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Short Note

Bis(μ -iodo)-tetrakis(*O*-methyl *N*-phenylthiocarbamate)-tetraiodo-dibismuth

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Abstract: In order to investigate the coordination chemistry of *O*-alkyl *N*-aryl thiocarbamate ligands, BiI₃ was reacted with two equivalents of MeOC(=S)N(H)Ph in MeCN solution to afford the dinuclear title compound complexes $[\{I_2Bi(\mu_2-I)_2BiI_2\}\{\kappa^1\text{-MeOC(=S)N(H)Ph}\}_4]$ **1**. Compound **1** was characterized by IR, UV and NMR spectroscopy, the formation of a dinuclear framework is ascertained by a single-crystal X-ray diffraction study performed at 100 K.

Keywords: bismuth triiodide; thiocarbamate; thione; crystal structure; hirshfeld analysis



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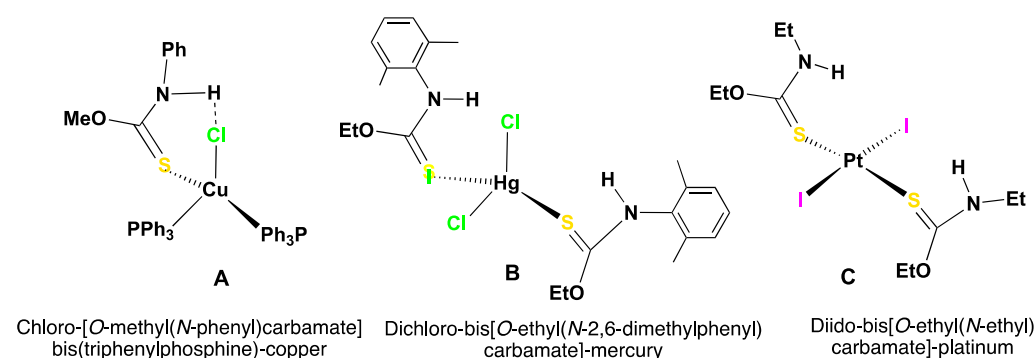
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1. Introduction

Thiocarbamates, also called thiocarbamides of general formula ROC(=S)N(H)R', play not only a role in organic chemistry as building blocks for further transformations, but found also application in various domains such biological and pharmacological activity or catalysis [1–5]. Furthermore, they have attracted the attention of coordination chemists, since the soft C=S thione function (according Pearson's HSAB principle) [6] readily coordinates to a wide range of transition metal complexes giving complexes with Cu(I), Ag(I), Au(I), Pd(II), Rh(III), etc. Some crystallographically characterized complexes ligated by *O*-alkyl *N*-aryl and *O*-alkyl *N*-alkyl thiocarbamates are presented in Scheme 1 [7–9].



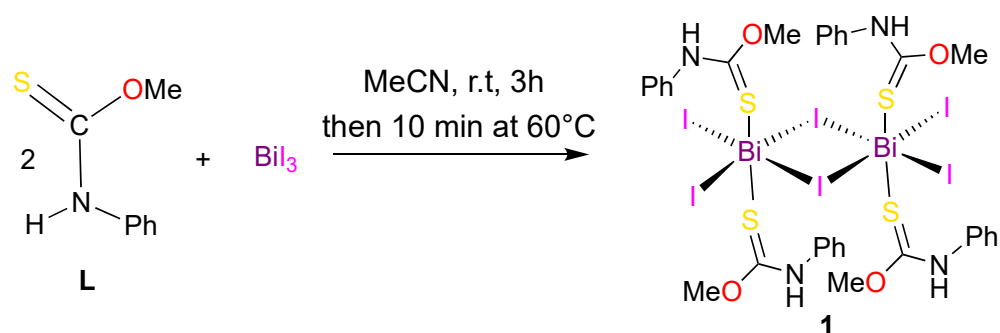
Scheme 1. Examples of some *O*-alkyl *N*-aryl(or alkyl) thiocarbamate complexes.

Surprisingly, despite the growing number of transition metal complexes bearing such type of thione ligands, there is a lack of *p* block metal complexes coordinated with *O*-alkyl *N*-aryl thiocarbamates. Since BiX₃ complexes with thione-type ligand are literature-known (see below) and may even display a biological activity [10–12], we reacted BiI₃ with *O*-methyl *N*-phenyl thiocarbamate and describe therein the crystal structure of the isolated

complex. This research is a continuation of our investigations on the coordination chemistry of thione-type ligand on diverse metal centers [13–16].

2. Results

The hitherto unknown complex $[\text{I}_2\text{Bi}(\mu_2\text{-I})_2\text{BiI}_2]\{\kappa^1\text{-MeOC(=S)N(H)Ph}\}_4$ **1** was obtained by addition of two equivalents of *O*-methyl *N*-phenyl thiocarbamate **L** to a suspension of BiI_3 in MeCN (Scheme 2). After stirring for 3 h followed by short heating to 60°C , a deep orange solution formed. Slow evaporation of the solvent yielded dark-orange air-stable crystals, whose IR-ATR spectrum confirmed the complexation of **L** on Bi(III). According to the elemental analysis, two **L** molecules are attached per BiI_3 motif.



Scheme 2. Synthesis of the title compound **1**.

The $^1\text{H-NMR}$ recorded in d_6 -acetone reveals a broad hump at δ 4.04 for the methoxy group, whereas the aryl signals are well resolved. Furthermore, two distinct N-H resonances are found at δ 9.32 and 10.03. A further indication of dynamic processes occurring in solution is provided by the $^1\text{H NMR}$ spectrum of **1** recorded at 323 K, in which the OMe resonance at δ 4.05 is considerably sharpened (Figure 1). There is also a noticeable high-field shift of the N-H signals. This dynamic behavior has not been investigated in more detail.

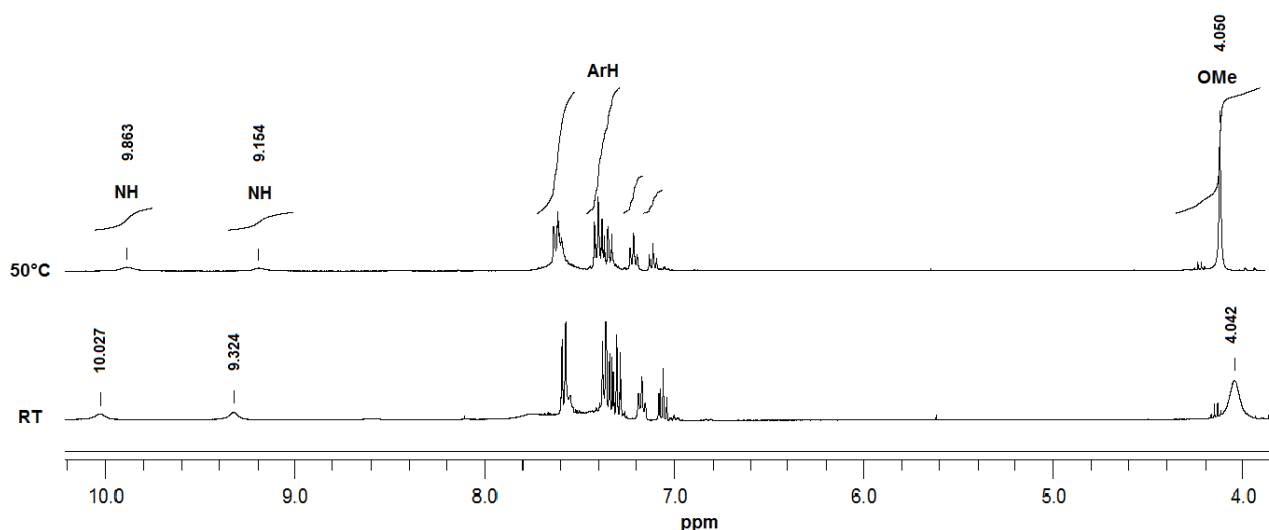


Figure 1. $^1\text{H NMR}$ spectra (400 MHz, acetone- d_6) of compound **1** at RT and 50°C .

Since according to a literature survey, no Bi(III) complexes ligated by thiocarbamates have been crystallographically characterized yet, we examined the product crystallizing in the triclinic space group $P\bar{1}$ by an X-ray diffraction study performed at 100 K. As shown in Figure 2, a dinuclear species has formed, in which the two crystallographically different coordinated Bi(III) centers are linked mutually through two μ_2 -bridging I3 and I4 iodido ligands. The Bi...Bi separation of 4.720 Å excludes any intermetallic interaction. The

octahedral coordination sphere around each Bi atom is completed by two terminal iodide ligands with a mean Bi–I_{term} distance of 2.924(3) Å and two *trans*-arranged thiocarbamate ligands. Each of the four L molecules is crystallographically different with Bi–S bond lengths varying from 2.8290(10) to 2.8952(11) Å. The mean C=S bond is slightly elongated with respect to that of non-ligated MeOC(=S)N(H)Ph (1.701(4) vs. 1.6708(11) Å) [17]. The two bridging I2 and I4 atoms are quite symmetrically bridging, the mean Bi–I_{bridg} bond distance of 3.225(3) Å being far longer than the Bi–I_{term} one.

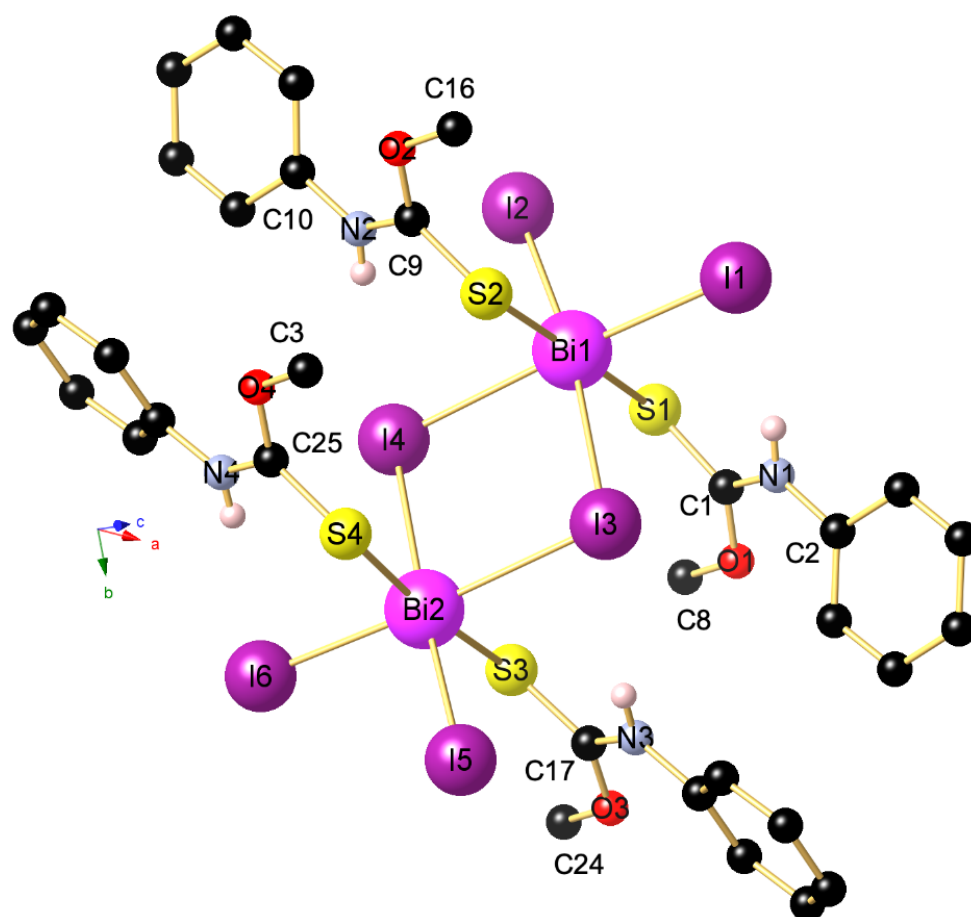


Figure 2. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg) of **1**. Bi1–I1 2.9650(3), Bi1–I2 2.8848(3), Bi1–I3 3.2832(3), Bi1–I4 3.2010(3), Bi1–S1 2.8309(11), Bi1–S2 2.8733(12), Bi2–I3 3.2040(3), Bi2–I4 3.2512(3), Bi2–I5 2.8941(3), Bi2–I5 2.8941(3), Bi2–I6 2.9507(3), Bi2–S3 2.8952(11), Bi2–S4 2.8290(10), S1–C1 1.707(4), O1–C1 1.317(5), O1–C8 1.453(5), O2–C9 1.314(5), O3–C17 1.320(5), N1–C1 1.323(5), N1–C2 1.422(5); I1–Bi1–I3 88.884(8), I1–Bi1–I4 174.132(9), I2–Bi1–I1 99.236(9), I2–Bi1–I3 171.720(8), I2–Bi1–I4 85.776(9), I4–Bi1–I3 86.031(7), S1–Bi1–I1 91.54(2), S1–Bi1–I2 84.53(2), S1–Bi1–S2 178.91(3), S2–Bi1–I1 89.05(2), I3–Bi2–I4 86.520(7), I5–Bi2–I3 91.078(8), I5–Bi2–I6 95.627(9), S3–Bi2–I3 86.14(2), S4–Bi2–I3 90.37(2), O1–C1–S1 123.1(3), O1–C1–N1 115.3(3), N1–C1–S1 121.6(3), C3–C2–N1 115.9(3), C7–C2–N1 124.1(3), C7–C2–C3 120.0(3).

In the packing, several secondary weak interactions are present such as between atoms I1ⁱ–H22 (3.081 Å), C14ⁱ–H24A (2.757 Å), H5–H8Bⁱ (2.293 Å) and I3ⁱ–H29 (3.128 Å). Furthermore, as shown in Figure 3, loose intramolecular S···H and N···H contacts occur.

These interactions have also been assessed by means of a Hirshfeld surface analysis using the *CrystalExplorer17* software (Figure 4) [18,19]. The Hirshfeld surface was mapped over d_{norm} in the range from -0.0743 to -1.2577 (arbitrary units). The corresponding fingerprints plots are presented in the Supporting Material.

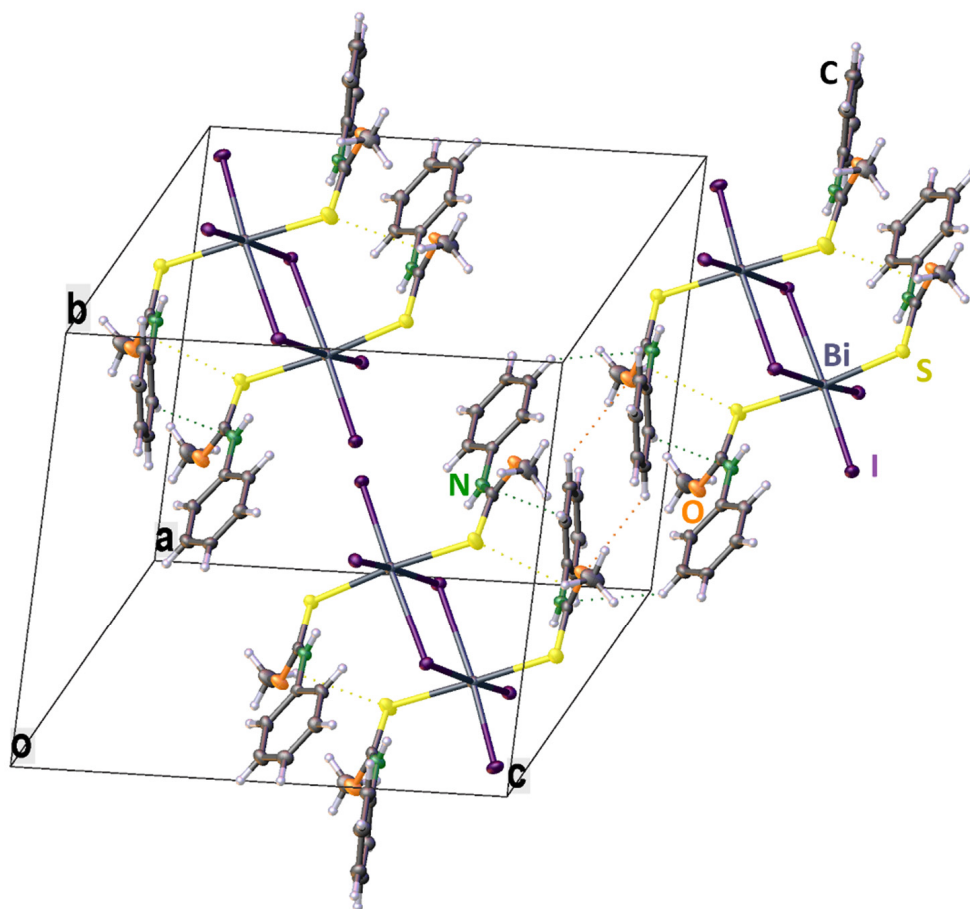


Figure 3. OLEX-generated view of the unit cell of **1** indicating several weak intra- and intermolecular interactions by dotted lines ($S2\cdots H32C$ 2.98094(15) Å, $S3\cdots H8A$ 3.05129(15) Å and $N3\cdots H7$ 2.90335(11) Å).

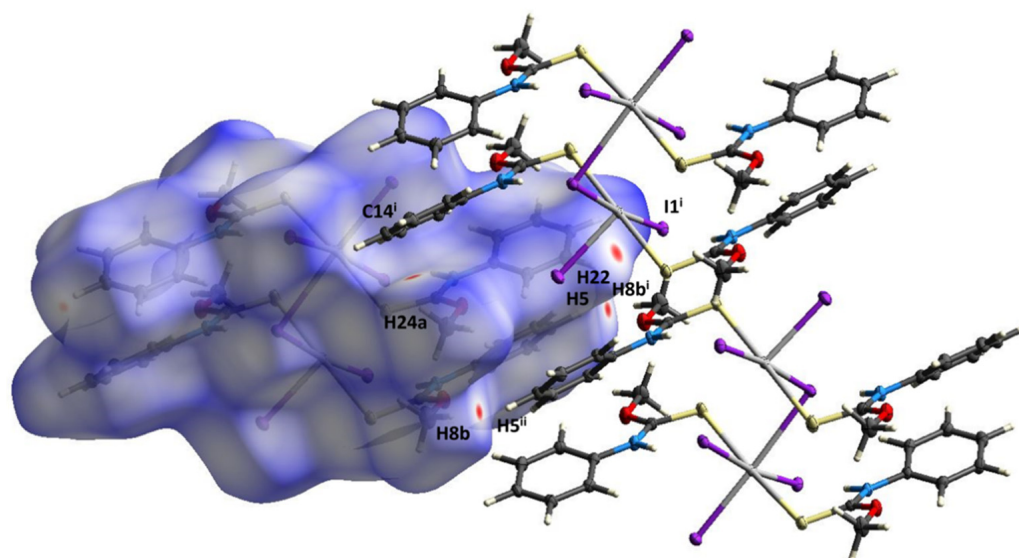


Figure 4. View of the Hirshfeld surface of compound **1** revealing some loose contacts in the crystal structure. Molecule *i* was generated by the symmetry operation $1+x, +y, +z$ and molecule *ii* by the symmetry operation $1-x, 1-y, 2-z$.

3. Discussion

A survey of the Cambridge Structural Database (CSD) reveals that in addition to several mononuclear tris(thione) complexes of type $[X_3Bi(\text{thione})_3]$ such as tris(2-benzylidenehydrazine-1-carbothioamide)-tribromo-bismuth (refcode QASQAG) or tris(1,3-diazinane-2-thione)-triiodo-bismuth (refcode BOSDAR) [12], there are some other examples of dinuclear complexes with a $[(X_2Bi(\mu_2-X)_2BiX_2)(\text{thione})_4]$ motif. One example is tetrakis(1-allyl-3-(2-pyridyl)-thiourea-S)-bis(μ_2 -chloro)-tetrachloro-dibismuth bismuth (refcode ALPBIA), but in this compound the thione ligands on each $BiCl_3$ unit are *cis*-arranged and not in *trans*-position as in compound **1** [20]. An example for a complex with a $[(Cl_2Bi(\mu_2-Cl)_2BiCl_2)]$ core bearing four *trans*-arranged thione ligands is bis(μ_2 -chloro)-tetrachloro-tetrakis(2-[1-(3-ethylpyrazin-2-yl)ethylidene]-*N*-methylhydrazine-1-carbothioamide)-di-bismuth (refcode KOTNAL). However, the only representative of a iodido complex $[-25]trans-[I_2Bi(\mu_2-I)_2BiI_2](\text{thione})_4$ is bis(μ_2 -iodo)-tetrakis(5-methoxy-1,3-dihydro-2*H*-benzimidazole-2-thione)-tetraiodo-di-bismuth (refcode MADZAW), recently described by the research group of Ozturk et al. [10]. Maybe the fluxional behavior revealed by NMR spectroscopy is due to a *trans*-*cis* isomerization occurring in solution, involving dissociation and re-coordination of L (facilitated by the polar solvent acetone). Alternatively, the four *O*-alkyl *N*-aryl thiocarbamate ligands may adopt somewhat different arrangements at ambient temperature due to N-H... contacts and are getting more equivalent on the NMR time-scale when rising the temperature. Formation of weak hydrogen bonding between the N-H groups of L and the O=C function of acetone used as solvent may also be taken in account.

4. Experimental

To a slurry of BiI_3 (294.8 mg, 0.5 mmol) in 10 mL of acetonitrile, *O*-methyl *N*-phenylthiocarbamate L (167.2 mg, 1 mmol) was added in several portions. The reaction was first stirred at room temperature for 3h, and then heated to 60 °C for 10 min. After reaching ambient temperature, the solvent was allowed to evaporate partially. After 2 days, dark orange crystals of **1** were formed and then collected by filtration. Yield: 79%. Anal. Calc. for $C_{32}H_{36}Bi_2I_6N_4O_4S_4$ (M.W = 1848.3 g.mol⁻¹): C, 20.79; H, 1.96; N, 3.03; S, 6.93%. Found: C, 20.73; H, 1.94; N, 2.99; S, 6.89%. IR-ATR: 1230 ν (C=S), 1483 ν (C-N), 1548 ν (N-H), 3281 ν (N-H bonded) cm⁻¹. ¹H NMR (acetone-*d*₆) at 298 K: δ 4.05 (*s*, br, 3H, OCH₃), 7.04–7.59 (*m*, 5H, aryl-H), 9.32 and 10.03 (2*s*, br, 1H, NH) ppm. UV-vis (acetone) [λ_{max} nm (ϵ M⁻¹ cm⁻¹): 247 (30100), 275 (25900), 375 (4100), 465 (3500).

Crystal data for $C_{32}H_{36}Bi_2I_6N_4O_4S_4$, $M = 1848.25$ g.mol⁻¹, dark orange crystals, crystal size 0.15 × 0.113 × 0.073 mm³, triclinic, space group $P\bar{1}$, $a = 12.8215(6)$ Å, $b = 13.5748(6)$ Å, $c = 15.1534(8)$ Å, $\alpha = 85.829^\circ$ (2), $\beta = 73.537(2)^\circ$, $\gamma = 68.789(2)^\circ$, $V = 2356.7(2)$ Å³, $Z = 2$, $D_{calc} = 2.605$ g/cm³, $T = 100$ K, $R_1 = 0.0286$, $Rw_2 = 0.0470$ for 104,055 reflections with $I \geq 2\sigma(I)$ and 14,441 independent reflections. Largest diff. peak/hole/e Å⁻³ 1.48/-1.51. Data were collected using graphite-monochromated MoK α radiation $\lambda = 0.71073$ Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2165826. (Supplementary Materials). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXL,2015 [21,22]).

5. Conclusions

We have crystallographically evidenced that not only transition metals, but also p-block salts such as BiI_3 , can constitute interesting targets for the coordination of thiocarbamate ligands via their thione function.

Supplementary Materials: The following supporting information can be downloaded, CIF file, Check-CIF report, UV-Vis spectrum and Hirshfeld fingerprint plot.

Author Contributions: W.A. prepared the compound; C.S. and A.S. collected the X-ray data and solved the structure; A.K. and M.K. designed the study and analyzed the data and M.K. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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

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