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An unprecedented silver-decavanadate dimer investigated using ion-mobility mass spectrometry†

Thomas McGlone, Johannes Thiel, Carsten Streb, De-Liang Long and Leroy Cronin*

A silver(I)-linked decavanadate system has been synthesised, and characterised in both the solid-state and solution showing that two cluster units are held in a specific, dimeric arrangement wholly supported by cooperative hydrogen bonds, and ion-mobility mass spectrometry (IM-MS) was used to analyse the system yielding significant information on the secondary building units and aggregation behaviour supported by hydrogen bonding.

The assembly routes of polyoxometalate (POM)-based systems, while traditionally accepted as complicated and somewhat difficult to probe, can now in the case of many examples, be regarded with a much increased level of understanding thanks to the design of rational experimentation and sophisticated analytical techniques.[1,2] The presence of active templating species,[3] thermodynamically stable secondary building units[4] and intelligent use of non-covalent forces of attraction have been proven to play significant roles in the construction of huge supramolecular assemblies based on core inorganic entities approaching dimensions of up to 5 nm.[5,6] Hence it has become increasingly evident that the serendipitous discovery of novel cluster types is fast becoming an outdated approach in the development of POM-based research and the real challenge is the rational selection of appropriate building blocks towards the assembly of advanced functional materials.

While POM clusters comprising tungsten and molybdenum largely dominate this field of research,[7–9] polyoxovanadates also contribute a significant amount, with an array of highly versatile structures already reported. The tendency of these systems to incorporate mixed valent arrangements with reduced (V^{IV}) and fully oxidized (V^V) vanadium centres has also generated much interest.[10,11] The lower acidic nature of the polyoxovanadates, compared to tungstates and molybdates, allows protonation at moderate pH values and hence unique supramolecular assemblies can result, due to the acceptance of hydrogen bonds at non-protonated oxygen atoms and donating hydrogen bonds at

protonated oxygen ones.[12] The decavanadate cluster, $[H_xV_{10}O_{28}]^{y-}$ is a well established secondary building unit[13] and can be found with up to four protons per cluster, with respect to the level of acidity during preparation. A study by Day and Klemperer revealed the location of the protons in a triprotonated decavanadate dimer, $\{[H_3V_{10}O_{28}]_2\}^{6-}$, as a *n*-tetrabutyl-ammonium (TBA) salt in a $CH_3CN/CHCl_3$ mixture and also showed that the addition of H_2O to CH_3CN mixtures of $(TBA)_3[H_3V_{10}O_{28}]$ dissociates dimers of decavanadate anions into monomers.[14] Ozeki *et al.* recently described a report on the association/dissociation behaviours of the decavanadate anions proving reversibility driven by the protophobic/protophilic nature of the solvent. Under protophobic acetone rich conditions the decavanadate anion prefers a self-associated hydrogen bonded dimer of $\{[H_3V_{10}O_{28}]_2\}^{6-}$ which is dissociated into a monomeric species as the concentration of protophilic dioxane is increased.[12,15]

Herein, we describe the association of a silver(I)-linked decavanadate dimer species, $\{(Ag(CH_3CN)_3)_3[H_3V_{10}O_{28}] \cdot CH_3CN\}_2$ (**1**), prepared from $(TBA)_3[H_3V_{10}O_{28}]$ in acetonitrile. The dimeric assembly fits well with previous hypotheses that aprotic, protophilic solvents (including acetonitrile) drive the formation of the specific supramolecular assembly as a direct result of protonated cluster positions inducing hydrogen bonding interactions.[15] The novel structure has been characterised by single crystal X-ray diffraction (SC-XRD), flame atomic absorption spectroscopy (FAAS), thermogravimetric analysis (TGA), IR and bond valence sum (BVS) calculations. In addition, **1** was investigated using ion-mobility mass spectrometry (IM-MS), a developing technique used to probe metal oxide systems, allowing size separation for the investigation of supra-molecular assemblies.[16] This system seemed ideal for such a study, with the potential aim of understanding the dimeric supramolecular assembly process driven by hydrogen bonding.

The straightforward synthesis of system **1** involved the reaction of $(TBA)_3[H_3V_{10}O_{28}]$ with silver nitrate in acetonitrile and subsequent crystallisation. Due to its high affinity for oxygen donor ligands, the silver(I) ion has been readily used to functionalise POMs and a diverse range of Ag(I)–POM complexes have already been obtained.[17–20] Analysis of the crystal structure of **1** revealed that each inorganic cluster unit, $[H_3V_{10}O_{28}]^{3-}$, is covalently coordinated to three silver centres with bond distances $d_{O–Ag}$ = 2.478(2), 2.635(4) and 2.647(4) Å. The silver centres themselves feature a tetrahedral environment with three acetonitrile

WestCHEM, School of Chemistry, The University of Glasgow, Glasgow, UK G12 8QQ. E-mail: L.Cronin@chem.gla.ac.uk; Web: http://www.croninlab.com; Fax: (+44) 141-330-4888; Tel: (+44) 141-330-6650
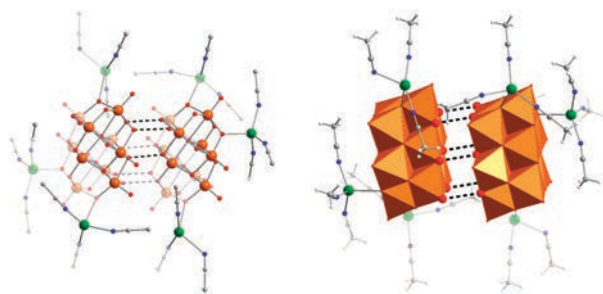
Fig. 1 Illustration of system **1** with the standard 'ball and stick' model (left) and polyhedral version (right) shown. Two $[H_3V_{10}O_{28}]$ clusters are held together *via* a series of six hydrogen bonds formed between protonated and non-protonated oxygen atoms on the POM cage and each cluster features three $\{Ag(CH_3CN)_3\}$ groups attached. V: orange polyhedra, O: red spheres, Ag: green, N: blue, C: grey. The oxygen centres involved in hydrogen bonding interactions are enlarged for clarity.
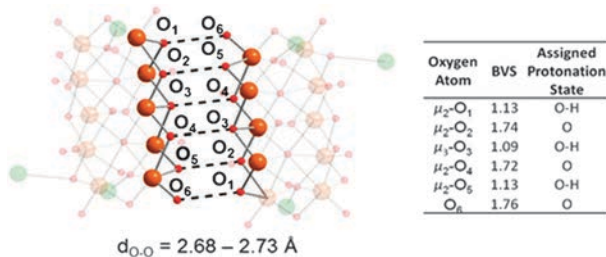

Oxygen Atom	BVS	Assigned Protonation State
$\mu_2\text{-}O_1$	1.13	O-H
$\mu_2\text{-}O_2$	1.74	O
$\mu_3\text{-}O_3$	1.09	O-H
$\mu_2\text{-}O_4$	1.72	O
$\mu_2\text{-}O_5$	1.13	O-H
O_R	1.76	O

$d_{O \cdot O} = 2.68 - 2.73$ Å

Fig. 2 Additional representation of system **1** highlighting the hydrogen bonding environment (left) and including BVS calculations (right) for the oxygen atoms involved. V: orange polyhedra, O: red spheres, Ag: green. Acetonitrile ligands have been omitted for clarity and the hydrogen bonds are shown as black, broken lines.

molecules in each coordination sphere. The overall system is illustrated in Fig. 1.

As can be clearly observed, two cluster units are held together *via* a cooperative array of six hydrogen bonds formed between protonated and non-protonated oxygen atoms on the $[H_3V_{10}O_{28}]^{3-}$ cluster cage. This indicates that the three cluster

protons are attached to specific oxygen centres on one side of the cluster. BVS calculations, in addition to establishing the presence of ten fully oxidised V^V centres, confirm the locations of the protons, see Fig. 2. The six hydrogen bonding interactions have distances in the range $d_{O-O} = 2.68$–2.73 Å and are represented as dashed black lines. Oxygen atoms $\mu_2\text{-}O_1$, $\mu_3\text{-}O_3$ and $\mu_2\text{-}O_5$ are mono-protonated and the two clusters comprising the overall dimeric structure are arranged in an anti-parallel fashion to allow maximum hydrogen bonding interactions. Interestingly, as this type of dimeric arrangement for the decavanadate anion has been observed previously,[15] and is believed to be solvent driven, this would strongly suggest that the clusters are assembled in solution prior to silver coordination, allowing these new centres to coordinate only to the outer parts of the cluster-based dimer, away from the established hydrogen bonding sites.

System **1** was studied using IMS/MS to further investigate the nature of the hydrogen bonding interactions that have been proven integral to the overall assembly positions of the inorganic cluster units. Analysis of the spectra revealed significantly different arrangements of the ionised clusters in the gas phase compared to that of the solid state, as is often observed for these types of system. In the lower m/z range **1** exhibits a high level of disassembly with cluster fragments ranging from four vanadium atoms, $[V_4O_{11}]^{2-}$, to ten, $[V_{10}O_{26}]^{2-}$ with missing oxo ligands. Many of these fragments are in perfect agreement with the assignments presented by Nagy-Felsobuki *et al.* in a comprehensive study of isopolyoxovanadates in aqueous solution using Electrospray Ionisation (ESI) MS.[21,22] Novel silver-containing vanadate fragments were also detected along with intact clusters including silver(I) or protons (or a mixture of both) for charge balance, see Fig. 3. Two assemblies have been identified that indicate hydrogen bonding, $\{H_6Ag_4[V_{10}O_{28}]_2\}^{2-}$ and $\{H_9Ag_6[V_{10}O_{28}]_3\}^{3-}$, see Table 1 and Supporting Information.

It has also been observed that under the given conditions, the weakly bound acetonitrile molecules are removed from the
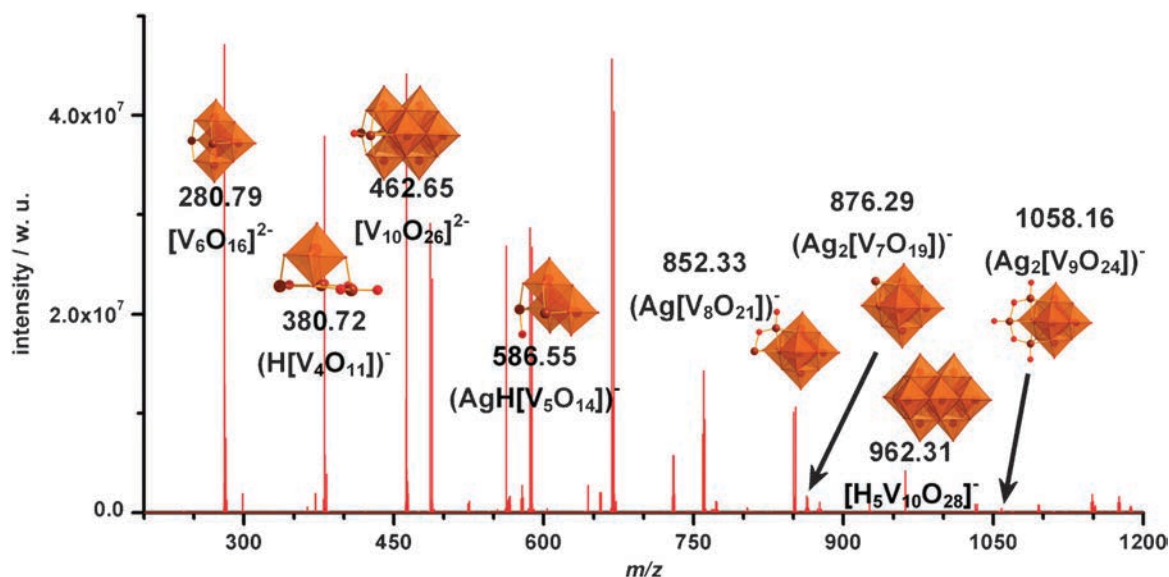

Fig. 3 MS of system **1** in the m/z range 200–1200 Da. An assignment for deduced clusters is depicted in the spectrum. These structural interpretations do not necessarily represent the actual arrangement in the mass spectrometer, *i.e.* in the gas phase.

Table 1 Fragments and poly-cluster assemblies of system **1** assigned by analysis of IMS/MS spectra. Species which required separation by ion-mobility are marked with an asterisk

m/z	Charge	Assignment
280.79	2−	$[V_6O_{16}]^{2-}$
380.72	1−	$(H[V_4O_{11}])^-$
462.65	2−	$[V_{10}O_{26}]^{2-}$
486.61	1−	$(Ag[V_4O_{11}])^-$
562.57	1−	$(H[V_6O_{16}])^-$
586.55	1−	$(AgH[V_5O_{14}])^-$
668.47*	1−	$(Ag[V_6O_{16}])^-$
668.47*	2−	$\{(Ag[V_6O_{16}])^-\}_2$
729.75	3−	$(Ag_3O[V_{10}O_{26}]_2)^{3-}$
760.40	4−	$\{(Ag_2[V_{10}O_{28}][V_4O_9])^{2-}\}_2$
852.33	1−	$(Ag[V_8O_{21}])^-$
926.29	1−	$(H[V_{10}O_{26}])^-$
962.31	1−	$[H_5V_{10}O_{28}]^-$
1032.18*	1−	$(Ag[V_{10}O_{26}])^-$
1032.18*	2−	$\{(Ag[V_{10}O_{26}])^-\}_2$
1058.16*	1−	$(Ag_2[V_9O_{24}])^-$
1058.16*	2−	$\{(Ag_2[V_9O_{24}])^-\}_2$
1149.08*	2−	$(Ag_4[V_{10}O_{28}][V_{10}O_{25}])^{2-}$
1149.08*	4−	$\{(Ag_4[V_{10}O_{28}][V_{10}O_{25}])^{2-}\}_2$
1176.10*	2−	$(H_6Ag_4[V_{10}O_{28}]_2)^{2-}$
1176.10*	3−	$(H_9Ag_6[V_{10}O_{28}]_3)^{3-}$

silver(I) centres during the ionisation process. The then vacant coordination sites allow for further linkage of additional clusters giving rise to dimeric and trimeric species such as $\{Ag_6[V_{10}O_{27}]_2\}^{2-}$, $\{Ag_9[V_{10}O_{27}]_3\}^{3-}$ and $\{Ag_4[V_{10}O_{28}][V_{10}O_{25}]\}^{2-}$ which have only been observed so far in the MS. In general as coordination O–Ag bonds are much stronger than hydrogen bonds between protonated and non-protonated oxygen atoms, this explains why the former are more prominently observed in the spectra. A summarised list of the peak assignments is shown in Table 1 and species which required separation by ion-mobility due to the same m/z ratio are marked with an asterisk. The resolved spectra of these peak envelopes can be found in the supporting information.

In summary, a new silver(I)-linked decavanadate system has been prepared, utilising facile synthetic conditions, and exhibiting a distinctive dimeric configuration wholly supported by cooperative hydrogen bonds. Not only does this system corroborate previous findings regarding the association of decavanadates in specific solvent media, but also provides an insight into the self-assembly processes involved in its construction. The system was also investigated using ion-mobility mass spectrometry, yielding significant results on thermodynamically stable POM-based secondary building units and aggregation behaviour fuelled by hydrogen bonding. Truly this developing

analytical technique is proving invaluable in studying such subtle interactions.

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