



## Synthesis, Crystal Structure and Characterization of a new Polyoxovanadate $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$

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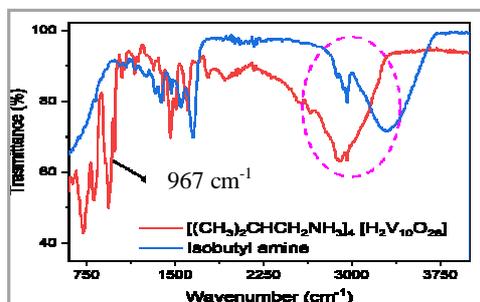
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### ABSTRACT

Polyoxovanadates (POVs), formed by vanadium and oxygen, possess a wide variety of applications in the field of chemical-, physical- and biological sciences as they are capable of exhibiting various structural motifs, like a baskets, cages, belts, barrels, etc., from different vanadium polyhedra. Among POVs, decavanadates  $[\text{H}_n\text{V}_{10}\text{O}_{28}]^{(6-n)-}$  are extensively studied and structurally characterized because of its potential uses in materials chemistry, industrial chemistry and electrochemistry; moreover, it shows a vast biological activity. Here we report a structurally characterized decavanadate compound,  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  (1). The title compound has been prepared by one-pot aqueous (acidic) synthesis involving  $\text{V}_2\text{O}_5$ ,  $\text{HCl}$ , isobutylamine, resulting in single crystals of compound 1. Compound 1 has been characterized by FTIR, TGA, Raman, FESEM-EDX microscopy and PXRD studies. It is unambiguously characterized by single-crystal X-ray diffraction analysis (Figure 1). The title compound  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  crystallizes in the centrosymmetric monoclinic  $P2(1)/c$  space group. In the crystal structure, the asymmetric unit consists of half of the cluster unit  $[\text{V}_5\text{O}_{14}]^{3-}$  anion and two isobutylammonium cations,  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]^+$ . Thus there are four  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]^+$  cations and one full decavanadate cluster anion present per formula unit. We have added two protons to the decavanadate cluster to counterbalance the charge of the cluster anion. The decavanadate anion is made up of ten edge-sharing  $[\text{VO}_6]$  octahedra. The V-O bond length and O-V-O bond angles are in agreement with the reported data. In the crystal structure, the isobutyl ammonium cations are hydrogen bonded to the decavanadate cluster via  $\text{N-H}\cdots\text{O}$  bonds.

### Graphical Abstract:



FTIR spectra of compounds 1 and Isobutylamine

**Keywords:** Polyoxovanadates, Vanadium polyhedra, Decavanadate, Single-Crystal X-ray diffraction.

## INTRODUCTION

Polyoxometalates (POMs) represent a fascinating class of inorganic compounds that have captured the attention of chemists for their unique structural diversity [1-3] and wide-ranging applications in catalysis [4, 5], medicine [6, 7], materials sciences [8], electrochemistry and redox processes [9], photochemistry [10] and magnetism [11]. Among the diverse family of POMs, the chemistry of polyoxovanadates (POVs), especially decavanadates, stands out as an intriguing subset due to their distinctive molecular architecture and intriguing properties. Decavanadate  $[H_nV_{10}O_{28}]^{(6-n)-}$  is easily isolated from acidic medium (pH 3 to 5) [12], structurally characterized, and extensively studied due to their applications in biological activities [13,14], material chemistry, industrial chemistry, electrochemistry, magnetochemistry, etc. [15]. Thus, the research community is attracted to decavanadate chemistry for its fascinating properties.

Decavanadate, an important building unit composed of ten vanadium atoms arranged in a particular structural motif, is used in the construction of inorganic-organic hybrid materials [16] and was first reported by Rossotti in 1956 on the basis of spectrophotometric and potentiometric measurements [17]. pH dependent studies of vanadium solutions were reported by Jander and Jahr in 1933. X-ray structure of decavanadate was reported by Evans in 1966 [18] which is made up of ten edge-sharing  $VO_6$  octahedra arrangement of these vanadium atoms, along with surrounding oxygen atoms, leads to unique properties that make decavanadates of interest in various fields, making them a subject of ongoing investigation and exploration in the scientific community [19-21].

In this work, we report a synthesis, Crystal structure, and characterization of a new polyoxovanadate  $[(CH_3)_2CHCH_2NH_3]_4[H_2V_{10}O_{28}]$  compound 1. The title compound has been prepared by one-pot aqueous (acidic) synthesis involving  $V_2O_5$ , HCl, and isobutylamine, resulting in single crystals of compound 1, Which has been characterized by FTIR, TGA, Raman, FESEM-EDX microscopy and PXRD studies and unambiguously characterized by single-crystal X-ray diffraction analysis.

## MATERIALS AND METHODS

All the chemicals are of analytical reagent grade and used as received from commercial sources without any further purification and deionized water is used to perform all the experiments.

### Experimental Section.

**Synthesis of  $[(CH_3)_2CHCH_2NH_3]_4[H_2V_{10}O_{28}]$ :** To a suspension of vanadium pentoxide (10 mmol, 1.81g, in 15 mL of water), isobutyl amine (6 mL) was added and the resultant mixture was stirred to dissolve completely. The pH of the resultant mixture is found to be 9.23 which were then adjusted to  $P^H$  3.56 using dilute HCl to get a clear dark orange solution. The obtained solution was filtered, and the filtrate was left for crystallization at room temperature. The orange shiny crystals were grown in the transparent filtrate within a week. Yield: 1.39 g.

**Physical Measurements:** Bruker D8-Advance diffractometer equipped with graphite-mono-chromated  $Cu K\alpha_1$  (1.5406 Å) and  $K\alpha_2$  (1.54439 Å) radiation was used to record the powder X-ray diffraction (PXRD) plots. FTIR spectra were collected on Bruker Tensor II equipped with a platinum attenuated total reflection (ATR) accessory. Raman spectra were obtained with a Wi-Tec alpha 300 AR laser confocal optical-microscope (T-LCM) facility equipped with a Peltier-cooled CCD detector using a 633 nm Argon ion laser. TGA-DSC study was performed in a nitrogen atmosphere in an  $Al_2O_3$  crucible at a heating rate of  $10^\circ C \text{ min}^{-1}$  using an SDT Q600 V20.9 Build 20 thermal analyzer. Field-emission scanning electron microscopy energy-dispersive X-ray spectroscopy (FESEM-EDS) analysis was performed with a Carl Zeiss model Ultra 55 microscope equipped with Oxford Instruments X-MaxN SDD (50 mm<sup>2</sup>) system operated with INCA software.

**Single-crystal X-ray diffraction:** A nascent single-crystal of  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  compound (1) was selected from the mother liquor and mounted on a glass fibre tip using lubricant grease for X-ray diffraction data collection at 100 K. The Rigaku Oxford XtalLAB Synergy diffractometer, equipped with a Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) graphite monochromatic X-ray beam source, was used for data collection; a crystal-to-detector distance of 40 mm was maintained. The collected data reduction was accomplished with AutoLab software. Empirical absorption corrections were accomplished with the SADABS program.<sup>45</sup> Structure solutions and full-matrix least-squares refinement were done by standard crystallographic software Olex2-1.3-ac4 embedded with SHELX 2018/1 package for the title compound [22, 23]. The crystallographic details and structure refinement parameters for compound 1 are listed in table 1.

**Table 1.** Crystal data and structure refinement parameters for compound 1

Parameter	Compound 1
Empirical formula	$\text{C}_{16}\text{H}_{38}\text{N}_4\text{O}_{28}\text{V}_{10}$
Formula weight	1243.6
T(K)/ $\lambda$ ( $\text{\AA}$ )	293 (2) K/ 0.71073
Crystal system, Space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.2556(5) $\text{\AA}$ b = 10.1818 (3) $\text{\AA}$ c = 16.2500(4) $\text{\AA}$ $\alpha = 90^\circ$ $\beta = 105.132(3)$ $\gamma = 90^\circ$
Volume	2117.15(12) $\text{\AA}^3$
Z, Density (calculated)	2, 1.891 mg/m <sup>3</sup>
Absorption coefficient (M)	2.189 mm <sup>-1</sup>
F (000)	1156
Reflections collected / unique	3559/4419 [R(int) = 0.0679]
Theta range for data collection	2.385 to 27.009 $^\circ$
Goodness-of-fit on F <sup>2</sup>	1.05

## RESULTS AND DISCUSSION

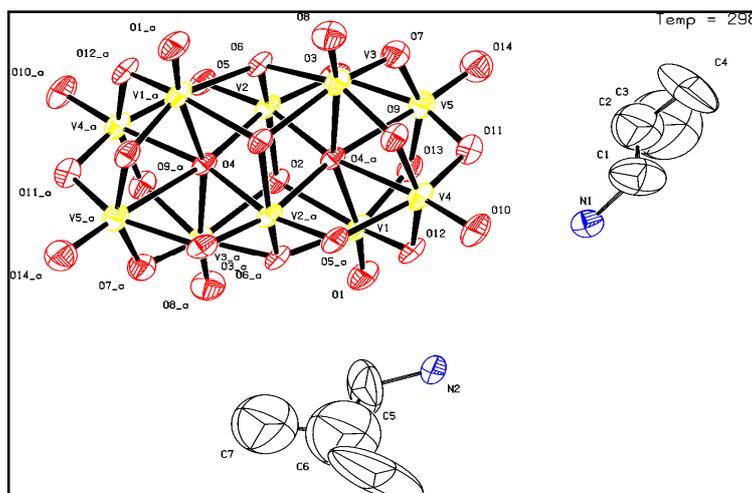
**Synthesis:** The orange shiny crystals were isolated in a one-pot wet synthesis by reacting vanadium pentoxide with isobutyl amine (see Experimental Section for detailed procedure). The isolated compound has been subjected to diverse characterization techniques, e.g., FT-IR-, Raman-, and TGA-DSC, besides its unambiguous characterization by single-crystal X-ray diffraction (SCXRD). The complete characterizations of compound 1 have been discussed as follows.

**SCXRD Analysis:** Compound 1 crystallizes in the centrosymmetric monoclinic P2(1)/c space group. The unit cell dimensions of compound 1 are given in table 1.

In the crystal structure (figure1) the asymmetric unit consists of half of the cluster unit  $[\text{V}_5\text{O}_{14}]^{3-}$  anion and two isobutylammonium cations,  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]^+$ . Thus there are four  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]^+$  cations and one full decavanadate cluster anion present per formula unit. We have added two protons to the decavanadate cluster to counterbalance the charge of the cluster anion [24]. The decavanadate anion is made up of ten edge sharing  $\{\text{VO}_6\}$  octahedra. The V-O bond length and O-V-O bond angles are in agreement with the reported data. In the crystal structure, the isobutyl ammonium cations are hydrogen bonded to the decavanadate cluster via N-H $\cdots$ O bonds. In view of the centrosymmetric nature of the decavanadate ion, the asymmetric unit of compound 1 is half of the formula unit, with the other half being symmetrically generated.

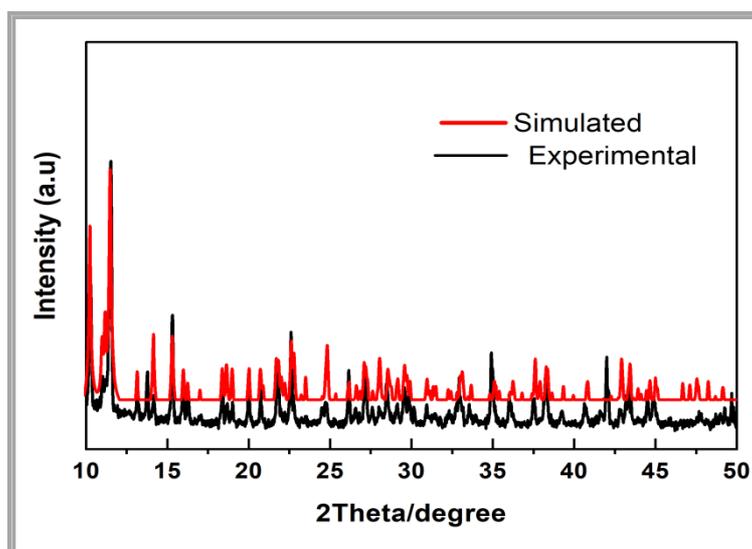
**Microscopy:** Field emission scanning electron microscopy (FESEM) energy-dispersive X-ray spectroscopy (EDS) analyses were carried out to probe the microscopic morphology and surface elemental composition of compound  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  (1). Figures 3a and b illustrate

the crystalline particle morphology of compound 1 in FESEM, which was collected in different magnifications. Figures 3c and d show the surface EDS elemental mapping plots of compound 1.



**Figure 1.** Single-crystal structure of compound 1 molecular structure with thermal-ellipsoid (50%) representation.

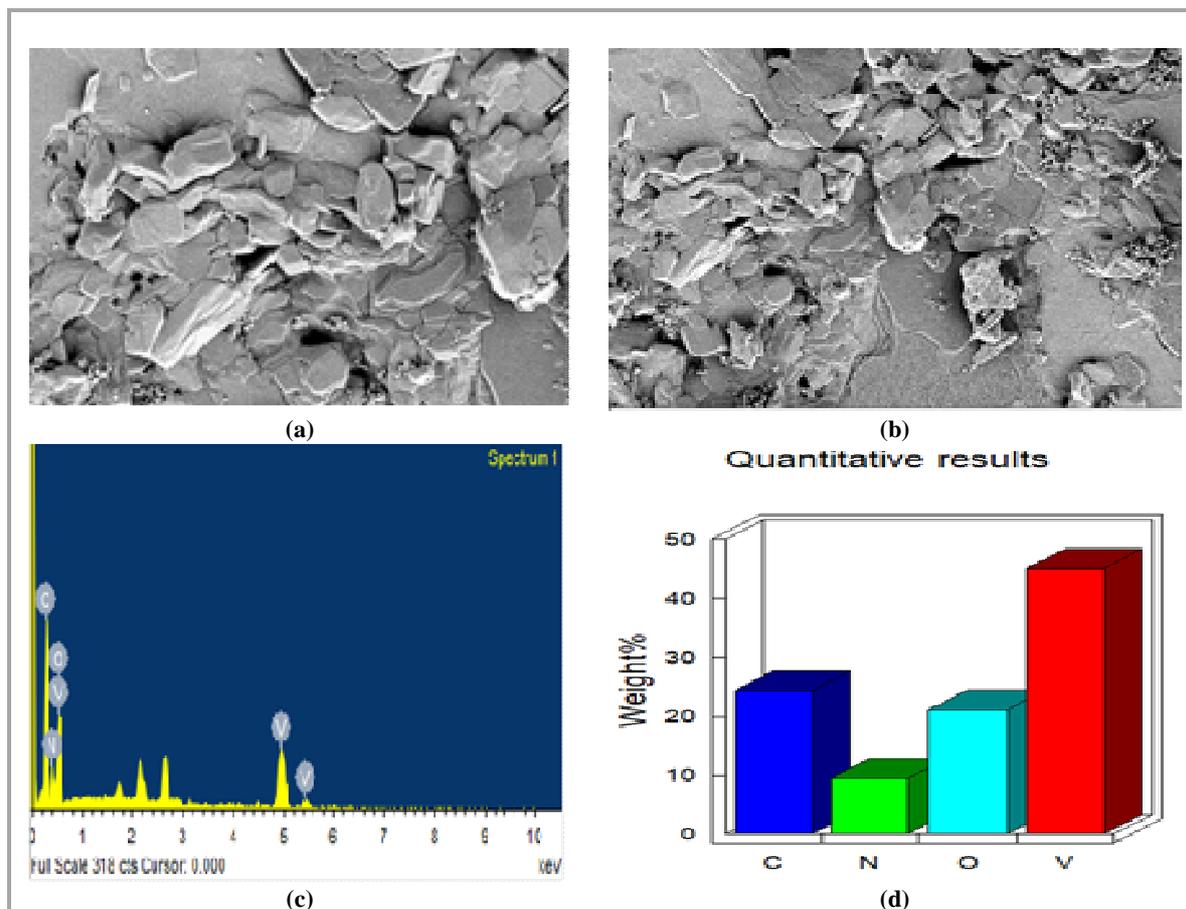
**PXRD Analysis:** The phase purity of compound 1 is confirmed by comparing its experimental powder X-ray diffraction pattern with the simulated pattern, generated from the SCXRD data file as shown in figure 2.



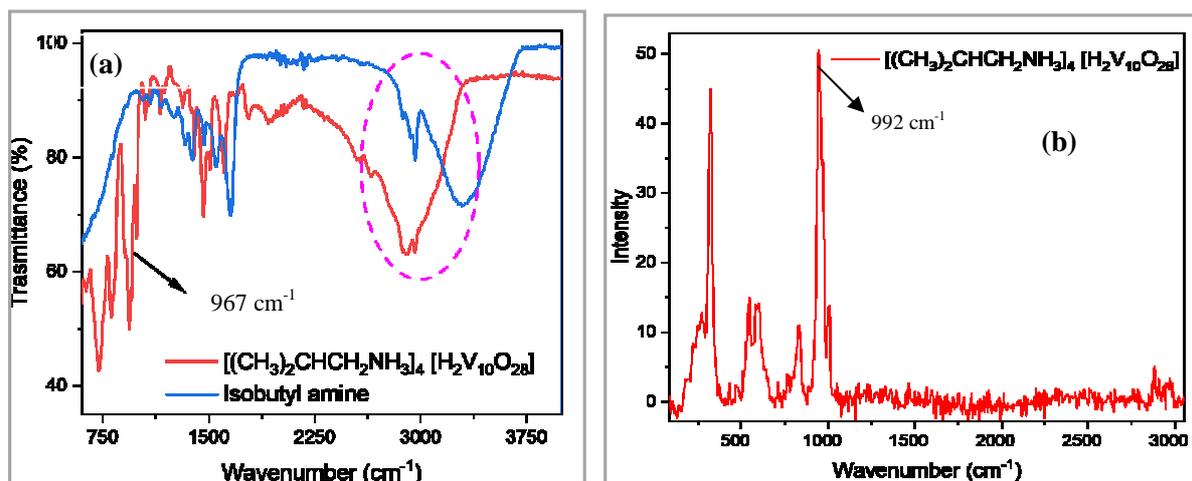
**Figure 2.** Powder X-ray diffraction patterns for compound 1 along with its simulated profile, generated from its single crystal X-ray data.

**Spectroscopy:** To understand better the behaviour and nature of compound 1, we have performed all the possible spectroscopic analyses of compound  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  (1). **FTIR** spectra of compound 1, as shown in figure 4 (a), several signals in the mid-IR region indicating the presence of organic cation. The bands at 967 and 941  $\text{cm}^{-1}$  are assigned to the stretching vibrations of the terminal V–O bonds, and the bands at 821 and 755  $\text{cm}^{-1}$  are assigned to the bridging anti-symmetric vibrations of V–O–V and the bands at 594 and 411  $\text{cm}^{-1}$  are due to the V–O–V symmetric vibrations. It is clearly shown in the IR spectra that the peaks at 3380  $\text{cm}^{-1}$  and 1650  $\text{cm}^{-1}$  in isobutylamine are which due to NH stretching and bending vibrations were shifted to lower frequency region i.e. 2950

$\text{cm}^{-1}$  and  $1460 \text{ cm}^{-1}$  in compound 1 thus conforming formation of compound 1 $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ .



**Figure 3:** (a, b) FESEM images of compound 1 recorded in different magnifications; (c, d.) EDS elemental mapping of compound 1.

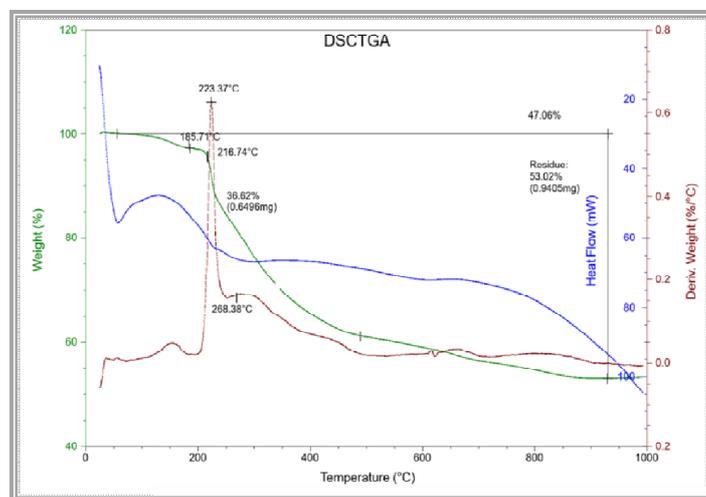


**Figure 4:** (a) FTIR spectra of compound 1 and Isobutylamine; (b) Raman spectra of compound 1.

Raman spectra of as-synthesized compound 1 were collected on solid samples and have been shown in figure 4b. The symmetric stretching vibration of the decavanadate unit is observed as an intense band

in the Raman spectrum at  $992\text{ cm}^{-1}$  and the strong signal at  $948\text{ cm}^{-1}$  can be attributed to the symmetric stretching vibration of V-O bonds.

The thermal study of compound 1 reveals that it is stable up to  $185^\circ\text{C}$  as evidenced by the TGA curve [figure 5](#) indicating the absence of any water molecules. DTA curve exhibits an endothermic and two exothermic signals by gradual weight loss.



**Figure 5.** TGA-DSC curves of compound 1.

## APPLICATION

Ployoxovanadates, especially Decavanadate, have been studied for various applications, including their catalytic activity in oxidation reactions, electrochemical properties in energy storage devices, and potential use in biomedical and environmental applications.

Its organic amine component enhances its solubility in organic solvents and facilitates its use in organic reactions and electrochemical systems. The decavanadate anion provides redox-active sites and catalytic centers, making it useful in various chemical transformations and energy storage applications.

Thus, the compound 1 decavanadate serves as an example of an organic amine-functionalized decavanadate with potential applications across multiple fields, including catalysis, electrochemistry, materials science, and environmental science.

## CONCLUSION

In conclusion, we have successfully synthesized compound 1  $[(\text{CH}_3)_2\text{CHCH}_2\text{NH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  in one pot synthesis. Compound 1 has been characterized by FTIR, TGA-DSC, Raman, FESEM-EDX microscopy and PXRD studies. The FTIR bands at  $967$  and  $941\text{ cm}^{-1}$  are assigned to the stretching vibrations of the terminal V-O bonds and the intense band in the Raman spectrum at  $992\text{ cm}^{-1}$  and the strong signal at  $948\text{ cm}^{-1}$  can be attributed to the symmetric stretching vibration of V-O bonds clearly confirms the formation of compound 1. The phase purity of the compound is confirmed by PXRD analysis. Finally, it is unambiguously characterized by single-crystal X-ray diffraction analysis. The title compound 1 crystallizes in the centrosymmetric monoclinic  $P2(1)/c$  space group. Thus, the synthesis, crystal structure, and characterization of as-synthesized decavanadate compound 1 aid advancement in fields such as catalysis, electrochemistry, materials science, and environmental

science. Continued research in this area promises to further expand our understanding of decavanadates and unlock their full potential for a wide range of practical applications.

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**Conflict of Interest Statement:** The authors declare that they have no conflict of interest

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