

New 12-Tungstophosphate-Based Organic-Inorganic Hybrid. Synthesis, Spectroscopic Characterization, X-Ray Determination and Thermal Behavior

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(Received 23 November 2007, Accepted 17 December 2007)

12-Tungstophosphate-based organic/inorganic hybrid, $[\text{HNMPA}]_3[\text{O}_{40}\text{PW}_{12}]\cdot 0.5\text{NMPA}\cdot 2\text{H}_2\text{O}$ (NMPA = N-methylpropionamide) was synthesized and characterized by IR, UV-Vis, ^1H , ^{13}C and ^{31}P NMR spectroscopies, elemental analysis, TGA, DTA and single crystal X-ray determination. Full decomposition of the hybrid leads to WO_3 powder was studied by IR, SEM and XRD.

Keywords: Organic/inorganic hybrid, Crystal structure, Keggin, WO_3

INTRODUCTION

Connection between new molecular and supramolecular structures on the basis of covalent bonds or non-covalent forces is one of the major challenges in crystal engineering, because the produced hybrid materials may exhibit cooperative properties of their different building blocks [1,2]. A remarkable area is the exploitation of polyoxometalates (POMs) as building blocks to construct the solid materials with organic substrates. Polyoxometalates are excellent molecular acceptors forming the hybrid materials with N, O, S-donor molecules [3-5]. These materials were extremely applied to catalysis, photochemistry, nano-material sciences and antibacterial application [6-9]. In the previous works we reported the structures of salt and hybrid materials based on 12-molybdophosphate [10-13]. In this study the investigation on a new 12-tungstophosphate-based organic-inorganic hybrid and its full decomposition to prepare WO_3 powder is reported.

EXPERIMENTAL

Chemicals and Apparatus

All chemicals were purchased commercially and used without further purification. ^1H , ^{13}C and ^{31}P NMR spectra were determined on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shift relative to 85% H_3PO_4 as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-PAPID apparatus. The thermal behavior was measured with PLSTA 1500 apparatus. UV-Vis spectra were recorded on a double-beam Shimadzu 2550 spectrophotometer. The morphology of WO_3 powder was studied by scanning electron microscopy (SEM, Philips XL30). Powder phase identification was performed by X-ray diffraction (XRD) obtained on Philips X-pert diffractometer using $\text{Cu K}\alpha$ line ($\lambda = 1.54056 \text{ \AA}$) radiation. X-ray structural analysis on single crystal of title compound was carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation.

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Synthesis of $[\text{HNMPA}]_3[\text{O}_{40}\text{PW}_{12}]\cdot 0.5\text{NMPA}\cdot 2\text{H}_2\text{O}$

The hybrid $[1-(\text{Methylamino})\text{propylidene}]$ oxoniumdodecatungstophosphate, N -methylpropionamidesolvate, hydrate (1/0.5/2) was synthesized as follows. A solution of N -methylpropionamide (0.358 g, 4.10 mmol) in HCl (10 ml, 1 M) was added dropwise to a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (2.360 g, 0.82 mmol) in H_2O (90 ml) and stirred 1.5 h. The solution was filtered and kept until the colorless crystals obtained. IR (KBr): $\tilde{\nu} = 3320\text{m}, 3210\text{w}, 2975\text{w}, 1682\text{m}, 1586\text{m}, 1450\text{w}, 1397\text{m}, 1152\text{w}, 1073\text{s}, 974\text{s}, 885\text{s}, 792\text{vs}, 636\text{m}, 587\text{m}, 510\text{m}$. ^{31}P NMR ($(\text{D}_6)\text{DMSO}$): -15.34. ^1H NMR ($(\text{D}_6)\text{DMSO}$): 0.98 (t, $J = 7.5$ Hz, 10.5H, 3.5 CH_3), 2.06 (q, $J = 7.5$ Hz, 7H, 3.5 CH_2), 2.55 (s, 10.5H, 3.5 CH_3), 6.5-8.0 (b, 10.5H, 3.5NH, 3OH $^+$, 2H $_2\text{O}$). ^{13}C NMR ($(\text{D}_6)\text{DMSO}$): 174.26, 28.40, 25.52, 9.90. Anal. Calcd. for $\text{C}_{14}\text{H}_{38.5}\text{N}_{3.5}\text{O}_{45.5}\text{P}_1\text{W}_{12}$: C, 5.22; H, 1.20; N, 1.52. Found: C, 5.27; H, 1.18; N, 1.51.

Decomposition of the Hybrid Material to Achieve WO_3 Powder

The hybrid compound was decomposed by heating at 650 $^\circ\text{C}$ (2 h) to obtain WO_3 powder. The powder was suspended in ethanol under ultrasound (20 min). IR (KBr): $\tilde{\nu} = 492\text{-}580$ (broad)s, 816-855 (broad)s, 986s.

RESULTS AND DISCUSSION

The hybrid material $[\text{HNMPA}]_3[\text{O}_{40}\text{PW}_{12}]\cdot 0.5\text{NMPA}\cdot 2\text{H}_2\text{O}$ (NMPA = N -methylpropionamide, $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{NHCH}_3$) was obtained by the reaction of 12-tungstophosphoric acid with NMPA (1:5 ratios) in acidic (HCl) solution.

IR Spectroscopy

The IR spectrum of hybrid material contains the characteristic peaks at 792 cm^{-1} ($\text{W-O}_\text{c}\text{-W}$), 885 ($\text{W-O}_\text{b}\text{-W}$), 974 (W-O_d) and 1073 cm^{-1} (P-O_a) which demonstrate the *Keggin* structure of W atom (O_d , O_a , O_b and O_c oxygen atoms are the terminal, the ones bonded to P and W, the ones corner-shared of WO_6 octahedra and the ones edge-shared of WO_6 octahedra, respectively). The band at 1682 cm^{-1} is assigned to C=O .

NMR Spectroscopy

Phosphorus-31 NMR spectrum shows one signal at -15.34

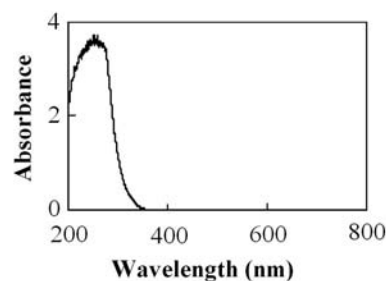


Fig. 1. UV-Vis absorbance spectrum of $[\text{HNMPA}]_3[\text{O}_{40}\text{PW}_{12}]\cdot 0.5\text{NMPA}\cdot 2\text{H}_2\text{O}$ in water (1.2×10^{-4} M), $\lambda_{\text{max}} = 253.5$ nm.

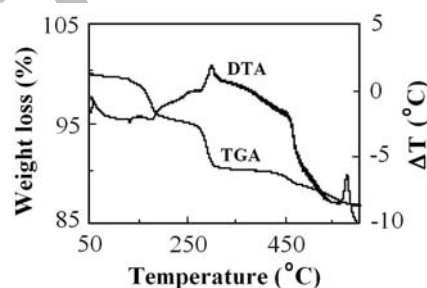


Fig. 2. The TGA and DTA curves.

ppm demonstrating the *Keggin* polyoxoanion of W. ^1H NMR spectrum indicates three signals in aliphatic region (triplet for CH_3 , quartet for CH_2 and singlet for the CH_3 which linked to N atom). The lines at 9.90, 25.52 and 28.40 ppm in ^{13}C NMR spectrum are related to CH_3 , CH_2 and the CH_3 (which linked to N) carbon atoms. C=O signal appears at 174.26 ppm.

UV-Vis Spectrum

UV-Vis spectrum (Fig. 1) of a 1.2×10^{-4} M aqueous solution of the compound shows an absorption band with $\lambda_{\text{max}} = 253.5$ nm (O to W charge transfer).

Thermogravimetric and Differential Thermal Analysis (TG-DTA)

The experiment was performed in the range of 30-600 $^\circ\text{C}$. The DTA diagram (Fig. 2) shows endothermic peaks at 133 and 180 $^\circ\text{C}$ followed by the exothermic peaks at 301 and 576 $^\circ\text{C}$. The endothermic peaks may be due to the release of physisorbed H-bonded H_2O and NMPA molecules and decomposition of HNMPA^+ cations. The exothermic peaks are

assigned to *Keggin* anion decomposition to yield WO_3 . The TG analysis (in the range of 30 to 600 °C) shows that the hybrid material undergoes a loss of 13.2% (calcd.: 13.6%), corresponding to removal of water and solvated molecules, organic cations and *Keggin* anion decomposition (loosing 0.5 mole P_2O_5 for each mole of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ polyoxoanion and remaining WO_3).

Description of the Crystal Structure

The crystal structure analysis reveals that the hybrid

material consists of one heteropolyanion which has absorbed 3.5 molecules of the organic part (three by protonating NMPA to produce HNMPA^+ cations and 0.5 H-bonded NMPA molecule) and two crystal water molecules. The crystal data and the details of X-ray analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2. The inorganic anion shows a classical “ α -*Keggin*” structure (Fig. 3) of W with 4 different types of O atoms including 12 terminal, 4 oxygen bonded to P and W, 12 WO_6 octahedra corner-shared and 12 WO_6 octahedra edge-shared oxygens. The P-O bond

Table 1. Crystal Data and Structure Refinement for $[\text{HNMPA}]_3[\text{O}_{40}\text{PW}_{12}]\cdot 0.5\text{NMPA}\cdot 2\text{H}_2\text{O}$

| | |
|--|---|
| Empirical formula | $\text{C}_{14}\text{H}_{38.5}\text{N}_{3.5}\text{O}_{45.5}\text{PW}_{12}$ |
| Formula weight | 3221.15 |
| Temperature | 120(2)K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a = 12.942(4)$ Å, $b = 13.017(4)$ Å $c = 17.932(5)$ Å $\alpha = 72.878(9)^\circ$ $\beta = 80.672(7)^\circ$ $\gamma = 78.157(7)^\circ$ |
| Volume | $2808.8(15)$ Å ³ |
| Z | 2 |
| Density (calculated) | 3.744 g cm^{-3} |
| Absorption coefficient | 24.581 mm^{-1} |
| F(000) | 2760 |
| Crystal size | $0.1 \times 0.1 \times 0.08 \text{ mm}^3$ |
| Theta range for data collection | 1.62 to 28.00° |
| Index ranges | $-17 \leq h \leq 17, -17 \leq k \leq 17, -23 \leq l \leq 23$ |
| Reflections collected | 28261 |
| Independent reflections | 13453 [$R(\text{int}) = 0.0807$] |
| Completeness to $\theta = 28.00^\circ$ | 99.2% |
| Absorption correction | Semi-empirical from equivalents |
| Max and min transmission | 0.140 and 0.081 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 13453/22/594 |
| Goodness-of-fit on F^2 | 1.058 |
| Final R indices [for 6886 rfln with $I > 2\sigma(I)$] | $R1 = 0.0770, wR2 = 0.1617$ |
| R indices (all data) | $R1 = 0.1294, wR2 = 0.1754$ |
| Largest diff. peak and hole | 4.078 and -2.695 e Å^{-3} |

Table 2. Selected Bond Lengths and Angles for [HNMPA]₃[O₄₀PW₁₂].0.5NMPA.2H₂O

| | | | |
|-------------------|-----------|-------------------|-----------|
| W(1)-O(7) | 1.704(19) | W(9)-O(5) | 1.914(17) |
| W(4)-O(6) | 1.884(16) | W(12)-O(4) | 2.435(15) |
| W(3)-O(14) | 1.743(15) | W(6)-O(2) | 2.439(14) |
| P(1)-O(1) | 1.566(16) | C(14)-C(15) | 1.509(10) |
| P(1)-O(2) | 1.515(13) | N(1)-C(3) | 1.310(5) |
| O(1S)-C(3) | 1.300(10) | N(2)-C(8) | 1.472(10) |
| O(4S)-C(15) | 1.298(10) | N(4)-C(16) | 1.477(10) |
| O(7)-W(1)-O(5) | 102.9(8) | O(9)-W(1)-O(6) | 153.6(7) |
| O(15)-W(3)-O(1) | 82.3(6) | O(14)-W(3)-O(16) | 103.7(7) |
| O(19)-W(4)-O(17) | 100.5(8) | O(17)-W(4)-O(2) | 73.3(6) |
| O(27)-W(7)-O(30) | 154.4(6) | O(29)-W(7)-O(3) | 70.2(6) |
| O(31)-W(8)-O(29) | 99.8(8) | O(31)-W(8)-O(3) | 169.9(8) |
| O(34)-W(9)-O(20) | 104.4(8) | O(34)-W(9)-O(30) | 100.1(8) |
| O(35)-W(10)-O(27) | 104.3(7) | O(37)-W(10)-O(36) | 86.0(8) |
| O(39)-W(11)-O(38) | 101.1(9) | O(40)-W(12)-O(22) | 104.4(8) |
| O(3)-P(1)-O(1) | 112.1(9) | O(2)-P(1)-O(4) | 108.6(8) |
| W(3)-O(1)-W(2) | 89.9(5) | P(1)-O(1)-W(3) | 126.8(8) |
| P(1)-O(3)-W(8) | 127.9(9) | W(7)-O(10)-W(2) | 153.3(9) |
| C(3)-N(1)-C(4) | 146(5) | P(1)-O(3)-W(7) | 123.0(9) |
| C(11)-N(3)-C(12) | 117(5) | C(15)-N(4)-C(16) | 122(3) |
| C(3)-C(2)-C(1) | 138(10) | C(7)-C(6)-C(5) | 143(5) |
| N(2)-C(7)-C(6) | 114(4) | N(4)-C(15)-C(14) | 130(4) |

lengths in the polyoxoanion are single (1.515(13)-1.566(16) Å), the P heteroatom has a tetrahedral configuration and the O-P-O angles are in the range of 108.6(8)°-112.1(9)°. The tetrahedron PO₄ is surrounded by 12 distorted octahedron of WO₆. The W-O bond distances of polyoxometalate are in the range of 1.67(2) Å-1.751(15) Å for the terminal oxygens, 1.862(19) Å-1.978(16) Å for the bridging oxygens and 2.425(15) Å-2.467(15) Å for the oxygen atoms bonded to P and W. All organic cations are symmetrically different from each other. Their differences are relevant to bond lengths, angles and torsion angles. In contrast to typical form of NMPA syn/trans (assigned by calculation) in the gas phase [14], both syn and anti forms of the title compound's organic parts are existed in the solid state. In the crystal network, non-covalent forces lead to a 3-D supramolecular aggregation. A view of polyoxoanions packing is shown in Fig. 4. As can be

seen in Fig. 4, each of the 2-D inorganic layers lay between two other layers with 'short' and 'long' spatial distances in the network. As the polyoxoanions are directly interacting *via* O...O electrostatic interactions, the spatial distances are shortened but in the other sides, the organic components lie between the 2-D layers of polyoxoanions. A view of unit cell packing of title compound is given in Fig. 5 in which the polyoxoanions are shown as polyhedra representation.

Decomposition of Title Material Hybrid

The full decomposition of the material hybrid leads to WO₃ powder. SEM image of the resulting powder is shown in Fig. 6. Meanwhile, the XRD pattern was found to be similar to that reported by Loopstra & Boldrini [15]. The Scherrer equation was used assuming a shape factor of 0.9 [16] to estimate average crystalline sizes of WO₃ (about 144 nm).

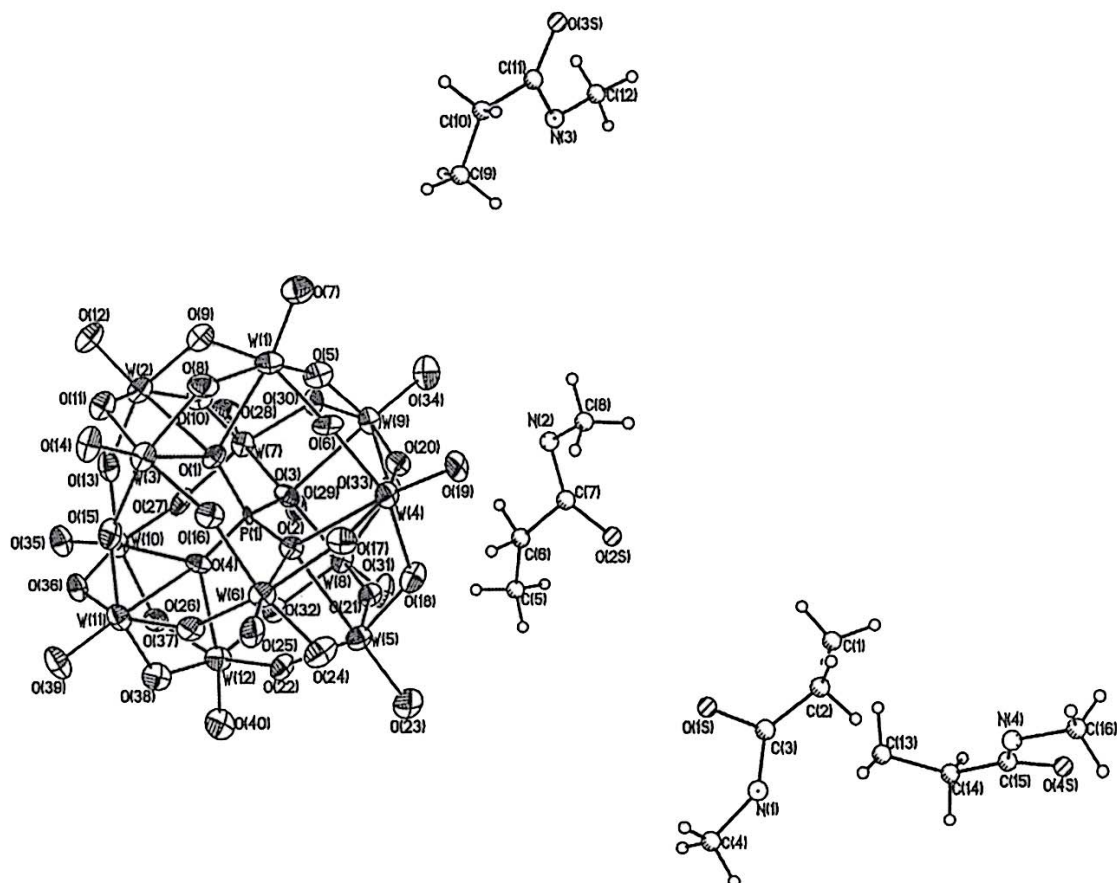


Fig. 3. A view of polyoxoanion, organic cations and H-bonded molecule.

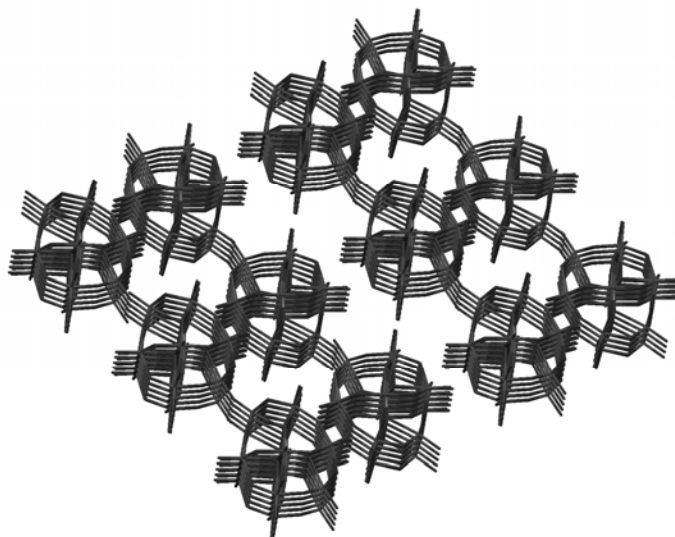


Fig. 4. A view of polyoxoanions packing in the 3-D network.

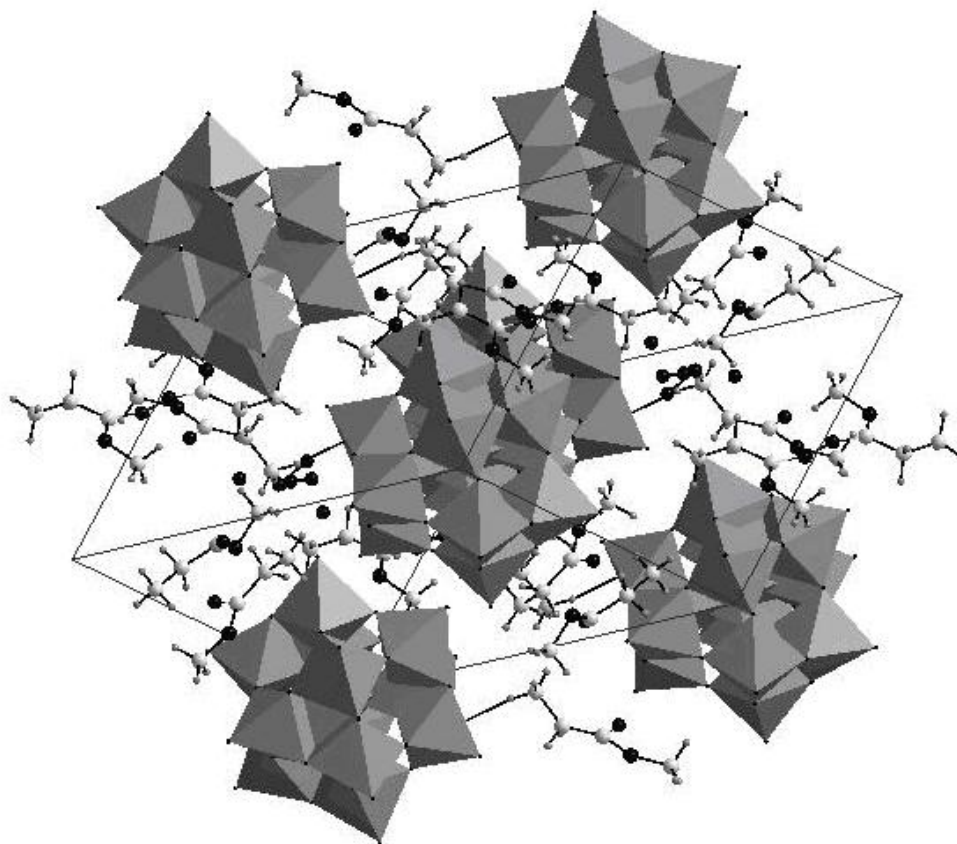


Fig. 5. A View of crystal packing of $[\text{HNMPA}]_3[\text{O}_{40}\text{PW}_{12}]\cdot 0.5\text{NMPA}\cdot 2\text{H}_2\text{O}$.

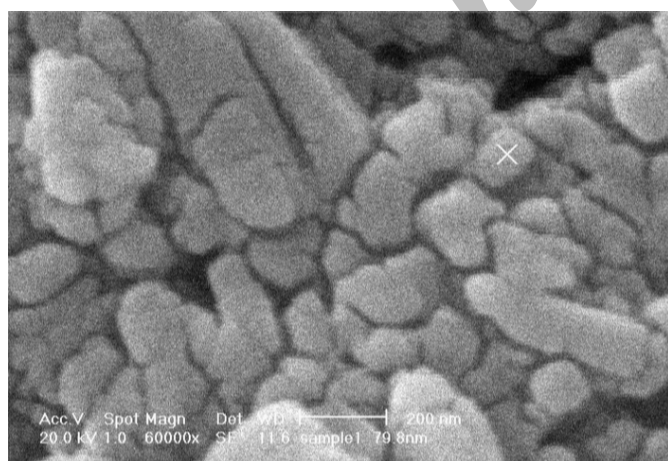


Fig. 6. SEM image of WO_3 powder which is obtained by thermal decomposition of material hybrid, selected (with symbol \times) nano-particle's size in the image is 79.8 nm.

ACKNOWLEDGEMENTS

Support of this investigation by Tarbiat Modares University is gratefully acknowledged.

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