Synthesis and structure of Anderson cluster based organic–inorganic hybrid solid, $[\{\text{Cu}(2\text{-}pzc)(\text{H}_2\text{O})_2\}_2\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}] \cdot 17\text{H}_2\text{O}$ and its dye adsorption properties

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Abstract. An inorganic–organic hybrid compound, namely $[\{\text{Cu}(2\text{-}pzc)(\text{H}_2\text{O})_2\}_2\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}] \cdot 17\text{H}_2\text{O}$ was synthesized based on Anderson–Evans cluster by the normal stirring process at room temperature. Its structure consists of metal coordination polymer covalently linked with Anderson–Evans cluster forming a 2D-sheet with void space containing water chains as determined by Single-Crystal X-ray Diffraction technique. This material owing to its void space of approx. 13 Å was utilized for adsorption of organic dyes like Methylene Blue (MB), Basic Violet 1 (BV1) and shows ultra-high uptake (more than 90%) within 5 min.

Keywords. Polyoxomolybdates; Anderson–Evans cluster; dye adsorption.

1. Introduction

The synthesis of organic–inorganic hybrid compounds has received much attention, not only because of their numerous potential applications in the field of catalysis, storage and separation of chemical matter, but also from their intriguing variety of architectures and topologies.¹ Polyoxometalates, as a large family of metal–oxygen clusters, have become attractive inorganic building blocks due to their large numbers of structural diversity and various applications in different areas, including catalysis, medicine, and material science.^{2,4–6} Polyoxomolybdates (POM), a class of polyoxometalates, are versatile nanosized molybdenum oxide clusters with various topologies.⁷ POM based hybrid solids are mostly crystallized from aqueous solution by reacting Ammonium heptamolybdate/Sodium Molybdate with appropriate metal salts and organic ligands in the temperature range from room temperature to 200 °C; the higher temperature reactions are mostly performed under hydrothermal/solvothermal condition.^{8,9}

There are different kinds of POM clusters based on their different structural features. In the first case, stable POM cluster like Octamolybdates,^{10,11} Keggin,^{12,13}

Wells–Dawson,¹⁴ Lindquist,¹⁵ and Anderson–Evans^{9,16} appear as building blocks; these may occur either as discrete counter anions or coordinatively bonded to metal complexes extending into multi-dimensions. In the second case, molybdates with extended –Mo–O–Mo– interactions dominate the structure-building with metal complex occurring as counter cations or bridging/pillaring units.¹⁷ In the third case, the metals form coordination polymers with the organic and the POM can further be coordinated to the metal or occur as counter anions.¹⁸

Polyoxomolybdates, being rigorously studied, are not yet widely explored for their applications. Due to the presence of Molybdenum atom and its varied oxidation states, POMs are recently being explored as electrocatalysts and photocatalysts for hydrogen evolution reactions (HER).¹⁹

One of the most common polyoxometalates (POMs) is the Anderson–Evans archetype with the general formula $[\text{Hy}(\text{XO}_6)\text{M}_6\text{O}_{18}]^{n-}$, where $y = 0–6$, $n = 2–8$, $\text{M} =$ addenda atoms (Mo^{VI} or W^{VI}) and $\text{X} =$ a central heteroatom. The Anderson–Evans archetype is a highly flexible POM cluster that allows modification from several points-of-view: (i) it can incorporate a large number of different heteroatoms differing in size and oxidation state,²⁰ (ii) it can incorporate inorganic and organic cations and molecules demonstrating different coordination motifs,²¹ and (iii) covalent attachment

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with 5-tris(hydroxymethyl)methane ligands allows it to be combined with specific organic functionalities. The catalog of available heteroatoms counter cations and organic ligands have witnessed a tremendous expansion during the recent past ranging from small inorganic anions that act as building blocks for larger structures to anions in the nanometre range exhibiting multifunctional properties.

With the rapid development of industries for manufacturing medicine, textile, leather, printing and plastics, more than 100,000 commercially available dyes with over 7×10^5 tons are discharged annually to the detriment of the water quality worldwide.²² Due to ecological and environmental importance, removing

and further separating cationic or anionic dye molecules from mixed dyes solution by host–guest electronic interactions and/or guest–guest exchange interactions but still facing the challenges of either time consume or operating in non-aqueous solutions.

Herein we report the synthesis and structure of an Anderson–Evans cluster based solid $[\text{Cu}(2\text{-}pzc)(\text{H}_2\text{O})_2]_2\{\text{H}_7\text{AlMo}_6\text{O}_{24}\} \cdot 17\text{H}_2\text{O}$ (**1**) which can rapidly and efficiently adsorb organic dyes like Methylene Blue (MB), Basic Violet 1 (BV1) from their aqueous solution. To the best of our knowledge, such high uptake of two dyes namely Methylene Blue and Basic Violet 1 has never been reported for any Anderson–Evans type cluster based solid.

Methylene Blue

Basic Violet 1

organic dyes with high toxicity and difficulties in their degradation from the wastewater have become a hot research topic.²³ Furthermore, considering sustainable development, it is extremely desirable to recover and reuse the enriched organic dyes if they could be selectively separated from their mixtures.

Various methods, such as electrochemical oxidation,²⁴ photodegradation,^{10,25,26} enzymatic biodegradation,²⁷ adsorption²⁸ and catalytic wet air oxidation (CWAO)²⁹ have been used for removing/treating and recovering organic dyes in wastewater. Among these technologies, adsorption has been given growing interest owing to their low cost, high efficiency, and ease of operation. Thus, it is indispensable to explore new adsorbents with ultra-high adsorption efficiency and capacity towards dyes, as well as highly selective ability to separate different organic dyes from their mixtures. Multifunctional organic–inorganic hybrid crystalline materials, which assemble molecular components into a periodic framework, have captured considerable attention owing to their diverse and easily tailored structures and their various potential applications in catalysis, separation, gas storage, carbon dioxide capture, photocatalysis and so on. Very recently, some ionic hybrid crystalline materials were also used for selectively adsorbing

2. Experimental

All the chemicals were purchased from commercial sources and used as such without further purification.

2.1 Synthesis

Initially, two different aqueous solutions were prepared. The experimental conditions were optimized to enable homogeneity of the solution before and after mixing. Solution A was prepared by adding $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2.35 mmol, Merck, 99%) to the solution of AlCl_3 (anhydrous) (1.57 mmol, CDH, 99%) in 15 mL of water; this was further acidified by 5 mL of glacial acetic acid. Solution B was prepared by mixing 2-pyrazine carboxylic acid (2.52 mmol, Merck, 99%) to the solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.68 mmol, Merck, 99%) in 10 mL of water and 10 mL of methanol. The solution A was then added to the solution B with stirring. The resulting clear blue colored solution was left for crystallization at room temperature. The blue block crystals were obtained after 2 weeks approximately in about 75% yield (based on Mo). The product was filtered, washed with distilled water and dried in air. IR: (KBr pellet, cm^{-1}): 1645(s) 1470(m) 1416(s) 1353(s) 1290(s) 1060(s) 940(w) 890(m) 795(m) 745(w) 643(m) 495(w).

Table 1. Crystal data and structural refinements for **1**.

Parameter	$[\{\text{Cu}_2(2\text{-}pzc)_2(\text{H}_2\text{O})_4\}\{\text{H}_7\text{AlMo}_6\text{O}_{24}\} \cdot 17\text{H}_2\text{O} (\mathbf{1})]$
Formula	$\text{C}_{10}\text{H}_6\text{AlCu}_2\text{Mo}_6\text{N}_4\text{O}_{49}$
Formula weight, g	1695.91
T (K)	293(2)
Wavelength ($\text{\AA}$)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
a ($\text{\AA}$)	10.880(2)
b ($\text{\AA}$)	17.031(3)
c ($\text{\AA}$)	13.617(3)
α ($^\circ$)	90
β ($^\circ$)	107.73(3)
γ ($^\circ$)	90
V ($\text{\AA}^3$)	2403.4(8)
Z	2
dcalc (g cm^{-3})	2.343
$\mu_{\text{MoK}\alpha}$, (cm^{-1})	2.528
R1(I > 2 σ I)	0.0450
WR2 (all)	0.1261
CCDC/CSD No.	1871912

2.2 Dye adsorption process

Methylene Blue shows the absorbance peak between 600 and 700 nm and Basic Violet 1 shows between 550 and 600 nm.

For dye adsorption studies 1 mM stock solution of both MB and BV1 was freshly prepared, other solutions of various concentrations i.e., 10 μM , 20 μM and 50 μM concentrations of MB and 50 μM , 100 μM and 150 μM of BV1 was prepared by dilution. Firstly, the studies were carried out using a different concentration of dye. 10 mL of dye solution was taken in a beaker. To this, 10 mg of the catalyst was added. The mixture was kept under stirring for 30 min. After this, the catalyst was separated from the dye solution by centrifuge and filtration. The filtrate was analysed using UV-visible spectroscopy to monitor the removal of dyes from the solution. Based on the results obtained from studies carried out with different concentration of dyes (discussed later), 50 μM of MB and 150 μM of BV 1 was used for carrying out time-dependent studies. For this, a sample suspension (2 mL) was taken out after a fixed interval. The dye absorption studies were also performed at different pH. pH of the solution was maintained by addition of 1 M HCl for pH < 7 and 1 M NaOH for pH > 7.

2.3 Characterization

2.3a Single crystal X-ray diffraction: For single crystal X-ray diffraction studies, a suitably sized crystal was mounted

Figure 1. (a) 1-D copper pyrazine carboxylate coordination polymer covalently linked to Anderson–Evans cluster forming a 2-D sheet. (b) Aggregation of water molecules forming water chains. The sheets contain water chains in the cavities (13.758 $\text{\AA}$ $\times$ 13.59 $\text{\AA}$) projecting along *a* axis.

Figure 2. Space-filling model showing the adjacent sheets (pink and blue) in $[\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4]\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$, **1** are stacked over each other through H-bonding between coordinated water and cluster oxygen.

on a capillary. A BRUKER AXS SMART-APEX three-circle diffractometer with a CCD area detector ($K\alpha = 0.71073 \text{ \AA}$, monochromator: graphite) was used for data collection.³⁰ Frames were collected at $T = 293$ or 100 K by ω , φ and 2θ -rotation at 10 s per frame with SAINT.³¹ The measured intensities were reduced to F^2 and corrected for absorption with SADABS.³¹ Structure solution, refinement, and data output were carried out with the SHELXTL program.³² Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model. O–H hydrogen atoms were localized by difference Fourier maps and refined in subsequent refinement cycles. Images were created with the Diamond program.³³ Hydrogen bonding interactions in the crystal lattice were calculated with SHELXTL and Diamond. Crystallographic details are summarized in Table 1.

2.3b Other analytical techniques: Room-temperature Powder X-ray diffraction (XRD) data were collected on a Bruker D8 – Avance Eco Powder X-ray Diffractometer using Ni-filtered $\text{Cu-K}\alpha$ radiation ($1.5418 \text{ \AA}$). Data were collected with a step size of 0.05° and at count time of 1 s per step over the range $2^\circ < 2\theta < 60^\circ$. Rietveld analysis of powder diffraction data of powder sample was carried out using the software Topas 5 (Bruker) to ascertain homogeneity of the synthesized product. Scanning electron microscope (SEM)

studies were carried out on powder mounted on carbon tape coated with gold with JSM –300 at an accelerating voltage of 20 kV . UV-Visible spectra were recorded on a UV-2600, Shimadzu. FTIR spectroscopy studies (using KBr) were carried out using Agilent Cary 600 series Fourier transform infrared (FT-IR) spectrometer in the range of $400\text{--}4000 \text{ cm}^{-1}$. TG analysis was carried out using Perkin–Elmer STA 8000 system on well ground samples in a flowing nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

3. Results and Discussion

3.1 Structural description of $[\text{Cu}_2(2\text{-pzc})(\text{H}_2\text{O})_2]_2\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$ (**1**)

The reaction of a 2-pyrazine carboxylic acid with copper yielded $[\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4]\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$. The structure of **1** is isostructural to its Chromium analogue.¹⁸ Single crystal X-ray analysis revealed that the structure consists of 1-D co-ordination polymer coordinated to aluminium molybdate cluster. The asymmetric unit of **1** contains Al-based Anderson–Evans type of cluster covalently linked to $\{\text{Cu}_2(2\text{-pzc})(\text{H}_2\text{O})_2\}_2$ unit and nine lattice water molecules. Cu exhibits distorted

Figure 3. H-bonding among lattice water molecules and coordinated water and carboxylate oxygens resulting in a 3D packing of $[\{\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4\}\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}]\cdot 17\text{H}_2\text{O}$, **1**. Pink and yellow represent two different 2D sheets.

octahedral geometry with the 2-*pzc* acting as bidentate and monodentate on either side, two water molecules and one oxygen from the molybdate cluster. Cu is coordinated to nitrogen of 2-*pzc* on equatorial positions and four oxygen atoms on an axial plane such that it forms 1-D CP of the composition $\{\text{Cu}(2\text{-pzc})(\text{H}_2\text{O})_2(\text{O}_{2/2})\}$. Out of four oxygens, two are from coordinated water molecules, one is from the carboxylate group of 2-*pzc* and the remaining one is cluster oxygen. Each Cu is linked to one Anderson–Evans cluster in the alternative direction forming a ladder-like sheet structure containing cavities of approx. $13.59 \times 13.75 \text{ \AA}$ as shown in Figure 1a. Seventeen water molecules are present in a unit cell. The water molecules interact among themselves via strong H-bonding to form zigzag water chains ($2.17\text{--}3.20 \text{ \AA}$) (Figure 1b). Water chains pointing perpendicular to *a*-axis occupy the cavities formed in sheets. The sheets are stacked over each other (Figure 2) through H-bonding between coordinated water and cluster oxygen ($2.2\text{--}3.150 \text{ \AA}$) forming a

3-D network structure. Water chains also show extensive H-bonding with the cluster oxygens and co-ordinated water molecules to form a 3-D network (Figure 3).

3.2 Rietveld analysis of powder X-ray diffraction data

Phase purity of the solid was established by full profile Rietveld refinement using Topas 5 as shown in Figure 4. It is clear from the plot that the solid was obtained in pure form.

3.3 Scanning electron microscopy

Scanning Electron Microscopy was performed on the powdered sample mounted on carbon tape coated with gold. It was observed that rods with diameter $\sim 200 \text{ nm}$ were formed for $[\{\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4\}\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}]\cdot 17\text{H}_2\text{O}$, **1** (Figure 5).

Figure 4. Rietveld refinement plot for $[\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4]\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$, **1**. The blue corresponds to the experimental data while red represents the calculated profile. Grey line gives the difference between the experimental and calculated diffraction profiles.

Figure 5. SEM images of $[\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4]\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$, **1**.

3.4 Thermogravimetric analysis

TG analysis of $[\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4]\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$, **1** showed weight loss in two steps (Figure 6). The first step is due to the loss of seventeen lattice water molecules. The broad second step corresponds to the loss of four co-ordinated water molecules and 2-*pzc* ligand and degradation of aluminium molybdate cluster.

3.5 Dye adsorption studies

Dyes coming out from textile industries are toxic and hazardous for human health as well as for aquatic life; therefore, their effective removal from wastewater is necessary. Generally, the methods used for dye removal are time-consuming and costly. Herein, we used an inorganic–organic hybrid compound for dye removal from its aqueous solution by adsorption process. To the best of our knowledge, this is the first time that any Anderson–Evans type cluster based solid is showing such high uptake of two dyes namely Methylene Blue and Basic Violet 1. However, octamolybdate cluster

based solids have been used earlier for dye adsorption³⁴ and degradation properties.^{35,36} The intriguing layer-like structure, porosity and acidic nature of title compound motivated us to use it for dye uptake. Methylene Blue (MB) and Basic Violet 1 (BV1) were tried as both have basic nature. Our catalyst shows high uptake of both the dyes from aqueous solution. Dye removal efficiency was calculated by equation (1) and their corresponding UV-Vis spectra after the treatment with the catalyst.

$$\text{Removal (\%)} = [(A_0 - A)/A_0] \times 100 \quad (1)$$

Where, A_0 is initial dye concentration and A is dye concentration after adsorption. Methylene Blue shows the absorbance peak between 600 and 700 nm and the basic Violet 1 shows between 550 and 600 nm. The decrease in the peak intensity of MB at 600–700 nm and for BV1 at 550–600 nm confirms that the dye is being adsorbed by the catalyst.

3.5a Uptake of Methylene Blue: For optimizing the concentration of the dye, dye uptake was measured in aqueous solution at different concentrations i.e., 10 μM ,

Figure 6. TG analysis plot of $[\text{Cu}_2(2\text{-pzc})_2(\text{H}_2\text{O})_4]\{\text{H}_7\text{AlMo}_6\text{O}_{24}\}\cdot 17\text{H}_2\text{O}$, **1**.

20 μM and 50 μM MB solution. It was found that catalyst shows good uptake in higher as well as in lower concentrations. Figure 7 shows dye uptake by the

Figure 8. Percentage uptake of MB dye at various time intervals (Dye conc. 50 μM).

catalyst at a different concentration of MB solutions. The dye removal efficiency increases as MB concentration increases and becomes constant above 50 μM concentration (97% uptake; 19 mg/g). The effect of contact time between catalyst and dye molecules on

(a)

(b)

(c)

(d)

Figure 7. The adsorption by the compound in MB solutions of (a) 10 μM , (b) 20 μM and (c) 50 μM concentration, respectively. The compound shows the highest uptake in 50 μM MB solution i.e., about 97% {colour removal of MB solution after 5 min stirring, as shown in Figure 7(d)}.

Figure 9. Percentage uptake of MB dye in acidic and basic pH range. The compound shows approximately same efficiency in acidic as well as in basic medium (Dye conc. $50\ \mu\text{M}$).

uptake efficiency was measured to check how fast catalyst can adsorb dye. For this, MB solution ($50\ \mu\text{M}$, 10 mL) was taken as a target in a cuvette. Initial UV

absorbance of MB solution was measured and after that 10 mg catalyst was put into the solution and stirred. After 5 min, 2 mL solution was taken out and the catalyst was recovered by centrifugation and filtration. UV absorbance of the filtrate was recorded. The same process was repeated after 10 min, 15 min and 20 min and the result is shown in Figure 8. It was found that the title compound shows almost 90% (18 mg/g) uptake within 5 min.

In order to be used as an efficient catalyst for dye uptake from industrial effluents, it is important that the catalyst is equally efficient in acidic as well as in basic medium. Therefore, we checked the catalytic efficiency in both the mediums. As done earlier, 10 mg catalyst was added to each solution, stirred for 30 min and then the catalyst was recovered by centrifugation and filtration. The filtrate was monitored spectroscopically. It was observed that the catalyst is equally efficient in acidic (more than 99% uptake) as well as in basic medium (97% at pH 9 and 91% at pH 11) (Figure 9).

Figure 10. The adsorption by the compound in BV1 solutions of (a) $50\ \mu\text{M}$, (b) $100\ \mu\text{M}$ and (c) $150\ \mu\text{M}$ concentration, respectively. The compound shows the highest uptake in $150\ \mu\text{M}$ BV1 solution i.e., about 93% (colour removal of the BV1 solution after adsorption, as shown in Figure 10(d)).

Figure 11. Percentage uptake of BV1 dye at various time intervals (Dye conc. 150 μ M).

3.5b Uptake of Basic Violet 1: Same procedure as above was applied to check the efficiency of the catalyst towards uptake of another hazardous dye i.e., Basic Violet 1 (BV1) and it was found that catalyst is equally efficient for Basic Violet 1. For optimizing the concentration of the dye, the dye uptake was measured in aqueous solution at different concentrations i.e., 50 μ M, 100 μ M, and 150 μ M MB solutions (Figure 10). Optimization of dye concentration shows that catalytic efficiency is similar for higher as well as lower concentrated solutions. For adsorption of Basic Violet 1, less amount of catalyst was sufficient (0.5 g/L) in comparison to Methylene Blue solution (1 g/L). Time-dependent study shows that catalyst can adsorb $\sim$ 90% (36 mg/g) of the dye from the solution within 5 min (Figure 11).

It was found that Basic Violet 1 was not stable in basic medium and hence we checked catalyst efficiency only in acidic medium i.e., in pH 3 and pH 5. It was found

that the catalyst was quite efficient in both the pH, as shown in Figure 12.

Methylene Blue and Basic Violet 1 can be removed completely from the catalyst after repeated washing with fresh methanol several times. Moreover, it was also found that other solvents such as ethanol and acetone can also be used to desorb MB and BV from the catalyst.

4. Conclusions

An Al-supported Anderson–Evans cluster based hybrid solid has been synthesized under mild conditions and its structure has been characterized using Single Crystal XRD technique. The title compound possesses an alternative layer-like the arrangement of inorganic POM anions with organic cations. In addition, hydrogen bonds and $\pi \cdots \pi$ interactions play important roles in constructing 3-D crystal supramolecular frameworks. Dye adsorption properties on Anderson-type cluster-based solid has been analysed for the first time to the best of our knowledge. The dye adsorption properties of the catalyst were checked with two hazardous dyes, Methylene Blue and Basic Violet 1 and it shows very good uptake of both the dyes in aqueous solution. The catalyst can adsorb approx. 90% of both the dyes within 5 min. It was also observed that the catalyst was equally efficient in acidic as well as in basic conditions. However, the stability of this Anderson cluster based solid in the acidic and basic medium are yet to be explored for use as a potential catalyst for removal of dyes from wastewater. Further work on designing these types of POM-based structures and exploring their diverse properties are currently underway.

Figure 12. The adsorption by the compound in BV1 solutions at (a) pH 3 and (b) pH 5.

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