INVESTIGATION OF THE CATALYTIC ACTIVITY OF HYBRID DECAVANADATE MATERIALS

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ABSTRACT. Three decavanadate $(V_{10}O_{28})^{6-}$ containing compounds were used to test their catalytic activity in the sulfoxidation reaction of diphenyl sulfide using environmentally friendly conditions (low temperature, non-toxic solvent). The compounds of interest for our study, $(NH_4)_2(H_2en)_2\{V_{10}O_{28}\}\cdot4H_2O$, $(H_2en)_3\{V_{10}O_{28}\}\cdot6H_2O$ and $\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$, were evaluated, showing good activity in sulfoxidation reaction and leading to complete conversion of the sulfide even after three runs. The tetraammonium decaaqualithium decavanadate, with the formula $\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$ was obtained through a modified literature method and its structure re-determined and investigated, giving similar results as previously described and confirming the structure of the used material.

Keywords: decavanadate derivatives, catalytic sulfoxidation, green and sustainable chemistry

INTRODUCTION

Sulfinyl (–SO–) and sulfonyl (–SO$_2$–) functional groups can be found in numerous compounds, [1,2] applied in many fields, such as biologically relevant derivatives, [2,3,4,5,6] fine chemicals, [7] pharmaceuticals, [2,8,9] ligands in catalyst structures, [10,11,12] etc. Because of these, their synthesis

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presents an interest in the scientific community. There are several different methods known in the literature for the synthesis of sulfoxides or sulfones. [1,13,14] Among the most commonly used methods for obtaining sulfoxides or sulfones is to oxidize the corresponding sulfide. [1,15] Different oxidation procedures are known, for example employing meta-chloro-perbenzoic acid (mCPBA), HIO_4, oxone, H_2O_2 as oxidizing agents. [14,16,17] In these cases, the central issue is represented by the formation of both the sulfone and the sulfoxide, which requires a laborious separation process to purify the desired products. Thus, the selective synthesis of the sulfoxide or sulfone represents a constant challenge. It is intensely studied to find easy, cheap, and sustainable methods for oxidizing sulfides to sulfoxide or sulfone, respectively. [14,16] In this context, different homogeneous and heterogeneous systems are used as catalysts, [14,17,18] mainly based on tungsten, vanadium, titanium. [6,17,18] Since vanadium containing compounds are well known in catalytic oxidation reactions, [19,20] among these the oxidation of sulfides, [21,22,23] hence for testing the catalytic activity of the decavanadates, the choice fell on this process.

Sulfoxidation reactions represent an interest in our research group as well, since one of our research areas has been focused on studying ligands that contain sulfinyl and sulfonyl groups. In the last few years, pincer-type ligands that contained such moieties were designed, synthesized then used. [24,25,26,27] For example, pincer ligands containing two sulfonyl groups, [27] or a sulfonyl group and a sulfinyl one [25] were used to obtain germylene and stannylene systems, [24,25,27,28] transition metal complexes [29] or p-block element containing compounds. [30] Furthermore, a ligand containing two sulfinyl groups in ortho position was also obtained, and it was used as ligand for obtaining phosphorus and silicon containing derivatives. [26] Our promising results in synthesizing such derivatives made us work on finding new methods for obtaining sulfoxides that are easy, cheap and more sustainable.

Examples of different polyoxometalates can also be found among the catalysts used for sulfide oxidation, [31] for example polyoxovanadates, among which are decavanadates. Decavanadate anion $(V_{10}O_{28})^{6-}$ containing compounds became frequently investigated in the scientific community for their diverse applications, [32] in materials chemistry, [33,34,35] energy conversion and storage, [35] catalytic [36] or biological activity. [37,38,39] Their properties can be tuned by selecting the appropriate charge balancing counter cations, [40] constructing structures with various application possibilities. They can be encountered in the role of catalyst in different processes as well. [19] However, using decavanadate-based materials for sulfide oxidation processes is not as standard. Some examples are known where $(V_{10}O_{28})^{6-}$ anion-containing materials were tested as catalyst for such processes, having different charge

balancing counter cations like organic phosphonium- or ammonium-salts [41,42], Mn-decavanadate clusters, [43] imidazole-decorated transition metal hybrid decavanadates, [44] aryl sulfonium moieties. [45]

In the present work, we aimed to present the catalytic activity of the decavanadate-based materials obtained and studied in our research groups. [38,39] These compounds presented varied structural features and were tested for their antimicrobial, antioxidant, or corrosion-inhibiting activity. [38,39] Given the ease of the synthetic procedure through which these materials could be obtained and investigated, we also decided to evaluate their role as catalyst. This determination was prompted by the general knowledge that cheap and easily obtained catalysts are needed to achieve sustainable synthetic procedures.

RESULTS AND DISCUSSIONS

Three different decavanadate-based materials were used as catalysts to test their activity in sulfide oxidation reactions: diethylenediammonium diammonium decavanadate tetrahydrat $(NH_4)_2(H_2en)_2\{V_{10}O_{28}\}\cdot4H_2O$ [38] (**Cat1**), triethylenediammonium decavanadate hexahydrated $(H_2en)_3\{V_{10}O_{28}\}\cdot6H_2O$ [39] (**Cat2**) and tetraammonium decaaqualithium decavanadate, with the formula $\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$ (**Cat3**) (**Table 1**).

Table 1. Formula and abbreviation of the tested decavanadate catalysts.

Formula	Abbreviation
$(NH_4)_2(H_2en)_2\{V_{10}O_{28}\}\cdot4H_2O$	**Cat1**
$(H_2en)_3\{V_{10}O_{28}\}\cdot6H_2O$	**Cat2**
$\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$	**Cat3**

The derivatives tested as catalysts were selected taking into account their facile synthesis, following the sustainability guidelines. [46] Vanadium-containing polyoxometalates seemed like a good starting point because of their already proven use in sulfoxidation reactions, as detailed in the introduction. Furthermore, none of the elements on which these materials were based are critical from the availability point of view. [47] The materials were prepared in an aqueous solution, using straightforward and readily available reagents.

As described in the previous papers of the research groups, both **Cat1** [38] and **Cat2** [39] were synthesized via wet chemistry, using ammonium metavanadates and ethylenediamine as structure-directing agents under acidic conditions, leading to the protonation of the organic moieties within the structure,

then the crystals were obtained via slow evaporation. Single-crystal X-ray diffraction analysis showed that the structural integrity of **Cat1** was maintained by hydrogen bonds involving nitrogen and oxygen atoms among ammonium ions, ethylenediamine, water, and decavanadates. In contrast, the structure of **Cat2** was stabilized by similar hydrogen bonds but with no presence of ammonium ions. [38,39] The promising results obtained in these studies encouraged us to continue their investigation and to test these materials for their catalytic role in sulfoxidation reactions.

Besides these derivatives, we aimed to obtain new decavanadate materials as well, containing lithium counterions. Using straightforward, easy synthesis, we aimed to evaluate the effect of starting materials and synthetic conditions in forming such new decavanadates. For this, ammonium metavanadate (NH_4VO_3) was dissolved in nitric acid, then a solution of lithium hydroxide (LiOH, 10 % solution) was added until the pH was adjusted to 5, the solution was then maintained under stirring at 50 °C. Single crystals of **Cat3** suitable for crystallographic studies were obtained after filtration and gradual evaporation at ambient temperature. The analysis of the crystals through single-crystal X-ray diffraction showed that the structure of the compound we obtained is identical to one described previously in the literature. [48,49] The X-ray diffraction analysis on a single crystal of the compound revealed the existence of four ammonium cations, a decaaquadilithium cation $[Li_2(H_2O)_{10}]^{2+}$ and the arrangement is surrounded by decavanadate cluster anion $[V_{10}O_{28}]^{6-}$. The solid-state structure is shown in **Figure 1**.
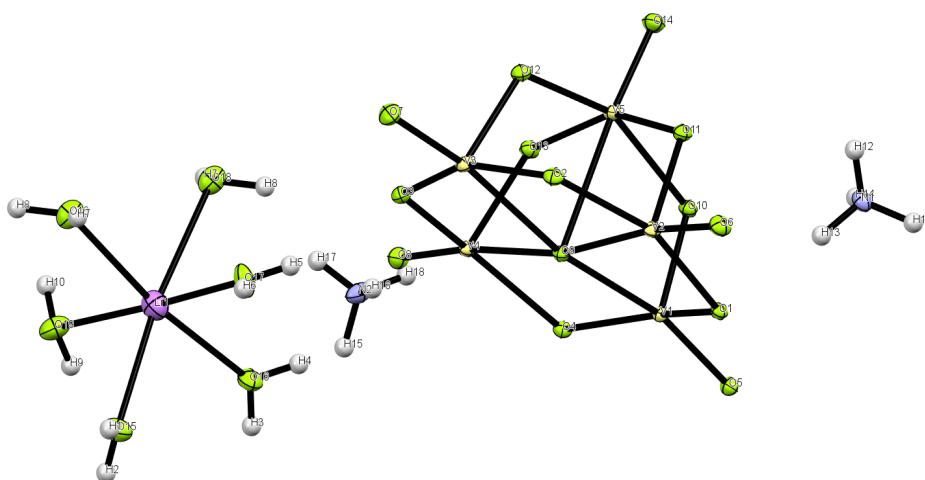

Figure 1. The ORTEP image of the asymmetric unit of **Cat3** with non-hydrogen atom displacement ellipsoids drawn at a 60% probability level.

The X-ray measurement was performed at low temperature (T= 100 K), this leading to better results in the structure analysis. The study of the structure revealed that the V–V distances within the decavanadate cluster anion $[V_{10}O_{28}]^{6-}$ range from 3.0631(3) to 3.1195(3) Å, (**Table 4** in Experimental Section), which is consistent with those found in comparable structures containing such anions. [50] The average V–O distances within the decavanadate entity also have values similar to those observed in known structures. [37,39,50,51,52,53] The dication $[Li_2(H_2O)_{10}]^{2+}$ consists of Li atoms surrounded by six water molecules, two of which act as a bridge between the two neighbouring $[LiO_6]$, with a Li–Li distances of 3.228(5) Å. Decavanadate, decaaqualithium and ammonium cations are all linked via N-H...O and O-H...O as hydrogen bonds, which are the primary basis of the structural cohesion of the system. The interaction between ammonium cations, decaaquated lithium cations, and decavanadate anions, all connected by a network of hydrogen bonds, defines the architecture of this compound's crystal structure. The system's structural backbone and basic building components are the decavanadate anions. The decaaqualithium cations are arranged in a superposition pattern around these anions. (**Figure 2**)
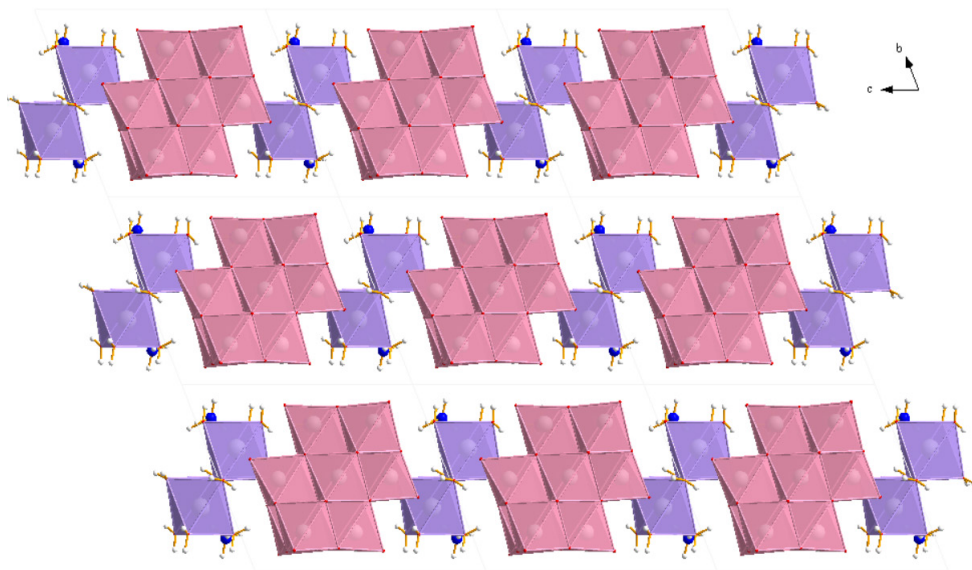

Figure 2. Illustration of the compound **Cat3** along the *a* axis, with decavanadate polyhedra = old rose, decaqualithium polyhedra = lavender.

The obtained **Cat3** was analyzed through FT-IR (Fourier transformed IR) and thermal analysis, showing similar characteristics to those previously presented in the literature. [48,49] For example bands at 984-950 cm^{-1} and 840-733 cm^{-1} for ν(V=O) and ν(O-V-O) vibrations, bands at 3180 cm^{-1} and 1418 cm^{-1} for N–H and H–N–H vibrations, and vibrations δ(OH) and ν(OH) in the range of 3450–3560 cm^{-1} and 1620 cm^{-1} in the infrared spectrum confirm the presence of all the moieties in the structure of **Cat3**.

Investigation of catalytic activity

In the present work, decavanadates **Cat1 - 3** were tested for their catalytic activity in a sulfoxidation process on a model substrate, namely diphenyl-sulphide. (**Scheme 1**)
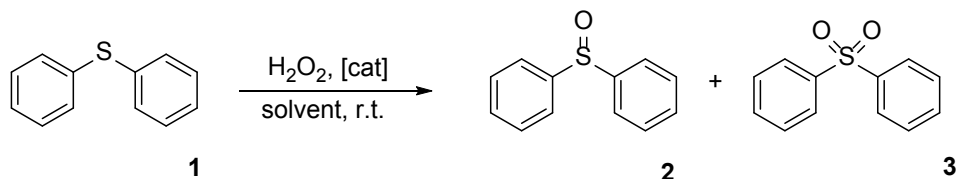
Scheme 1. Oxidation of diphenyl-sulfide.

For the catalytic test in the selection of the reaction conditions, the following criteria were taken into consideration: the reaction should take place at room temperature (22 °C ± 2), the reaction time should be as short as possible, the oxidant should be easily handled, the solvents should be easily accessible and with low toxicity.

For the selection of solvents, first the guidelines of green and sustainable chemistry were followed, [54,55] that consider different safety, health and environment related criteria. All the solvent guides rank water, ethanol, 2-propanol and ethyl acetate as recommended solvents. In contrast, solvents like methanol, ethylene glycol, acetone, cyclohexanone, benzyl alcohol, tert-butyl alcohol are recommended with some warnings. Furthermore, literature data was also considered, following examples of catalytic sulfoxidation reactions, where solvents like methanol, [56] water, etc. were successfully employed. Thus, all three catalysts **Cat1 - 3** (**Table 1**) were tested in five different solvents, namely methanol (MeOH), ethylene-glycol (EG), water, ethanol (EtOH), 2-propanol (*i*-PrOH). An excess of hydrogen-peroxide was used as oxidant (35% solution), this being one of the most atom-economical next to molecular oxygen, but easier to handle.

The reactions were followed through ^1H NMR spectroscopy, where both the diphenyl sulfoxide **2** (($C_6H_5)_2SO$) and diphenyl sulfone **3** (($C_6H_5)_2SO_2$) present characteristic signals. In the ^1H NMR spectra the conversion and the percentage of compounds **2** and **3** could be easily calculated and followed (**Figure 3**). In the ^1H NMR spectra sulfone **3** gives a doublet signal at 7.95 ppm, while sulfoxide **2** gives a doublet of doublets at 7.65 ppm (both in $CDCl_3$), and neither overlaps with other signals; thus, following the progress of the oxidation, conversion and the ratio between the two products could be possible.
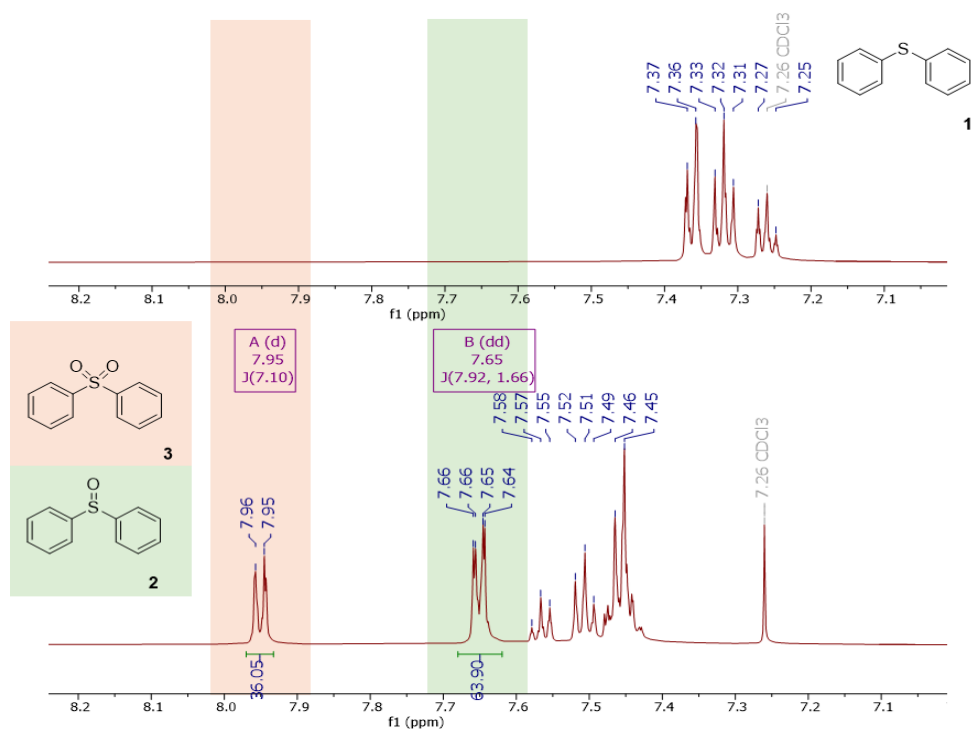
Figure 3. Use of ^1H NMR spectroscopy for following the oxidation process.

The data obtained from the investigation of the three decavanadate based materials **Cat1 - 3** in the oxidation reaction are presented in **Table 2**, showing conversion and the percentage of the obtained compound **2** and **3**.

In the chosen catalytic conditions, in most cases all three catalyst **Cat1 - 3** had similar performance. Full conversion of difenyl-sulfide was observed in MeOH, EtOH, *i*-PrOH, while in EG and H_2O lower conversion was obtained. (**Table 2**)

Table 2. Oxidation results.

Catalyst	Solvent	Conversion* (%)	Compound 2* (%)	Compound 3* (%)
none[a]	MeOH	13	100	0
Cat1[b] (no H_2O_2)	MeOH	0	0	0
Cat1	MeOH	100	64	36
	EG	100	27	73
	H_2O	52	68	32
	EtOH	100	16	84
	i-PrOH	100	42	58
Cat2	MeOH	100	22	78
	EG	81	28	72
	H_2O	100	11	89
	EtOH	100	24	76
	i-PrOH	100	32	68
Cat3	MeOH	100	13	84
	EG	52	53	47
	H_2O	100	34	66
	EtOH	100	10	90
	i-PrOH	100	40	60

Reaction conditions: diphenyl-sulfide (0.27 mmol), solvent (3 mL), 1 mL H_2O_2, catalyst (1.5 mol%), room temperature, 2h. [a]no catalyst was used. [b]no H_2O_2 was used. *without separation from reaction mixture, calculated from ^{1}H NMR measurements. Methanol (MeOH), ethylene-glycol (EG), water (H_2O), ethanol (EtOH), 2-propanol (*i*-PrOH).

In the case of **Cat2** and **Cat3** selectivity towards the sulfoxide **2** was better when using *i*-PrOH, then MeOH or EtOH (32-40% *vs*. 10-24%), while for **Cat1** selectivity towards sulfoxide was better in the case of MeOH (64%). However, when using EtOH, better selectivity towards sulfone **3** could be noted (>76%). No 100% selectivity towards sulfoxide **2** could be achieved, higher selectivity towards the corresponding sulfone **3** was predominant in most cases. However, in the case of **Cat1**, higher selectivity towards the sulfoxide could be observed when using MeOH or H_2O (>60%). Interesting to note, that high selectivity (90%) towards sulfone **3** could be observed in case of **Cat3** in EtOH.

For further assessing the properties of the catalytic system, up-scaling and catalyst recycling test were realized as well. The activity of **Cat3** was tested on 0.5 g substrate, using *i*-PrOH as solvent. The catalyst was then re-used in two more runs. Realizing the experiment on a larger scale (0.5 g substrate) led to full conversion, as seen in the screening test previously, however, in this case selectivity towards sulfone **3** was observed. It is noteworthy that even after the 3rd run the catalyst **Cat3** led to complete conversion of the diphenyl-sulfide in 2 hours. It is interesting the fact that after the 2nd run, the selectivity of the process was different then after the 1st and 3rd runs, leading to 64% of sulfoxide **2** in the product mixture.

These results reveal that the tested catalytic systems can be easily tuned to obtain a fast, environmentally friendly process towards obtaining sulfones. To note, that the catalyst **Cat3** led to complete conversion even after the 3rd run.

CONCLUSIONS

In this work we investigated the catalytic activity of three decavanadate species $(NH_4)_2(H_2en)_2\{V_{10}O_{28}\}\cdot 4H_2O$ (**Cat1**), $(H_2en)_3\{V_{10}O_{28}\}\cdot 6H_2O$ (**Cat2**) and $\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$ (**Cat3**), in sulfoxidation reactions. Compound **Cat3** was obtained through a modified literature procedure, then structurally investigated as well, in order to determine its structural features. The data obtained was in agreement with those previously reported in the literature, more than that, the single crystal X-ray diffraction analysis provided a solid-state structure with improved characteristics. In the case of all three catalysts **Cat1**-**3**, full conversion of the diphenyl-sulfide substrate was observed in a short reaction time (2h), in most solvents (MeOH, EtOH, *i*-PrOH), with low catalyst loading (1.5 mol%), however with no selectivity towards the sulfoxide or sulfone. Moreover, **Cat3** showed good results in the recyclability test, giving full conversion of the substrate even after three runs. Even though the selectivity of the chosen reaction condition was not as envisioned beforehand, it provides a quick and easy way to obtain sulfonyl and sulfinyl group containing compounds. In perspective, further adjustments will be made in the structure of the decavanadates and the reaction conditions in order to obtain a catalytic system with a cheap, simple catalyst in mild and environmentally favorable reaction conditions.

EXPERIMENTAL SECTION

Synthesis and crystallization of decavanadate derivatives

Catalysts were prepared according to literature procedures, as follows: **Cat1** and **Cat2** were prepared according to the procedures described in the literature [37,39], while **Cat3** was obtained using a modified literature procedure. [48,49]

$(NH_4)_2(H_2en)_2\{V_{10}O_{28}\}\cdot4H_2O$, **Cat1** – obtained using the previously described method [38].

Ammonium metavanadate $(NH_4)VO_3$ (300 mg, 2.5 mmol) was dissolved in 20 mL distilled water at 90 °C under continuous stirring. The obtained light-yellow solution was allowed to cool to 50 °C, then copper(II) chloride tetrahydrate $(CuCl_2\cdot4H_2O$, 80 mg, 0.4 mmol) and ethylenediamine (30 mg, 0.5 mmol) were added, obtaining a brown colored solution. The pH of this solution was adjusted to pH 5 by adding nitric acid $(HNO_3$, 3M solution) dropwise. The mixture was further stirred for 30 minutes then filtered and kept at room temperature until the apparition of an orange colored, crystalline solid.

$(H_2en)_3\{V_{10}O_{28}\}\cdot6H_2O$, **Cat2** – obtained using the previously described method [39]

Ammonium metavanadate (300 mg, 2.5 mmol) was dissolved in 20 mL distilled water at 95 °C. The light-yellow colored solution was then cooled to 50 °C and ethylenediamine (30 mg, 0.5 mmol) was added before adjusting the orange-colored solution to pH 4 by adding HNO_3. The resulting brown solution was filtered and slowly evaporated at room temperature to give orange crystals, which were separated, washed and dried in air.

$\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$, **Cat3** – obtained using modified literature procedure [48,49]

Ammonium metavanadate $(NH_4VO_3$, 300 mg, 2.5 mmol) was dissolved in nitric acid (10 ml, 3 M), yielding a measured pH of 2. Subsequently, a solution of lithium hydroxide (LiOH, 10 %) was added dropwise until the pH was adjusted to 5. The mixture was then stirred at moderate temperature (50 °C) for 30 min, filtered and cooled to room temperature. By gradual evaporation at ambient temperature, coral-like single crystals, suitable for crystallographic studies, were obtained after 3 days. It's important to note that this structure has been previously published, with its characterization conducted at room temperature resulting in a higher R-factor of 3%. However, through the redetermination at 100 K in the present work, a lower R-factor was achieved, leading to a more stabilized structure and a refined understanding of its configuration. [24,25].

General procedure

In a typical experiment 50 mg (0.27 mmol) diphenyl-sulphide, 3 mL solvent, 1 mL H_2O_2 35% solution, 5 mg catalyst (1.5 mol%) were added in a round bottom flask and stirred at room temperature for 120 minutes. Water and ethyl-acetate were added, the phases separated, the organic phase washed with water, then dried under vacuum and analysed by ^{1}H NMR spectroscopy. NMR was registered in $CDCl_3$.

General considerations

All chemicals were purchased from usual chemical suppliers and used as received. NMR spectra were recorded in deuterated chloroform on Bruker Avance 400 (operating frequency of 400.13 MHz for ^{1}H) as well as Bruker Avance 600 (frequencies of 600.13 MHz for ^{1}H) spectrometers. The chemical shifts are given in ppm relative to the solvent residual peak for the ^{1}H NMR spectra.

X-ray crystal structure re-determination of Cat3

The measurement was performed at low temperature (T= 100 K) using a Bruker D8 Venture diffractometer equipped with a CCD detector and a molybdenum (Mo) radiation source with Mo-Kα (λ= 0.71073 Å) at 100 K in the range of 3.0° < θ < 28.3° to perform a single-crystal X-ray diffraction measurement. Processing of the acquired data was performed using SHELXL software. [57]. Data reduction was carried out using SAINT [58] and the data was corrected for Lorentz polarisation and absorption effects using the SADABS program. [59] Refinement was carried out using APEX 3 software. [60] The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed and idealized positions and refined with a driving model and a mutual isotropic thermal parameter. The drawings of the molecular structures were created with the DIAMOND [61] and MERCURY [62] programs. **Table 3** presents the crystallographic data and experimental details of the data collection and structure refinements.

The use of single-crystal X-ray analysis allowed the thorough examination of the obtained material **Cat3**. It crystallizes in the triclinic space group P$\bar{1}$, with a = 8.4427 (2) Å, b = 10.1475 (2) Å, c = 11.0738 (3) Å, α = 68.445 (1)°, β = 86.957 (1)°, γ = 67.637 (1)°, and Z = 1. The structure has been refined to an R-factor of 1.5%. Hydrogen bonding interactions (O-H···O and N-H···O) tie water molecules and inorganic structures. Fourier-transform infrared spectroscopy results reveal distinct bands associated with water molecules, decavanadate, and ammonium cations, aligning with the crystalline structure.

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Table 3. Structure refinement, data collection and crystal data for **1**.

Chemical formula	$O_{28}V_{10}\cdot10(H_2O)\cdot4(H_4N)\cdot2(Li)$
Mr	1223.61
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	8.4427 (2), 10.1475 (2), 11.0738 (3)
α, β, γ (°)	68.445 (1), 86.957 (1), 67.637 (1)
V (Å^3)	811.85 (3)
Z	1
F(000)	604
Radiation type / λ Å)	Mo K / 0.71073
D_x (Mg,m^{-3})	2.503
R($_{int}$)	0.020
No. measured reflections	27842
No. independent reflections	4010
reflections with I > 2 σ(I)	3916
θ_{max}, θ_{min}	28.3°, 3.0°
Reciprocal space	h = -11$\rightarrow$11 k = -13$\rightarrow$11 l = -14$\rightarrow$14
$R[F^2 > 2\sigma\ (F^2)]$/ $wR(F^2)$/ S	0.015/0.041/1.12

The crystal structure reveals the existence of four ammonium cations, a decaaquadilithium cation $[Li_2(H_2O)_{10}]^{2+}$. The arrangement is surrounded by decavanadate cluster anion. $[V_{10}O_{28}]^{6-}$. With ten edges and ten corners shared by each $[VO_6]$ octahedra, the decavanadate anion has a cage-like structure.

Sharing edges, six octahedra are organized in a 2 x 3 equatorial plane; the other four octahedra are positioned above and below the equatorial plane, linked by inclined edges shared with the six octahedra in front. The average <V-O> distances within the decavanadate entity have the values shown in **Table 4**, which are similar to those observed in other structures comprising such oxoanions.[37,52,63,64,65]

As shown in **Table 5**, BVS calculations, using the I. D. Brown and D. Altermatt approach, [66] revealed that all vanadium atoms have valence sums ranging from 4.96 to 5.01, with an overall average of 4.98, close to the ideal value of 5 for V (V). The bond valences of the oxygen atoms range from 1.62 to 2.06, indicating that our structure contains a cluster of deprotonated decavanadate (**Table 6**).

The dication $[Li_2(H_2O)_{10}]^{2+}$ consists of two edge-shared $[LiO_6]$ octahedra. Each Li atom is surrounded by six water molecules, two of which act as a bridge between the two $[LiO_6]$. The distance between Li1 – Li1^{ii} ions within the cationic structure is of 3.228(5) Å. The oxygen atom O18, located precisely between the two lithium atoms making up the metal cation,

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therefore has the highest Li-O distance in this context. Cations and anions alternate in structure, forming an arrangement sequence, as illustrated explicitly in **Figure 1** along the *a* axis.

Table 4. Angles and distances selected in $\{V_{10}O_{28}\}^{6-}$ of **Cat3**.

$\{V_{10}O_{28}\}^{6-}$			
Distances (Å)		Angles (°)	
V1—O5	1.6869(8)	O1—V1—V3^i	90.23(2)
V1—O10	1.6994(8)	O5—V1—O9^i	166.20(4)
V1—O1	1.9091(8)	O10—V1—O1	96.99(4)
V1—O4	1.9240(8)	O5—V1—O4	97.07(4)
V1—O9	2.0914(8)	O10—V1—O4	96.59(4)
V1—O9^i	2.1115(8)	O1—V1—O4	156.34(3)
V2—O6	1.6155(8)	O6—V2—O11	104.06(4)
V2—O2	1.8178(8)	O2—V2—O11	94.58(4)
V2—O11	1.8288(8)	O6—V2—O4^i	98.47(4)
V2—O4^i	1.9948(8)	O2—V2—O4^i	90.14(4)
V2—O1	1.9954(8)	O11—V2—O1	89.71(4)
V2—O9^i	2.2458(8)	O4^i—V2—O1	76.43(3)
V3—O7	1.6038(9)	O14—V5—O13	102.96(4)
V3—O12	1.8250(8)	O12—V5—O13	89.45(4)
V3—O2	1.8685(8)	O11—V5—O13	153.21(4)
V3—O3	1.8895(8)	O14—V5—O10	100.68(4)
V3—O5^i	2.0566(8)	O12—V5—O10	154.43(4)
V3—O9^i	2.2908(8)	O11—V5—O10	84.75(3)
V4—O8	1.6267(8)	O7—V3—O5^i	97.51(4)
V4—O13	1.7994(8)	O12—V3—O5^i	157.42(4)
V4—O3	1.8117(8)	O2—V3—O5^i	83.94(3)
V4—O4	1.9946(8)	O3—V3—O5^i	82.83(3)
V4—O1^i	2.0358(8)	O7—V3—O9^i	171.80(4)
V4—O9^i	2.2196(8)	O12—V3—O9^i	83.11(3)
V5—O14	1.5982(8)	O13—V4—O4	91.33(4)
V5—O12	1.8522(8)	O3—V4—O4	154.84(4)
V5—O11	1.8543(8)	O8—V4—O1^i	98.68(4)
V5—O13	1.9054(8)	O13—V4—O1^i	155.89(4)
V5—O10	2.0218(8)	O3—V4—O1^i	88.71(3)
V5—O9^i	2.3580(8)	O4—V4—O1^i	75.53(3)

Table 5. BVS per Vanadium atoms of **1**.

Octahedral	V1O$_6$	V2O$_6$	V3O$_6$	V4O$_6$	V5O$_6$
BVS	5.00	4.98	5.01	4.99	5.02

Table 6. BVS per Oxygen atoms of **1**.

Atome	Σs	Atome	Σs
O1	1.853	O8	1.787
O2	1.825	O9	1.683
O3	1.826	O10	1.728
O4	1.789	O11	1.735
O5	1.732	O12	1.778
O6	2.051	O13	1.699
O(7)	1.764	O(14)	1.693

Decavanadate, decaaqualithium and ammonium cations are all linked via N-H...O and O-H...O as hydrogen bonds, which are the main basis of the structural cohesion of the system. The overall stability and order of these molecular arrangements is essentially maintained by the hydrogen bonds that make them up.

The structural configuration reveals the presence of multiple hydrogen bonds, uniformly characterized by their weak nature, with an average bond length of 2.99 Å. Refer to **Table 7** for a full list of these important interactions, where many of the hydrogen bonding details are carefully documented.

Table 7. Bond number (s) calculations for all the oxygen atoms
in the $\{V_{10}O_{28}\}^{6-}$ anion in **Cat3**.

D—H⋯A	D⋯A (Å)	D—H⋯A (°)
O17-H5⋯O3	2.78(17)	165.930(2604)
O16-H4⋯O8	2.92(18)	152.198(2337)
N2-H16⋯O8	2.85(16)	171.372(1978)
N1-H13⋯O11	3.06(16)	108.549(1904)
N1-H14⋯O10	3.01(19)	109.344(1600)
N1-H13⋯O1	2.89(17)	173.282(2341)

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