

Annexure I

List of publications

A. Publications in Journals

(i) Related to thesis work

1. Separation of ^{137m}Ba from ^{137}Cs using new ion exchanger $[\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]]$, **Sanjoy Dhara**, Sourav De, Sukalyan Basu, Michael G.B. Drew and Pabitra Chattopadhyay, *Radiochim. Acta*, 2007, **95**, 297-301.
2. Separation of ^{90}Sr - ^{90}Y pair over cerium(IV)iodotungstate cation exchanger, **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, *Appl. Radiat. Isot.*, Revised.
3. Separation of ^{137}Cs - ^{137m}Ba , ^{115}Cd - ^{115m}In and ^{198}Au - ^{110m}Ag at tracer level on aluminiumvanadate ion exchanger, **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, *Radiochim acta*, Revised.
4. Synthesis and characterization of quinolinephosphomolybdate ion exchanger and its application in the separation of ^{90}Y from ^{90}Sr , **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, (under preparation).
5. Synthesis, characterization and analytical applications of aluminium tungstate ion exchangers, **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, (under preparation).

(ii) Other work

6. Separation and determination of some metal ions on new chelating resins containing N, N donor sets, Sadhan Pramanik, **Sanjoy Dhara**, Shuvendu S. Bhattacharyya, Pabitra Chattopadhyay, *Anal. Chim. Acta*, 2006, **556**, 430-437
7. Separation of ^{90}Sr - ^{90}Y and ^{197}Au - ^{110}Ag pairs over cerium(IV)iodomolybdate cation exchanger, **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, (Under preparation).

B. Symposia paper

1. Separation of ^{137m}Ba from ^{137}Cs using new ion exchanger $[\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$, **Sanjoy Dhara**, Sourav De, Sukalyan Basu, Michael G.B. Drew and Pabitra Chattopadhyay, *Proceedings of DAE-BRNS Symposium of emerging trends in separation science and Technology, (SESTEC)*, 29th Sept.-1st Oct, 2006, Bhaba Atomic Research Centre, Mumbai, India.
2. Separation of ^{90}Sr - ^{90}Y pair over cerium(IV)iodotungstate cation exchanger, **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, *Proceedings of the Nuclear and Radiochemistry Symposium, NUCAR*, 14th Feb -17th Feb, 2007, Vadodara, Gujrat, India.
3. Separations of ^{137}Ba - ^{137m}Cs and ^{115}Cd - ^{115m}In mixtures on Aluminium vanadate Ion exchanger, **Sanjoy Dhara**, Pabitra Chattopadhyay, Sukalyan Basu, *Proceedings of DAE-BRNS Symposium of emerging trends in separation science and Technology, (SESTEC)*, 15th -17th March, 2008, Delhi University, Delhi, India.
4. Synthesis of aluminium tungstate and its application to the separation of ^{137m}Ba from ^{137}Cs at the tracer level, **Sanjoy Dhara**, Pabitra Chattopadhyay and Sukalyan Basu, *Proceedings of the Nuclear and Radiochemistry Symposium, NUCAR*, 7th Jan-10th Jan, 2009 (to be held), RC &1G, Mumbai, India.(Accepted).

C. Oral presentation

1. Separation of ^{137}Cs - ^{137m}Ba , ^{115}Cd - ^{115m}In and ^{198}Au - ^{110m}Ag at tracer level on aluminiumvanadate ion exchanger, **Sanjoy Dhara**, Sukalyan Basu, Pabitra Chattopadhyay, *UGC-Sponsored National Seminar on Advanced Spectroscopy, Theoretical Chemistry, Synthesis, Reactivity and Structure Evaluation*, 25th-27th April, 2008, Department of Chemistry, The University of Burdwan, Burdwan, India.

Separation of ^{137m}Ba from ^{137}Cs using new ion exchanger $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$

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Exchanger / Synthesis / Crystal structure / Radiochemical separation

Summary. A new polyoxometalate of chemical formula, $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ (**1**) containing Anderson type large anion has been synthesized and characterized by single-crystal X-ray structure determination and IR spectroscopic studies. The crystal of **1** is triclinic, spacegroup P-1 with cell dimensions, $a = 6.365(9)$ Å, $b = 10.37(1)$ Å, $c = 10.44(1)$ Å and $\alpha = 65.41(1)$, $\beta = 77.18(1)$, $\gamma = 86.58(1)$ and $Z = 1$. The compound **1** behaves as an ion exchanger and is stable in thermal, radiation and chemical environments. Radiochemical separation of the short-lived daughter ^{137m}Ba ($t_{1/2} = 2.50$ min) from its long-lived parent ^{137}Cs using this newly designed and synthesized ion exchanger has been developed.

1. Introduction

Polyoxometalates, in addition to their importance in catalysis, biochemical separation, medicinal chemistry [1–9] and in the design of new materials with novel electronic, magnetic and topological properties [10] have received significant attention in the field of radioanalytical chemistry as synthetic inorganic ion exchangers for trace level separations of cations due to the excellent stability of these materials towards thermal and radiation dose. Exchangers like stannic silicomolybdate and zirconium antimonate for the separation of $^{134}\text{Cs} - ^{134}\text{Ba}$ [11], ammonium phosphomolybdate and zirconium vanadate for parent-daughter separation between ^{90}Sr and ^{90}Y [12, 13], and the compounds like antimonate, molybdate, tungstate and silicate salts of zirconium and analogous compounds of titanium and thorium have been investigated [14, 15]. But in all cases, the preparation and evaluation of both poorly crystalline and amorphous compounds of polyoxometalates have been reported, with zirconium phosphate being the most widely studied [16, 17].

However, no attention has been paid to the structure-property relationships between the polyoxometalates and sorption behavior though the chemistry of such materials is of considerable interest because of their fascinating structural diversities [18–21]. Here we have syn-

thesized a new polyoxometalate of chemical formula, $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ containing an Anderson type large heteropolyanion suitable for column operation and it has been well characterized by single-crystal X-ray structure determination and IR spectroscopic studies. The exchange capacities of this exchanger for several cations of different oxidation states have been determined. The time of equilibration and the maximum weight of the exchanger for uptake of a fixed amount of radionuclide were also determined. The study of the extraction behavior and the mutual separation of cesium and barium radionuclides are of interest and importance to fulfil the increasing demand for the radioactive waste management for environmental protection. The results have revealed that this new compound is suitable for the separation of the carrier-free daughter nuclide (^{137m}Ba) from its parent (^{137}Cs).

2. Experimental

2.1 Apparatus and reagents

IR spectra were obtained by JASCO FT-IR model 420 using KBr disk and thermogravimetric analysis by Shimadzu TG50/DT50. The adjustment of pH was carried out with a systronics digital pH meter (Model 335). Radioactivity was measured with a scintillation counter equipped with a well type NaI(Tl) crystal detector.

The reagents for synthesis of the polyoxometalate were obtained from commercial sources and used without further purification. Stock solutions were prepared by dissolving the appropriate amount of analytical-reagent grade respective salts in doubly distilled water. The radio-tracer ^{137}Cs in equilibrium mixture of daughter ^{137m}Ba was obtained from Board of Radiation and Isotope Technology (BRIT), India.

2.2 Synthesis of $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$

The title compound was synthesized by dissolving $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (14.0 g, 57.84 mmol) and ammonium nitrate (0.1 g) in water (300 mL) followed by the addition of glacial acetic acid (40 mL) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (6.0 g, 24.84 mmol). The pH of the resulting solution was adjusted to 3.0 with nitric acid and the filtered solution kept in an open flask at room temperature for seven days; after which

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time the solution afforded block-shaped crystals of the compound (yield 0.8 g, 25% based on Mo). The crystals of the compound were characterized with IR spectra and single crystal X-ray diffraction, and the stability was assessed *via* thermogravimetric analysis.

2.3 X-ray analysis

Data were measured with Mo K_{α} radiation using the MAR-research Image Plate System. The crystal was positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 mins. Data analysis was carried out with the XDS program [22] to provide 3450 independent reflections. The structure was solved using direct methods with the Shelx86 program [23]. The hydrogen atoms on the $-\text{OH}$ groups bonded to Al were located in a difference Fourier and were refined with distance constraints with thermal parameters 1.2 times those of the atoms to which they were bonded. The hydrogen atoms on solvent water molecules could not be located and were not included. It was assumed that one water molecule of the five in the unit cell was protonated to give charge balance for $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$. The structure was then refined on F^2 using Shelxl-97.

2.4 Stability of 1 as exchanger

The stability of **1** as exchanger was determined in different chemical, thermal and radiation environments. Chemical stability was determined by taking a 0.5 g portion of the exchanger in 25 mL of acid or alkaline solution of various strengths. This mixture was then shaken for 48 h, the solid-exchanger was filtered off and washed with water. The exchange capacity of the compound for Na^+ was checked after this acid or alkali treatment. Thermal stability of the resins was studied employing a thermo-gravimetric analysis technique. Radiation stability was checked by measuring the exchange capacity of the exchanger, before and after γ -irradiation dose rate of 4.0 kGy/h by a ^{60}Co radiation source.

2.5 Determination of ion exchange capacity (IEC) of 1

Hydrogen ion capacity was determined by batch method. An accurately weighed (0.5 g) exchanger was treated with 2.0 M HCl and then filtered off, washed with distilled water and dried at 50°C for 2–3 h to remove free HCl. The acidic form of the exchanger was equilibrated with 20.0 mL 0.1 M NaOH solution for 1 h at room temperature at stirring condition and then the excess alkali was titrated with 0.1 M hydrochloric acid solution to determine the total acidic hydrogen content.

The exchange capacities of the exchanger for different alkali and alkaline metal ions were determined by batch method. To a glass-stoppered centrifuge tube (diameter 2.0 cm) containing 0.5 g of the dry solid-exchanger, 50 mL of 2.0 M solutions of different alkali and alkaline metal ions was added to the tube in each case; then the mixture was shaken for a period of 1 h. The exchanger was subsequently filtered and washed with doubly distilled water to remove the adhering H^+ ions. The exchange capacities for the metal ions were determined by measuring the liberated acid by titration with standard alkali.

2.6 Studies of separation

In column method, the glass column of 5 cm length and 1 cm inner diameter was packed with the exchanger (1.0 g). The column bed was first conditioned with 0.01 M HCl solution. A sample volume of 2.0 mL solution of measured radioactivity of cesium and barium radionuclides, where ^{137}Cs ($T_{1/2} = 30$ y) is in secular equilibrium with its daughter element $^{137\text{m}}\text{Ba}$ ($T_{1/2} = 2.55$ min), was passed through the column at a flow rate of 1.0 mL/min. After absorption of the mixture, 10 mL of 0.01 M HCl solution was passed through the column to ensure the total absorption of the mixture. Finally, the daughter fraction was eluted with 0.5% ascorbic acid which was followed by collecting the effluent in ten successive counting tubes (1.0 mL each). The γ -activity in each tube was measured with the help of NaI(Tl) γ -ray spectrometer several times with a time gap of 30 sec.

3. Results and discussion

3.1 Synthesis and characterization

The compound **1** was prepared by stirring the mixture of sodium molybdate and aluminium chloride in presence of ammonium nitrate at ambient temperature adjusting the pH of the mixture at 3.0. The compound was found to be insoluble in water, alcohol, moderately concentrated acid and alkali and other common organic solvents. The IR spectrum of the compound shows the characteristic peaks at 961, 872 and 779 cm^{-1} corresponding to the $\nu_{(\text{Mo}-\text{O})}$, $\nu_{(\text{Mo}-\text{O}-\text{Mo})}$ and $\nu_{(\text{Mo}-\text{O}-\text{Mo})}$ stretches, respectively [24].

By comparing the exchange capacity of sodium ion, the chemical stability of **1** in different acid and alkali media has been checked (Fig. 1). These experiments show that **1** is stable in mineral acid medium but in strongly oxidizing acids it undergoes degradation and the exchange capacity reduces. The exchanger is quite stable in normal chemical environment. In thermal analyses of **1**, a big endothermic peak appears near 100°C , indicating loss of water molecules, otherwise the compound is stable upto 150°C . Radiation stability of the exchanger was studied by determining the exchanging

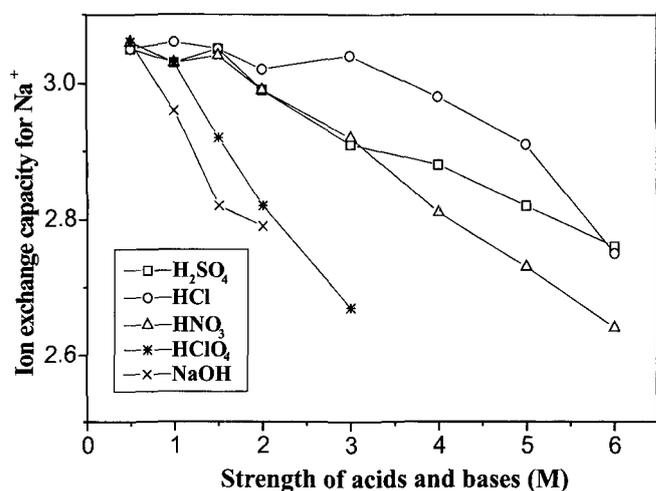


Fig. 1. Stability of the compound, $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ in different concentration of acids and base towards the exchange capacity.

capacity of **1** as exchanger before and after γ -irradiation at a dose rate of 4 kGy/h in dry condition. The exchanger was found to retain the exchange capacity for the metal ions up to a total dose of 40 kGy.

3.2 X-ray structure

The ORTEP view of **1** is illustrated in Fig. 2 together with the numbering scheme and the crystallographic data, and the selected bond distances and angles are listed in Tables 1 and 2, respectively. The $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ compound has the Anderson anion $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ based on $\text{Al}(\text{OH})_6$ octahedron surrounded by 6 MoO_3 octahedra. The crystal is triclinic, with space group P-1 and the anion is centrosymmetric around the aluminium atom. The structure consists of seven edge-shared-octahedra, six of which are Mo-octahedra arranged hexagonally around

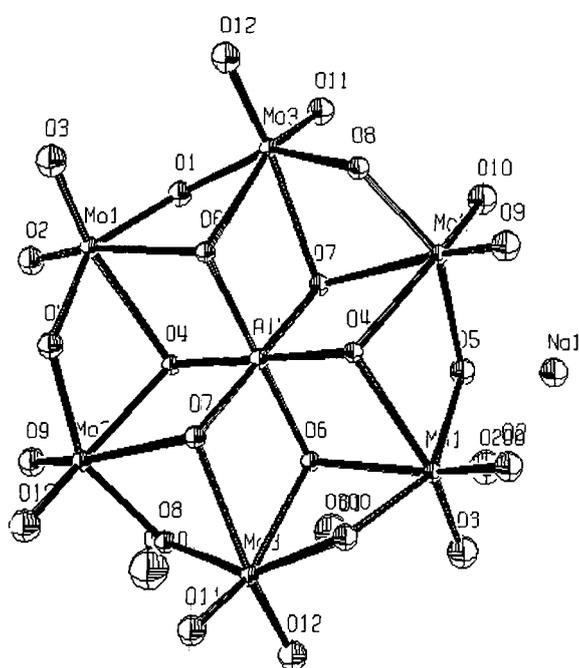


Fig. 2. Molecular structure of the exchanger, $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$.

Table 1. Crystallographic data of **1**.

Empirical formula	$\text{H}_{17}\text{AlMo}_6\text{Na}_2\text{O}_{29}$
Formula weight	1129.68
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	$a = 6.365(9)$ Å, $\alpha = 65.409(10)^\circ$ $b = 10.370(12)$ Å, $\beta = 77.178(10)^\circ$ $c = 10.443(12)$ Å, $\gamma = 86.585(10)^\circ$
Volume	$610.7(13)$ Å ³
Z, Calculated density	1, 3.072 g cm ⁻³
Absorption coefficient	3.178 mm ⁻¹
F(000)	536
θ range for data collection	2.16 to 25.63
Goodness-of-fit on F^2	1.126
Reflections: total	2075
Reflections: $I > 2\sigma(I)$	1958
Final R indices	$R1 = 0.0494$, $wR2 = 0.1321$
R indices (all data)	$R1 = 0.0533$, $wR2 = 0.1352$

the central octahedron containing hetero metal ion, which is Al^{3+} . In the crystal structure of **1** molybdenum-oxygen distances are divided into three groups: molybdenum-terminal oxygen [1.690(7)–1.734(6) Å]; molybdenum-bridging oxygen [1.932(6)–1.971(6) Å] and molybdenum- μ_3 -oxygen bridged to two molybdenum atoms and an aluminium atom [2.292(6)–2.341(6) Å]. The aluminium-oxygen distances are of three types having bond distances of Al4-O4, 1.892(6) Å; Al4-O6, 1.924(6) Å and Al4-O7, 1.919(6) Å though the last two types are very close to each other. From the angles around the molybdenum center it is obvious that four oxygens are in plane and another two in axial position. The three molybdenum atoms have similar geometries. To take Mo1 as typical, atoms O2, O3, O4 and O6 are in the equatorial plane (r.m.s. deviation 0.12 Å) with Mo1 in the plane while O1 and O5 are in axial position which is clear from the O-Mo-O angles as the angles are O2-Mo1-O3, 106.4(3)°; O4-Mo1-O5, 72.1(2)°; O4-Mo1-O6, 67.5(2)°; O5-Mo1-O6, 85.2(2)°; O1-Mo1-O5, 148.7(2)°. The charge of the neutral molecule has been satisfied by two $[\text{Na}(\text{H}_2\text{O})_2]^+$ ions and one $[\text{H}_3\text{O}]^+$ ion. The sodium ion is bonded to six oxygen atoms with an approximately octahedral environment. These include four terminal oxygen atoms O3, O2, O9 and O10 together with a bridging oxygen O5 and a water molecule O200. The packing of the molecules of the compounds shows the channel of the exchange of the ions (Fig. 3).

3.3 Sorption behavior of metal ions

The exchange capacities of different alkali and alkaline metal ions are tabulated in Table 3. The data show that the compound can be employed as an exchanger. The exchange capacity for sodium ion is the highest and the exchange capacities are in the order of $\text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Cs}^+ > \text{Ba}^{2+}$. The exchange capacity for alkaline metal ions is higher than that for the alkaline earth metal ions.

3.4 Radiochemical separation

Separation of barium from cesium of ^{137}Cs tracer solution has been carried out onto the column packed with this

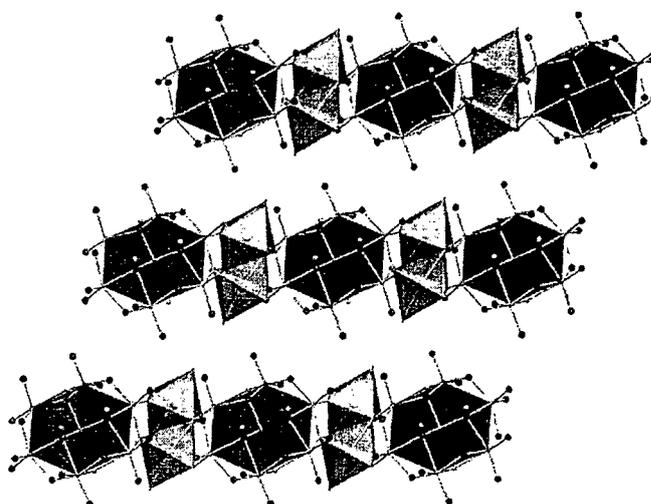


Fig. 3. Packing of the compound showing the path of the exchange having the counter cation with light black and the molybdate unit by deep black.

Table 2. Bond length (Å) and bond angle (°) of the title compound.

Bond distances (Å)					
Mo1–O2	1.713(6)	Mo2–O9	1.734(6)	Mo3–O11	1.723(6)
Mo1–O3	1.704(6)	Mo2–O10	1.690(7)	Mo3–O12	1.712(6)
Mo1–O1	1.971(6)	Mo2–O5	1.946(6)	Mo3–O1 ^a	1.932(6)
Mo1–O5	1.940(7)	Mo2–O8	1.941(6)	Mo3–O8	1.933(6)
Mo1–O4	2.311(6)	Mo2–O4	2.292(6)	Mo3–O6 ^a	2.298(6)
Mo1–O6	2.320(6)	Mo2–O7	2.341(6)	Mo3–O7	2.334(6)
Al4–O4	1.892(6)	Al4–O6	1.924(6)	Al4–O7	1.919(6)
Na1–O2 ^a	2.418(7)	Na1–O5	2.405(7)	Na1–O9 ^a	2.469(8)
Na1–O10	2.379(7) ^a	Na1–O200	2.315(8)	Na1–O2 ^a	2.560(8)
Bond angle (°)					
O2–Mo1–O3	106.4(3)	O1–Mo1–O2	96.5(3)	Al4–O4–Mo1	104.3(3)
O9–Mo2–O10	106.6(3)	O1–Mo1–O3	101.3(3)	Al4–O4–Mo2	104.6(3)
O11–Mo3–O12	105.9(3)	Mo1–O1–Mo3	116.6(3)	Al4–O6–Mo3	102.9(2)
O1–Mo1–O4	79.3(2)	Mo1–O5–Mo2	117.8(3)	Al4–O6–Mo1	102.9(2)
O1–Mo1–O5	148.6(2)	Mo1–O6–Mo3	91.8(2)	Al4–O7–Mo3	101.5(2)
O1–Mo1–O6	71.9(2)	Mo1–O4–Mo2	92.4(2)	Al4–O7–Mo2	102.0(3)
O2–Mo1–O4	96.0(3)	Mo2–O7–Mo3	90.5(2)	O4–Al4–O4	180.0(19)
O2–Mo1–O5	99.3(3)	Mo2–O8–Mo3	118.6(3)	O4–Al4–O7	85.4(3)
O2–Mo1–O6	161.2(2)	O4–Mo1–O5	72.2(2)	O4–Al4–O6	85.1(2)
O3–Mo1–O4	157.3(3)	O4–Mo1–O6	67.8(2)	O6–Al4–O7	86.4(2)
O3–Mo1–O5	100.1(3)	O5–Mo1–O6	85.1(2)	O7–Mo3–O8	72.5(2)
O3–Mo1–O6	90.7(3)	Mo1–O2–Na1	138.7(4)	Na1–O2–Na1	89.2(2)
Mo2–O5–Na1	113.7(3)	Mo1–O5–Na1	126.5(3)	Mo2–O9–Na1	136.9(3)

a: $-x, -y, -z$;b: $-1 + x, y, z$;c: $-1 - x, 1 - y, -z$;d: $-x, 1 - y, -z$.**Table 3.** Ion exchange capacity for different cations.

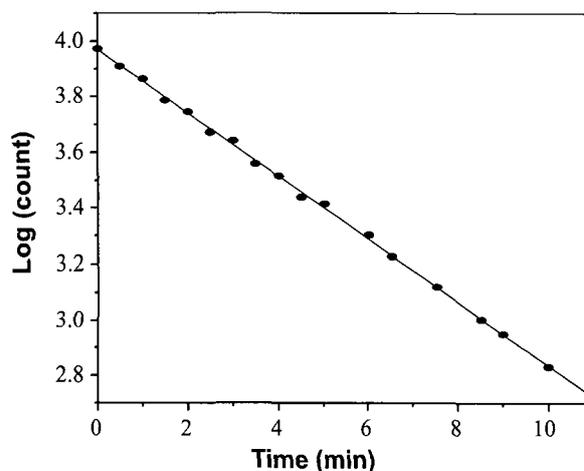
Cation	Exchange capacity ^a (mmol/g of exchanger)	Cation	Exchange capacity ^a (mmol/g of exchanger)
Li ⁺	2.73 ± 0.03	Be ²⁺	1.91 ± 0.02
Na ⁺	3.05 ± 0.03	Mg ²⁺	1.89 ± 0.03
K ⁺	2.44 ± 0.05	Ca ²⁺	1.81 ± 0.02
Cs ⁺	2.29 ± 0.03	Sr ²⁺	1.34 ± 0.04
NH ₄ ⁺	2.82 ± 0.08	Ba ²⁺	1.47 ± 0.05

a: Average of five determinations.

compound as exchanger. In this study, it has been observed that no activity was obtained when 0.01 M HCl solution was percolated through the bed of the exchanger after absorption of radioactive solution having the radioisotope ¹³⁷Cs. It indicates complete absorption of activity of both the radioactive nuclides (parent cesium nuclide as β⁻-emitter and γ-active daughter barium nuclide). But when 0.5% ascorbic acid solution as eluent was passed through the column, the eluted activity was due to the presence of the only barium ion confirmed by the characteristic half-life period ($T_{1/2} = 2.54$ min) of ^{137m}Ba (Fig. 4) and no growth of the activity due to the presence of long-lived ¹³⁷Cs was observed. It is an indication of complete retention of ¹³⁷Cs in the bed of the exchanger within the column. The results have revealed that this new material is suitable for the separation of carrier-free daughter nuclide (¹³⁷Ba) from its parent (¹³⁷Cs).

4. Conclusion

A new inorganic compound, Na₂(H₂O)₄(H₃O)[Al(OH)₆Mo₆O₁₈] has been synthesized and structurally characterized.

**Fig. 4.** Activity due to ^{137m}Ba after eluted with 0.5% ascorbic acid ($t_{1/2} = 2.6$ min).

This new material can be used as an exchanger in a generator system to have the carrier-free short-lived γ-active daughter product ^{137m}Ba from the long-lived ¹³⁷Cs. It is also predicted that this exchanger might be useful for the separation

of other alkali metals from selective alkaline earth metal ions.

5. Supporting material

Crystallographic data for the structural analyses of compound have been deposited with the Cambridge Crystallographic Data Centre, CSD No. 391 356. Copies of this information are available on request at free of charge from Klaus-Peter.Wirtz@FIZ-Karlsruhe.de.

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