text{Sm}$  units in the scaffold of **1**. To the best of our knowledge, the  $\text{Cp}^*\text{AsS}_2^{2-}$  anion is unknown so far.

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**Figure 1.** Solid-state structure of **1**. Hydrogen atoms are omitted for clarity.



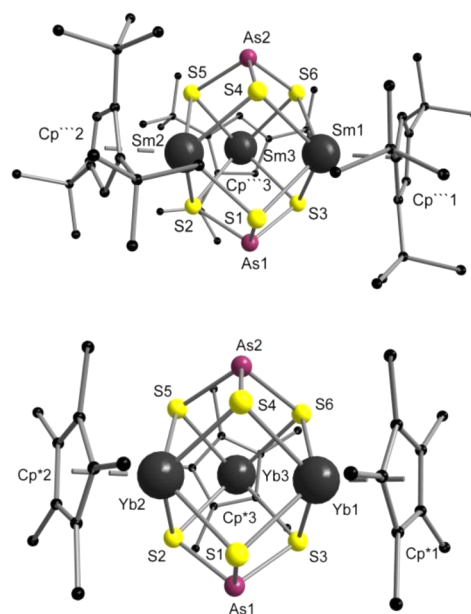
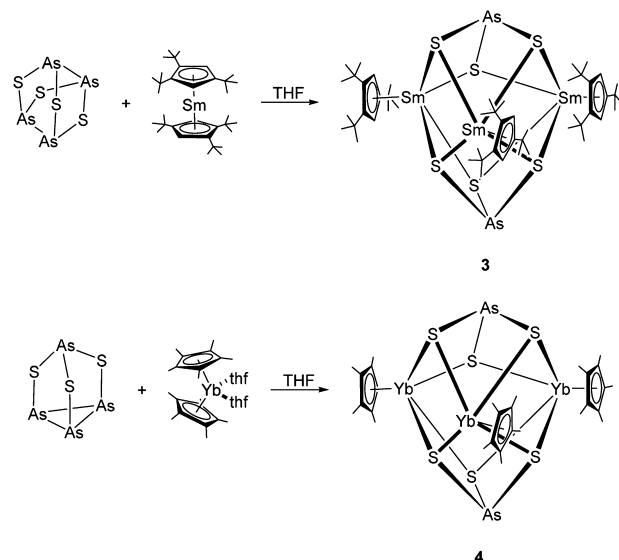
**Figure 2.** Solid-state structure of **2**. Hydrogen atoms are omitted for clarity.

Compound **2** is a trimetallic cluster (Figure 2), which features in the center a novel  $\text{As}_2\text{S}_4^{4-}$  bridge (S1,S2–As1–As2–S3,S4). The  $\text{As}_2\text{S}_4^{4-}$  bridge binds to three Yb atoms. In comparison to  $\text{As}_4\text{S}_4$  (2.566(1) Å) and  $[\text{Cp}^{\text{Et}}\text{Co}(\text{CO})\text{As}_4\text{S}_4]$  ( $\text{Cp}^{\text{Et}} = \text{Me}_4\text{EtC}_5$ ) (2.519(6) Å),<sup>25,26</sup> the As–As bond in **2** is shortened (As1–As2 2.487(2) Å). As observed for **1**, one  $\text{Cp}^*\text{AsS}_2^{2-}$  anion is formed due to the transfer of one  $\text{Cp}^*$  ligand. Both anions of compound **2** are unknown in coordination chemistry. Neither the  $\text{Cp}^*\text{AsS}_2^{2-}$  nor the  $\text{As}_2\text{S}_4^{4-}$  anion have been used as ligands so far.

Although similar reaction conditions were chosen for the synthesis of **1** and **2**, there are significant differences in the formation of both compounds. These differences are caused by the different redox potentials of Sm(II) and Yb(II).<sup>27</sup> However, in both compounds, we observe the coordination of the  $\text{Cp}^*\text{AsS}_2^{2-}$  anion to the lanthanide, which prevents, due to the low number of coordinating sulfur atoms, the formation of a closed cage species. To avoid this coordination for obtaining closed cage compounds, different strategies were tried. As it has been shown previously that the tendency for cyclopentadienyl (Cp) transfer depends on the steric demand of the ligand,<sup>28</sup> we tried to synthesize a closed cage species by increasing the steric bulk of the Cp ligands. For Sm this proved to be successful when using the more sterically demanding ligand  $\text{Cp}^{\text{III}}$  (1,2,4-*t*-Bu)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>). However, for Yb a different  $\text{As}_x\text{S}_y$  source ( $\text{As}_4\text{S}_3$ ) had to be applied. These strategies were individually adapted for each metal.

The reaction of  $[\text{Cp}^{\text{III}}_2\text{Sm}]$  with  $\text{As}_4\text{S}_4$  at room temperature in THF resulted in the formation of the highly symmetric trinuclear 11-vertex closed cage compound  $[(\text{Cp}^{\text{III}}\text{Sm})_3(\text{AsS}_3)_2]$  (**3**) (Scheme 2). Compound **3** forms a cage, which consists of two  $\text{AsS}_3^{3-}$  anions and three  $\{\text{Cp}^{\text{III}}\text{Sm}\}^{2+}$  cations (Figure 3, top). Both  $\text{AsS}_3^{3-}$  anions coordinate through each sulfur atom

**Scheme 2.** Synthesis of **3** and **4**



**Figure 3.** Solid-state structure of **3** (top) and **4** (bottom).

to a different samarium atom of the  $\{\text{Cp}^{\text{III}}\text{Sm}\}^{2+}$  units. The As–S bond distances range from 2.246(2) to 2.266(1) Å and thus are slightly elongated compared with  $[(\text{tepa})_2\text{La}_2(\text{AsS}_3)_2]$  (tepa = tetraethylenepentaamine) (2.227(1)–2.249(1) Å).<sup>14</sup> The Sm–As bond distances are in the range of **1**. Eleven-vertex cages are very rare but are found, for example, in  $\text{B}_{11}\text{H}_{11}^{2-}$ .<sup>29</sup> The Sm atoms are five-coordinate and a four-legged piano stool polyhedron is formed.

$\text{Sm}^{3+}$  complexes exhibit a characteristic absorption pattern in the NIR spectrum even in the presence of a strong visible absorption.<sup>30,31</sup> The spectra obtained for compound **1** and **3** show spectral patterns that are comparable to  $\text{Sm}^{3+}/\text{POCl}_3/\text{ZrCl}_4$ <sup>32</sup> and  $\text{Sm}^{3+}/\text{SeOCl}_2/\text{SnCl}_4$ .<sup>33</sup> The observed bands at 9232, 7801, 6698, and 6365  $\text{cm}^{-1}$  for **1** are assigned to the transitions of the states  ${}^6\text{F}_{9/2}$ ,  ${}^6\text{F}_{7/2}$ ,  ${}^6\text{F}_{3/2}$ , and  ${}^6\text{F}_{1/2}$ . Absorption bands at 9293, 7842, and 6529  $\text{cm}^{-1}$  for **3** can be assigned to transitions from  ${}^6\text{F}_{9/2}$ ,  ${}^6\text{F}_{7/2}$ , and  ${}^6\text{F}_{3/2}$  states (Figure S4, S5).

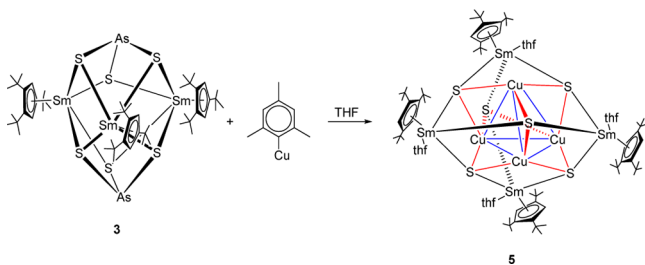
The reaction of  $[\text{Cp}^{\text{III}}\text{Yb}]$  with  $\text{As}_4\text{S}_4$  under the same conditions as used for the synthesis of **3** resulted in the formation of only a few crystals of  $[(\text{Cp}^{\text{III}}\text{Yb})_3(\text{AsS}_3)_2]$ , which could not be reproduced. As an alternative approach for the synthesis of a Yb/As/S cage related to **3**, we treated  $[\text{Cp}^{\text{III}}\text{Yb}(\text{thf})_2]$  with dimorphite ( $\text{As}_4\text{S}_3$ ) at room temperature in THF to obtain  $[(\text{Cp}^{\text{III}}\text{Yb})_3(\text{AsS}_3)_2]$  (**4**) (Scheme 2) in low yields. The core structure of the 11-vertex cage of compound **4** is closely related to **3** (Figure 3, bottom). The moderate to low yields of **1–4** are based on single crystalline material, which could be obtained reproducibly. As a result of the non-stoichiometric reactions, other byproducts could have been formed but a nonambiguous determination of their composition was not possible.

Since some near-infrared photoluminescence (NIR-PL) might be expected for the Yb compounds **2** and **4**, the corresponding PL measurements have been performed. At 17 K, both compounds show relatively weak, structured emission bands at  $\sim 1030$  nm (Figures S1, S2). This NIR emission corresponds to a  ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$  transition within the Yb(III) ions. The PL decays on the time scale of hundreds of nanoseconds (Figure S3), which indicates effective radiationless relaxation channels. The emission intensity decreases significantly upon raising the temperature.

The closed cage compounds **3** and **4** seem to be suitable starting materials for the synthesis of the desired heterometallic 3d/4f clusters. Derivatization of an isolated f-element cluster to a heterometallic system has not been reported, although the exchange of mercury in  $[(\text{py})_3\text{Eu}(\mu_2\text{-SPh})_2(\mu_3\text{-SPh})\text{Hg}(\text{SPh}))_2]$  by Zn or Cd has been shown.<sup>7</sup>

The coordination of copper halides to transition metal phosphides or polyphosphides is well-established.<sup>34,35</sup> In contrast, the coordination chemistry of copper halides or more general metal halides with transition metal As/S compounds is rare, e.g., the reactions of  $[(\text{Cp}^{\text{III}}\text{Mo})_2\text{As}_2\text{S}_3]$  with Cu(I) halides resulted in the formation of the one-dimensional polymers  $[(\text{Cp}^{\text{III}}\text{Mo})_2\text{As}_2\text{S}_3(\text{CuX})_2]_n$  ( $X = \text{Cl}, \text{Br}$ ) and in  $[(\text{Cp}^{\text{III}}\text{Mo})_2\text{As}_2\text{S}_3]_3(\text{CuI})_7$ . We chose  $[\text{CuMes}]$  ( $\text{Mes} = 2,4,6\text{-trimethylphenyl}$ ) as a reactive and soluble Cu(I) source.<sup>36</sup> The reaction of **3** with  $[\text{CuMes}]$  afforded the Sm/S/Cu cluster  $[(\text{Cp}^{\text{III}}\text{Sm}(\text{thf}))_4\text{Cu}_4\text{S}_6]$  (**5**), in which all arsenic atoms are lost (Scheme 3, Figure 4). The center of **5** consists of a  $\text{Cu}_4\text{S}_6^{8-}$  subcluster, in which the Cu atoms are arranged in a tetrahedral fashion and the S atoms in an octahedral scaffold (blue polyhedron in Figure 5). Alternatively, the endohedral cluster can be described as  $[\text{Cu}_4@(\text{Cp}^{\text{III}}\text{Sm}(\text{thf}))_4\text{S}_6]$ , in which a  $\text{Cu}_4$  tetrahedron (gray colored polyhedron in Figures 4 and 5) is encapsulated by the samarium sulfido cluster

### Scheme 3. Synthesis of **5**<sup>a</sup>



<sup>a</sup>The  $\text{Cu}_4$  tetrahedron is colored in blue. The  $\text{S}_6$  octahedron is colored in red.

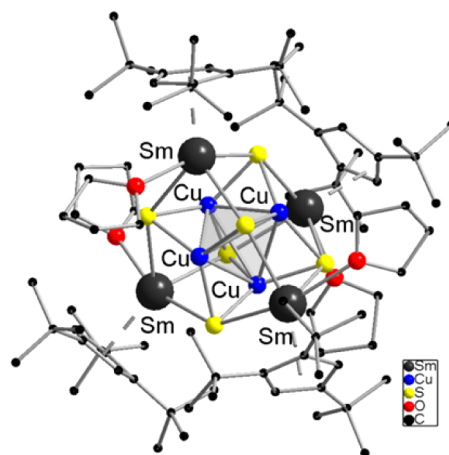


Figure 4. Solid-state structure of **5**, highlighting the endohedral  $\text{Cu}_4$  tetrahedron.

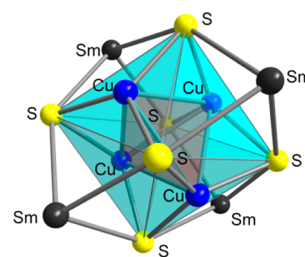


Figure 5. Central core of the solid-state structure of **5** showing the  $\text{Cu}_4$  tetrahedron (dark) and the  $\text{S}_6$  octahedron (blue), which is capped by four Sm atoms.

$\{(\text{Cp}^{\text{III}}\text{Sm}(\text{thf}))_4\text{S}_6\}$ . The  $\text{Cu}_4\text{S}_6^{8-}$  structural motif (Figure 5) has been described previously in  $[\text{Li}(15\text{-crown-5})(\text{thf})_2][\text{Cu}_4(\text{SPh})_6]$ <sup>37</sup> and  $[\text{Ph}_4\text{P}]_2[\text{Cu}_4(\text{SPh})_6]$ .<sup>38</sup> The observed Cu–S bond distances (2.240(3)–2.279(3) Å, av. 2.260 Å) are slightly shorter than in  $[\text{Li}(15\text{-crown-5})(\text{thf})_2][\text{Cu}_4(\text{SPh})_6]$  (av. 2.283 Å). The Cu–Cu distances range from 2.792(2) to 2.859(2) Å and thus are slightly longer than the Cu–Cu distances in  $[\text{Ph}_4\text{P}]_2[\text{Cu}_4(\text{SPh})_6]$  (av. 2.76 Å) and  $[\text{Li}(15\text{-crown-5})(\text{thf})_2][\text{Cu}_4(\text{SPh})_6]$  (av. 2.730 Å).<sup>37,38</sup> The outer shell of **5** is a  $\text{Sm}_4$  tetrahedron, in which the Sm atoms are capping the faces of the  $\text{Cu}_4$  tetrahedron. Each Sm atom binds to three sulfur atoms of the inner  $\text{Cu}_4\text{S}_6^{8-}$  subcluster. Furthermore, one molecule of THF and the  $\text{Cp}^{\text{III}}$  ring complete the coordination sphere. The bonding parameters of the Sm atoms are in the expected range. The oxidation state of the Sm atoms was unambiguously determined by NIR. The observed bands at 9288, 7991, 7338, and 6677  $\text{cm}^{-1}$  are assigned to the transition of the states  ${}^6\text{F}_{9/2}$ ,  ${}^6\text{F}_{7/2}$ ,  ${}^6\text{F}_{5/2}$ , and  ${}^6\text{F}_{3/2}$  (Figure S6). Although the structural pattern of **5** has so far not been described, it is known that Ln(III) carborane clusters<sup>39–41</sup> can incorporate other elements such as a  $\text{Li}_3\text{O}$  core.<sup>42,43</sup> Compound **5** has some unique properties and is a rare example of cluster derivatization. It is also the first f-element compound in which a transition metal chalcogenide cluster is encapsulated by f-elements.

In summary, we have prepared open and closed core lanthanide As/S clusters by reacting metallocenes of divalent Sm and Yb with the well-known main group cage compounds  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$ . In the open clusters, we observe a transfer of the  $\text{Cp}^{\text{III}}$  ligand, which results in the formation of a unique  $\text{Cp}^{\text{III}}\text{AsS}_2^{2-}$  anion. Furthermore, the novel  $\text{As}_2\text{S}_4^{4-}$  anion was

also formed. The closed Sm cluster **3** was treated with [CuMes] to give the unique Sm/S/Cu cluster **5**, in which the Sm atoms encapsulate a classical Cu<sub>4</sub>S<sub>6</sub><sup>8-</sup> cluster core.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Synthesis and characterization including cif files. Additional luminescence data, NIR and Raman data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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