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Cryst. Growth Des., **Just Accepted Manuscript** • DOI: 10.1021/acs.cgd.8b01258 • Publication Date (Web): 24 Oct 2018

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First Example of a Nonanuclear Silver Sulfate Hybrid Cluster: Green Approach for Synthesis of Lewis Acid Catalyst

Avijit Kumar Paul,* Kumari Naveen, Nikhil Kumar, Rajendiran Kanagaraj, V. M. Vidya and Tanmay Rom

Department of Chemistry, National Institute of Technology Kurukshetra, Kurukshetra-136119, Haryana, India.

Supporting Information Placeholder

ABSTRACT: Finding of high nuclearity hybrid framework with novel structure and properties in an environmentally benign approach is a really challenging task. Herein, a green strategy for synthesis of a new inorganic-organic hybrid framework solid has been described. The framework contains silver sulfate clusters with nine different silver ions with shortest silver-silver connectivity. Present compound is the first example of nonanuclear silver sulfate hybrid framework with a new topology. Hybrid solid compound shows highly active Lewis acidic nature for the various heterogeneous catalytic reactions such as cyanosilylation, ketalization and esterification with quantitative transformation and recyclability.

Functional organic-inorganic hybrid frameworks are intensively studied because of their fundamental scientific interest and potential applications in adsorption, separation, catalysis, sensor, ion-exchange and photoluminescence.[1-8] The bonding nature of inorganic ion plays vital role for structural variation whereas the organic moiety produces the multi-functional properties. Constant efforts on research in hybrid framework materials have evolved a variety of inorganic building moieties and organic linkers. From last few decades, silicate, phosphate, phosphite, sulfate, sulfite, selenate, selinite, borate, carbonate and thiosulfate ions are mainly used for the synthesis of new hybrid framework materials.[9-26] Sulfate based hybrid frameworks are not investigated comp1rehensively as few 3d-transition metals and lanthanum based sulfate frameworks are reported earlier.[27-31] Our past efforts have resulted few hybrid cadmium sulfate frameworks with versatile topology and catalytic activity.[31] As the nitrogen containing aromatic organic ligands are very significant to enhance the dimensionality and functionality of the hybrid framework structures, polyazaheterocyles and their derivatives are of particular interest in our present study. Any functional hybrid becomes more exciting when it can be synthesized with greener approach along with their sustainable applications.

Mechanochemical reaction, a promising synthetic technique, leads to form the product by applying the mechanical force with addition of negligible amount of solvent. This strategy is superior from Green Chemistry point of view which avoids the environment pollution. Hence, this alternative synthetic approach is readily acceptable for the synthesis of products in laboratory as well as in industry. Solvent-free or solvent-assisted mechanochemical reactions are widely used for the last few years to synthesize the metal-organic frameworks, coordination polymers or hybrid frameworks.[32-38] In this report, we have applied the high energy mechanochemical strategy to obtain the completely pure hybrid catalyst. Solvent drop grinding strategy was adopted to synthesize new silver sulfate, $[Ag_8(SO_4)_4(C_3H_6N_6)_3]$ (**I**), framework compound. The present three-dimensional extended solid has been used for various heterogeneous catalytic reactions due to its Lewis acidic nature. Herein, we are communicating the novel synthetic strategy, crystal structure, characterizations, topology and various heterogeneous catalytic behaviors.

Single crystal of the present compound was prepared by using solvothermal conditions in the presence of water and ethanol at 125 °C in a Teflon-lined autoclave (see ESI). Although the single crystal of compound **I** was synthesized in solvothermal condition, the complete phase pure product was not obtained under solvothermal conditions. Once the single crystal was obtained using above condition, the pure polycrystalline powder compound was synthesized by mechanochemical synthetic strategy with solvent drop approach. Exact molar ratio was ground for 2 hours to homogenize properly. Afterwards few drops of EtOH were added at the time of grinding for improvement of homogeneity. The finely ground mixture was kept inside the oven at 125 °C for 3 days. The pure white powdered compound was characterized by PXRD which shows the purity of the compound (See ESI, Fig. S1). Elemental analyses (using CHN analyser) were carried out for polycrystalline powdered compound and single crystals obtained from solvothermal synthesis. The observed results (C: 6.57%; H: 1.15%; N: 15.59%) of powdered sample well matched with single crystals (C: 6.60%; H: 1.13%; N: 15.55%) and calculated elemental percentage (C: 6.64%; H: 1.10%; N: 15.50%). Hence, all further characterizations and catalytic studies were performed using the powdered compound **I** synthesized by mechanochemical strategy.

The asymmetric unit of **I** contains 56 non hydrogen atoms, of which four S and nine Ag atoms are crystallographically independent (Fig. 1a). Out of nine silver atoms, Ag(6) and Ag(9) occupy special position (2i) with a site multiplicity of 0.5. Ag(1), Ag(3) and Ag(7) have the similar coordination environment (See ESI, Fig. S5-S6). They are coordinated with three oxygen atoms of sulfate units and one nitrogen atom of the melamine unit forming the distorted tetrahedral geometry (AgO_3N, CN = 4). Ag(2) and Ag(4) have also shown the similar geometry by coordinating with three oxygen atoms of sulfate units, one nitrogen atom of the melamine unit and one silver ion forming the distorted trigonal bipyramidal geometry (AgO_3NAg, CN = 5). Ag(5) and Ag(8) have the similar coordination environment. They are coordinated with two oxygen atoms from sulfate units, one nitrogen atom of the melamine unit and one silver ion forming the distorted tetrahedral geometry (AgO_2NAg, CN = 4). Ag(6) is coordinated with two oxygen atoms of sulfate units, one nitrogen atom of the melamine unit and two silver ions forming the distorted trigonal bipyramidal geometry (AgO_2NAg_2, CN = 5). The remaining Ag(9) is forming the distorted tetrahedral geometry by coordinating with one oxygen atom of sulfate unit, one nitrogen atom of the melamine unit and two silver ions ($AgONAg_2$, CN = 4). Interestingly, nine Ag-ions are showing five characteristic coordination environments possessing tetrahedral or trigonal bipyramidal geometry (See ESI, Fig. S5-S6). The Ag-O bond distances are in the range of 2.246(14) - 2.604(19) Å (av. Ag-O = 2.424 Å) and Ag-N bond distances are in the range of 2.216(15) - 2.305(15) Å (av. Ag-N = 2.251 Å). There are five distinguished Ag-Ag bonds present in the structure. Ag-Ag bonds are in the range of 2.389(7) - 3.315 (2) Å (av. Ag-Ag = 2.953 Å) which is comparable with the earlier literatures.[39-45] There are four sulfate units with average S-O bond distances of 1.443 Å. The sulfate unit possesses an average angle of 109.4°, which is indicative of a regular tetrahedral arrangement. The crystallographic parameters and selected bond distances are listed in Table T1-T2 (See ESI).

The present silver sulfate compound has three-dimensional extended structure. The structure can be understood in simplified way by taking the silver and sulfate coordination at first. As the structure has nine different silver ions and four different sulfate ions, the connectivity of both the ions make three-dimensional extended structure (See ESI, Fig. S8). Six silver ions and six sulfate units form a 12-membered ring in which the melamine unit is connected to three alternate silver ions (Fig 1b). The presence of melamine units eradicates the porosity of the open-framework structure. Such 12-membered rings grow along three directions to make the three-dimensional extended structure (Fig. 2). The coordination numbers of silver ions are four and five which include various Ag-O, Ag-N and most importantly Ag-Ag bonds. Interestingly minimum Ag-Ag distance is 2.39 Å which is observed for the first time though the metallic Ag-Ag bond distance is 2.91 Å. As silver exists in +1 oxidation state, so the present distance is slightly greater than the ionic distance (2.25 Å) of two silver ions.

The present compound possesses unusual structural diversity as the metal shows the variable bonding connectivity from four to five. Compared to the earlier reported silver sulfate framework compounds, the present structure shows the novel bonding connectivity with unique cluster formation. A list of the compounds with silver clusters and their observed properties have also been given (see ESI, Table 3). Mak and coworkers have reported two porous silver clusters $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]$ and $[Ag_{10}(SO_4)_5]$.[39] The complex containing $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]$ subunits exhibits two kinds of cages assembled with 12-connected $[Ag_{16}(SO_4)_8]$ units and 8-connected $[Ag_4(SO_4)_2]$ units. Second complex features 14-connected $[Ag_{10}(SO_4)_5]$ clusters with highest connectivity Ag(I) cluster SBU reported till the date. A series of silver sulfate coordination polymers have been synthesized in presence of bipyrazole ligands by Hou et. al.[40] Here, the structural diversity and dimensionality arises mainly due to the flexible orientation of bipyrazole ligands. Tong and coworkers have also reported one luminescent octanuclear silver (I) cluster $[Ag_8(SO_4)_2]$ with two-dimensional layer structure.[41] All the above silver sulfate compounds have weak argentophilic interactions with Ag-Ag distances above 3.00 Å. Such Ag···Ag interactions are more significant for silver based framework materials.[42,43] Beside the silver sulfate compounds, Jin et. al have also communicated one octanuclear Ag_8-cluster stabilized with adamentanedicarboxylic acid.[44] The compound exhibits 2D-layer of Ag-Ag interactions including ten kinds of Ag-Ag contacts ranging from 2.98 Å to 3.66 Å. Rao et al. communicated one dimeric silver cluster with cyanuric acid possessing silver sheets of average Ag-Ag distances around 2.95 Å.[45] Above literature survey clearly reveals the distinct connectivity as well as shortest Ag(I)-Ag(I) bonding interactions in our present silver sulfate hybrid framework compounds. The TOPOS analysis was also performed to understand the simplified structural-connectivity.[46-48] Three different nodes were presented for silver ions, sulfate units and melamine units as all the units are containing more than two coordination sites. Overall net is formed by 3-, 4-, 5-connected 16 nodal points. Point symbol of the net is $\{3.6^2.7^3.8^2.9^2\}\{3.6^2.7^3\}\{3^2.4.6^2.7\}^2\{4.6^3.8^2\}^2\{6.10^2\}\{6.8^2\}\{6^3.7^3\}^2\{6^3.8^3\}\{6^3\}^5$. The detailed analysis showed that the observed net is unique as it forms completely new topology (See ESI, Fig. S11).

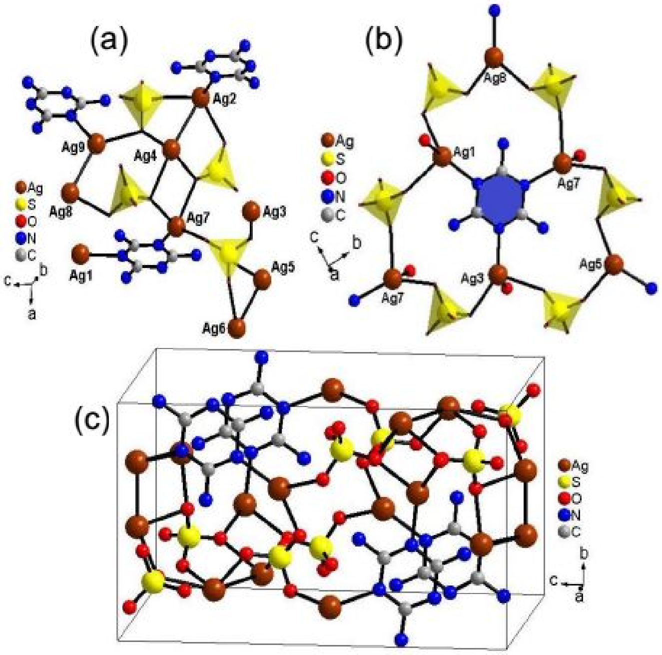


Figure 1. (a) Presence of nine different silver ions, four sulfate units and three melamine units in asymmetric unit of **I**. (b) Connectivity of one melamine unit with three different

silver ions forming 12-membered ring. (c) Unit-cell representation of the compound **I**.

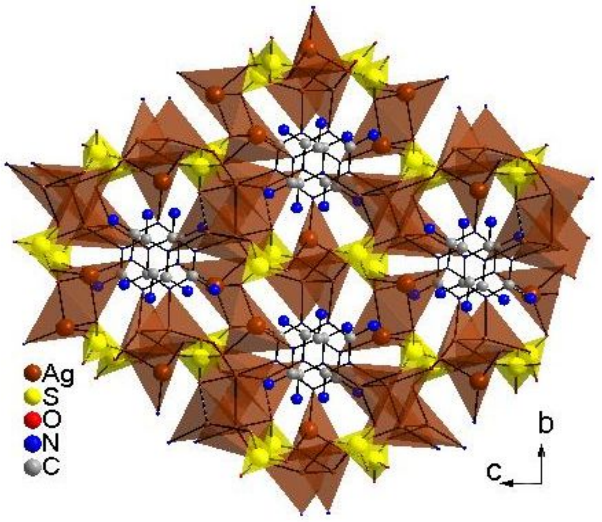
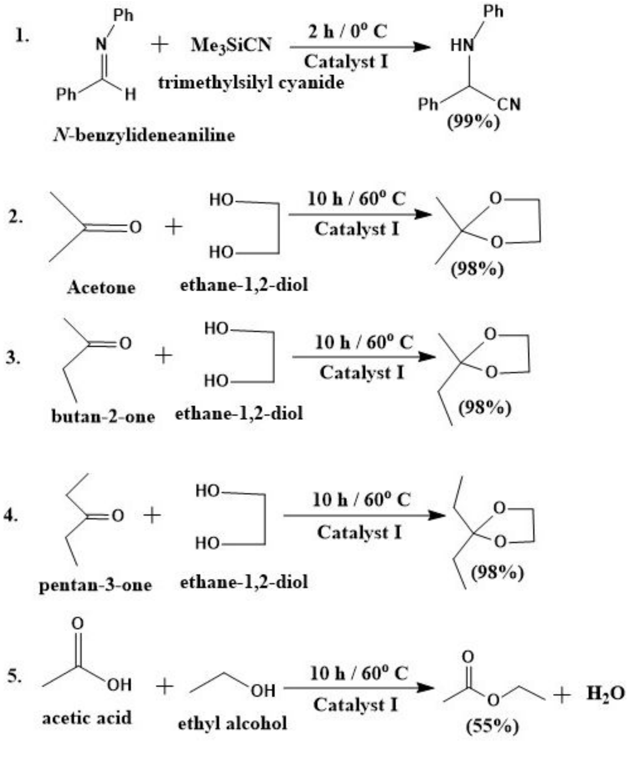


Figure 2. Three-dimensional polyhedral view of compound **I** along the *bc* plane.

Considering the lower coordination sites of Ag(I)-ions, we are keen to check its catalytic activity. A catalyst is designed in such a way that it provides negligible toxicity, higher recyclability and shows better cost effective performance in economic aspects. Recently, metal-organic frameworks and various metal-clusters are extensively used for heterogeneous catalysis reactions along with their multifunctional applications. [49-54] Our earlier efforts on cadmium sulfate catalysts proved that 4*d*-transition metal-based frameworks can be used as Lewis acid catalyst. It has been well established when a metal center with larger ionic radius is coordinately unsaturated; it can be served as Lewis acid catalyst. In the present compound **I**, the coordination numbers of silver ions vary from four to five which can accommodate additional coordinating ligands for heterogeneous catalytic activity. The Lewis acid character was examined through few well-known catalytic reactions i.e. cyanosilylation, ketalization and esterification. The above mentioned reactions generally require acid as the catalyst to increase the nucleophilicity of the carbonyl and imine-carbon. Instead of mineral acids, the acidity can be achieved by silver-ions as it works as Lewis acidic center with heterogeneous catalytic behavior.

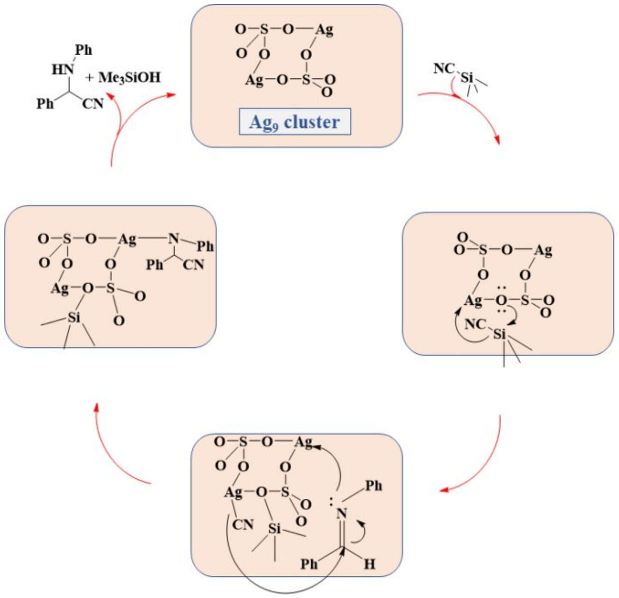
Initially, we checked the catalytic activity of compound **I** for cyanosilylation reaction as it was studied earlier with silver and cadmium based few hybrid framework compounds.[30-31,55] The addition of cyanide group occurs through the carbon-carbon bond formation in carbonyl carbon or imine compounds. The cyanohydrin products are intermediates in several organic compounds, e.g., aminoalcohal, hydroxyaldehydes, hydroxyacids. Here a model imine was taken to perform the catalytic reaction with the finely powdered polycrystalline compound (Scheme 1). The product was analyzed and evaluated for the conversion of the reactants (99%) through ^{1}H NMR spectra (See ESI). The catalyst to imine mole ratio was 1:100 which is notable and the present result shows better activity compared to many Cd based framework catalysts. The ketalizations of various ketones also reflect the Lewis acid nature of the present compound. For ketal formation, we used three different ketones i.e. acetone, 2-butanone and 3-pentanone. All product yields were determined by ^{1}H NMR spectra (See ESI). Three different aliphatic ketones have been converted quantitatively to the respective ketals (Scheme 1). In each reaction, we used catalyst and ketone ratio 1:800. Such high efficiency of this catalytic activity was successfully observed to various keton without depending on substrate structure.

At last, we carried out the esterification between acetic acid and ethanol with silver sulfate catalyst. Catalyst and substrate ratio was 1:800 similar to the ketalization. Esterification reaction gave a yield of 55% after 10 h reaction at 60 °C with continuous stirring. It was not observed any improvement to the yield even after longer reaction time. The yield for this reaction was considerably less, but the reactivity appears to be promising as observed in the ketal formation reaction. Blank experiments were carried out for each catalysis reaction under similar conditions without any catalyst, only negligible product formation confirming the effective catalytic activity of silver sulfate. The recyclability nature of the compound was checked for each reaction by performing three cycles. The similar yields were obtained in each cycles and the negligible weight loss of the catalyst was obtained after each cycle. To understand changes in the chemical environment or structure under catalytic conditions, we examined the powder *x*-ray diffraction patterns of the catalyst after each catalytic reaction. PXRD pattern of the catalyst remains completely same and the amount of the recovered catalyst matches well with the added catalyst (see ESI, Fig. S12). Overall, the high efficiency and reusability presented here prove that our new silver sulfate framework is a new example of Lewis acid catalyst for various heterogeneous catalysis reactions.



Scheme 1: Various heterogeneous catalytic reactions observed in presence of compound I.

The applicability of hybrid structures composed by d^{10} shell metal ions in the field of catalysis remains uninvestigated where the Lewis acidity arises due to the presence of low-coordinate open sites. The Lewis acidic nature of metal cations can be explained on the basis of e/r ratio (where e = charge and r = ionic radius), which is the basic criteria for the measurement of the electron-withdrawing ability of the metal cations. Although the charge of the silver ion is less but more number of coordinately unsaturated silver ions increase the efficiency in catalytic reactions. On the basis of present investigations, a plausible mechanism is displayed in Scheme 2. Here, electron-rich nucleophilic oxygen atoms present on the surface of Ag cluster framework initiate the reaction and transferred electrons to the trimethylsilyl group of TMSCN, with the formation of weak coordinated Si-O bond. The pentavalent silicon intermediate has weakened C-Si bond and increases the nucleophilicity of cyanide group, resulting attachment to the Lewis acidic Ag sites. The electron rich nitrogen atom of imines formed a weak bond with neighboring Lewis acidic Ag sites. Then, further nucleophilic CN group attacked to carbon and formed cyanosilylated species which comes out as a product in next step. In ketalization reactions, our cation-rich silver-based hybrid framework activates the oxygen of the carbonyl group and permits glycol to replace for the carbonyl group. The carbon atom of the carbonyl group undergoes nucleophilic attack by the hydroxyl group of ethyl alcohol resulted in the bond formation between the carbon atom of the carbonyl group and the hydroxyl group of ethyl alcohol with the removal of water. The similar activation will be observed with acetic acid also. But the electrophilicity of the carbonyl carbon will be the higher in carbonyl group compared to acid group. Hence the complete conversation can be observed in ketones as reported earlier.



Scheme 2: Plausible mechanism for the Lewis acid catalyzed cyanosilylation of imines.

In summary, we have reported solvent drop green synthesis of new silver sulfate hybrid cluster comprising stability upto 400 ºC. The crystal structure analysis has been shown the shortest Ag-Ag bond length consisting nine different silver atoms in asymmetric unit. The compound forms a new topology with 16-nodal points. The hybrid silver sulfate framework is applicable as heterogeneous catalyst for the cyanosilylation, ketalization and esterification reactions. Present compound is unique with its structural novelty along with potential applicability. The present study can motivate for the further research on synthesis of new heterogeneous solid acid catalyst by economical and environment-friendly mechanochemistry.

ASSOCIATED CONTENT

Supporting Information

Tables listing crystallographic data, selected bond lengths, PXRD patterns, IR spectrum, TGA plot, few structures, SEM image, Gas-adsorption plot, Topological analysis, ^{1}H-NMR plot for catalysis reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

Corresponding Author: *Email: apaul@nitkkr.ac.in

ACKNOWLEDGMENT

Authors acknowledge the financial support from the Department of Science and Technology through INSPIRE Award (No. IFA14-CH-144) & Science and Engineering Research Board, India in the form of Start-Up Research Grant (No. SB/FT/CS-098/2014). The authors thank Prof. S. Natarajan of Indian Institute of Science, for help with the Single Crystal data collection and fruitful discussion.

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(56) Crystal Data For **I**: Triclinic, P-1 (no. 2), a = 9.7628(2), b = 10.1956(4), c = 16.5042(5) Å, α = 87.646(3)°, β = 76.718(2)°, γ = 86.763(3)°, V = 1595.63(9) $Å^3$, Z= 2, ρcal = 3.346 g cm^{-3}, μ(Mokα) = 5.162 mm^{-1}, 28844 reflections, 5438 unique, 4595 observed I>2σ(I); R1 = 0.0933, wR2 = 0.2577 and GOF =1.042 for 481 parameters; CCDC No: 1496359.

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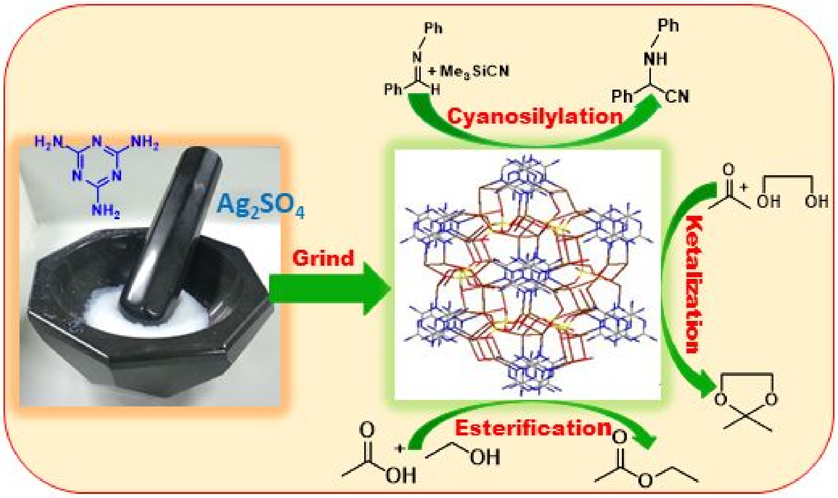
First Example of a Nonanuclear Silver Sulfate Hybrid Cluster: Green Approach for Synthesis of Lewis Acid Catalyst

Avijit Kumar Paul,* Kumari Naveen, Nikhil Kumar, Rajendiran Kanagaraj, V. M. Vidya and Tanmay Rom



A hybrid silver sulfate framework featuring nine silver atoms in the asymmetric unit with shortest Ag–Ag bond is synthesized under mechanochemical strategy. The framework has new topology and found to be very efficient heterogeneous catalyst for cyanosilylation, ketalization and esterification reactions.