

## An unprecedented silver – decavanadate dimer investigated using Ion – Mobility Mass Spectrometry

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### Supporting Information

#### Experimental

The precursor  $(\text{TBA})_3[\text{H}_3\text{V}_{10}\text{O}_{28}]$  was synthesised according to the literature procedure.<sup>1</sup> (TBA = *n*-tetrabutylammonium).

$(\text{TBA})_3[\text{H}_3\text{V}_{10}\text{O}_{28}]$  (290 mg, 0.172  $\mu\text{mol}$ ) was dissolved in 20 ml acetonitrile.  $\text{AgNO}_3$  (110 mg, 0.65 mmol) was dissolved in 10 ml acetonitrile and added to the mixture. The orange - red solution was stirred for 24 h and then centrifuged to remove any insoluble material. Diffusion of diethyl ether into the reaction mixture gave **1** as orange block crystals after *ca.* 4 days. These were collected by filtration. Yield: 112 mg (52.1  $\mu\text{mol}$ , 39.7 % based on V). Elemental analysis in wt.-% for  $\text{C}_{20}\text{H}_{33}\text{Ag}_3\text{N}_{10}\text{O}_{28}\text{V}_{10}$  (calculated values in brackets): C: 9.54 (14.18), H: 1.29 (1.96), N: 5.40 (8.27), Ag: 18.65 (19.13), V: 30.16 (30.12). The C, H and N values indicate the loss of 4 coordinated acetonitrile molecules upon air - drying. The Ag and V analysis was performed on a fully dried sample to eliminate systematic errors due to desolvation effects. Characteristic IR bands (in  $\text{cm}^{-1}$ ): 3297 (m, b), 2352 (vw), 1602 (m), 946 (vs), 921 (vs), 800 (vs).

#### Fourier - transform infrared (FT-IR) spectroscopy

**1** was prepared as a KBr pellet and a FT-IR spectrum was collected in transmission mode using a JASCO FT-IR-4100 spectrometer. Characteristic IR bands are shown above in  $\text{cm}^{-1}$ ; intensities denoted as vs = very strong, s = strong, m = medium, w = weak, b = broad, sh = sharp.

#### Microanalysis

Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the *Department of Chemistry, University of Glasgow* using a EA 1110 CHN, CE-440 Elemental Analyser.

#### Flame Atomic Absorption Spectrometry (FAAS)

FAAS was performed at the *Environmental Chemistry Section, Department of Chemistry, University of Glasgow* on a *Perkin-Elmer* 1100B Atomic Absorption Spectrophotometer.

#### Single Crystal X-ray Diffraction

The data was collected at 150(2) K on an *Oxford Diffraction Gemini S Ultra* diffractometer ( $\lambda$  ( $\text{MoK}\alpha$ ) = 0.7107 Å) equipped with a graphite monochromator. Suitable single crystals of **1** were selected and mounted onto the end of a thin glass fibre using Fomblin oil. Structure solution and refinement was carried out with SHELXS-97<sup>2</sup> and SHELXL-97<sup>2</sup> using WinGX.<sup>3</sup>

Empirical Formula	C <sub>20</sub> H <sub>33</sub> Ag <sub>3</sub> N <sub>10</sub> O <sub>28</sub> V <sub>10</sub>
M <sub>r</sub> [g mol <sup>-1</sup> ]	1694.57
Crystal System	Triclinic
Space Group	<i>P</i> -1
<i>a</i> [Å]	12.7703(4)
<i>b</i> [Å]	13.5522(4)
<i>c</i> [Å]	15.8528(6)
$\alpha$ [°]	74.740(3)
$\beta$ [°]	83.585(3)
$\gamma$ [°]	68.634(3)
$\rho_{\text{calcd.}}$ [gcm <sup>-3</sup> ]	2.284
V [Å <sup>3</sup> ]	2464.55(14)
Z	2
$\mu(\text{MoK}\alpha)$ [mm <sup>-1</sup> ]	3.054
T [K]	150(2)
RfIns. (measd.)	21255
RfIns. (uniq.)	8965
No. params.	650
R1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0309
wR2 (all)	0.0758

Table 1. Crystallographic data for system 1.

### Thermogravimetric Analysis (TGA)

TGA was performed on a *TA Instruments* Q 500 Thermogravimetric Analyzer under air flow at a heating rate of 10 °C min<sup>-1</sup> in a platinum pan.

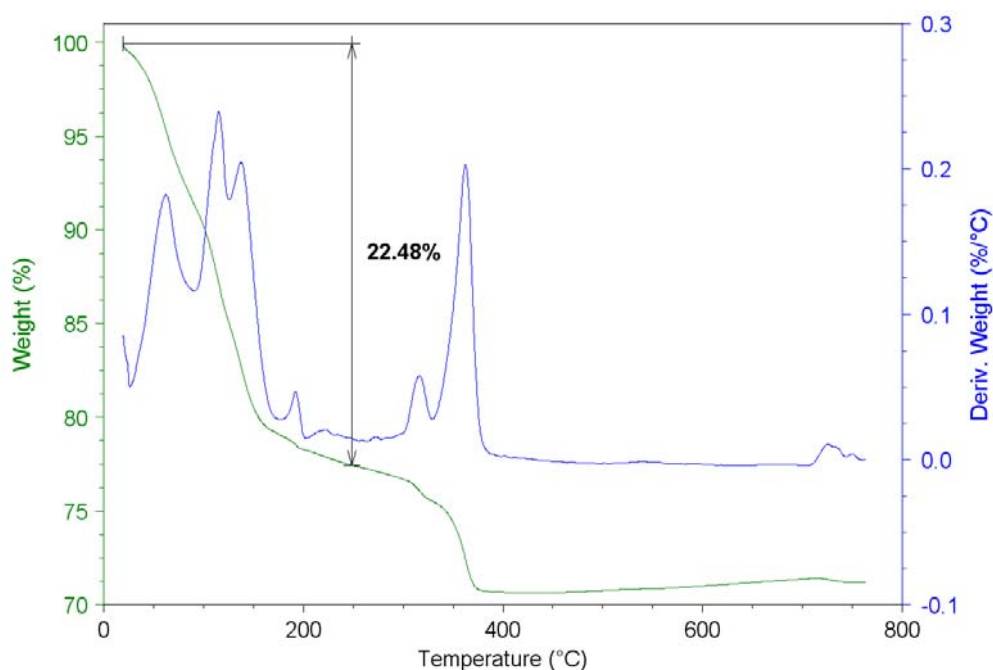


Figure 1. Thermogravimetric analysis for system **1**.

Thermogravimetric analysis of compound **1** shows a weight loss of 22.48 % attributed to the loss of all coordinated and solvent acetonitrile molecules. This is lower than the calculated value of 24.20 % due to some solvent evaporation during sample preparation.

#### Ion-Mobility Mass Spectrometry Measurements

HPLC solvent for IMS / MS analysis (acetonitrile, HPLC grade) was purchased from *Fisher Scientific* and used without further purification. All measurements were carried out on a *Waters Synapt G2 HDMS* in sensitivity mode equipped with a Quadrupole and time of flight flight (Q / ToF) module for MS analysis. The IMS section is a Travelling - wave IMS, located between the Q - and the ToF - section. It consists of a trap cell, an ion - mobility cell and a transfer cell.

Compound **1** was dissolved in HPLC grade acetonitrile and diluted to a concentration of *ca.*  $1 \times 10^{-5}$  M. This was injected at a sample flow rate of  $5 \mu\text{l min}^{-1}$  using a Harvard syringe pump. The parameters for IMS / MS measurements were set up as follows: ESI capillary voltage: 1.9 kV; sample cone voltage: 19 V; extraction cone voltage: 4.6 V; source temperature: 80 °C; desolvation temperature: 120 °C; cone gas flow:  $15 \text{ l h}^{-1}$  ( $\text{N}_2$ ); desolvation gas flow:  $500 \text{ l h}^{-1}$  ( $\text{N}_2$ ); source gas flow:  $0 \text{ ml min}^{-1}$ ; trap gas flow:  $2.5 \text{ ml min}^{-1}$ ; helium cell gas flow:  $200 \text{ ml min}^{-1}$ ; IMS gas flow:  $90.00 \text{ ml min}^{-1}$ ; IMS DC entrance: 25.0; helium cell DC: 35.0; helium exit: -5; IMS bias: 30; IMS DC exit: 0; IMS wave velocity:  $1500 \text{ m s}^{-1}$ ; IMS wave height: 40 V.

Analysis of MS spectra was carried out using Mass Lynx V4.1 Software supplied by *Waters*. Driftscope V2.1 was used for analysis of IMS / MS spectra. IMS chromatograms for two overlapping peak envelopes were extracted from the overall spectrum in order to resolve these envelopes and to show them in different spectra.

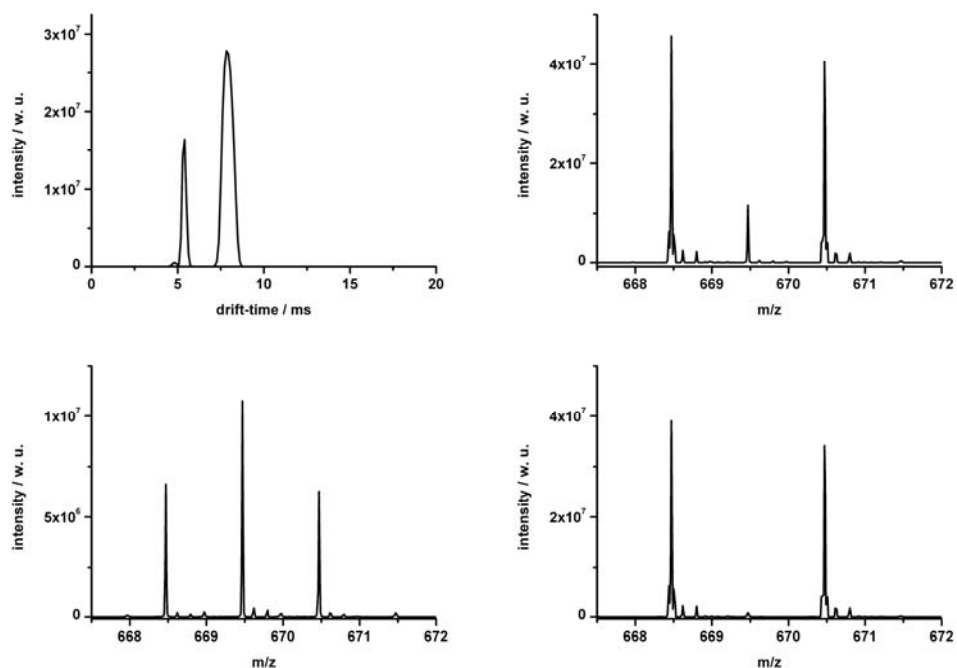


Figure 2. Top left: drift – time chromatogram of compound **1** in the  $m/z$  range from 667 to 672 Da. Top right: unresolved peak envelope, bottom left: resolved peak envelope for  $\{(Ag[V_6O_{16}])\}_2$  and bottom right: resolved peak envelope for  $(Ag[V_6O_{16}])^-$ .

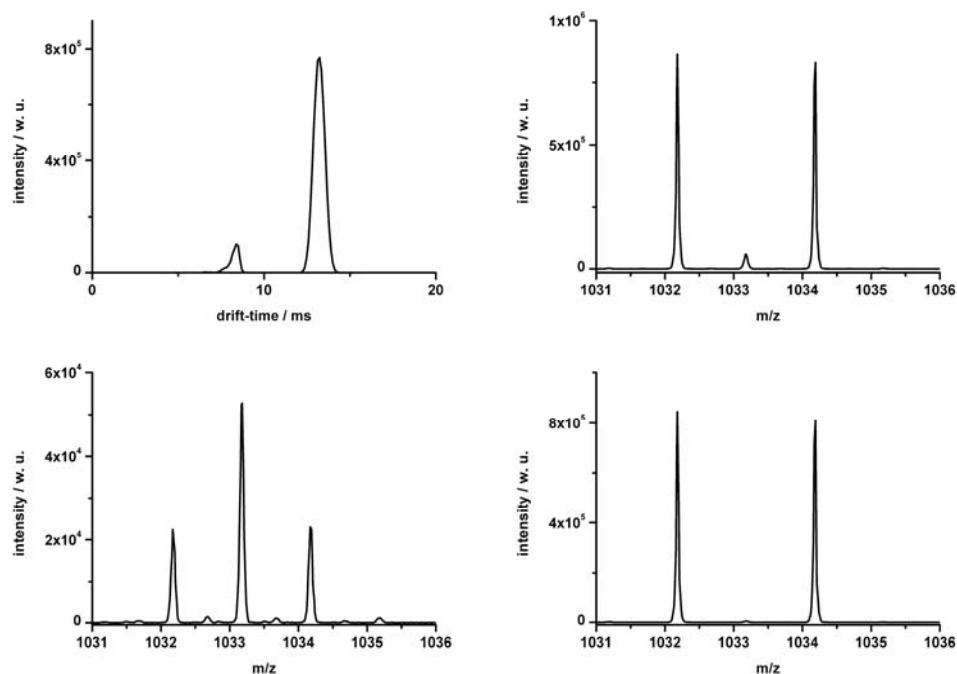


Figure 3. Top left: drift – time chromatogram of compound **1** in the  $m/z$  range from 1031 to 1036 Da. Top right: unresolved peak envelope, bottom left: resolved peak envelope for  $\{(Ag[V_{10}O_{26}])\}_2$  and bottom right: resolved peak envelope for  $(Ag[V_{10}O_{26}])^-$ .

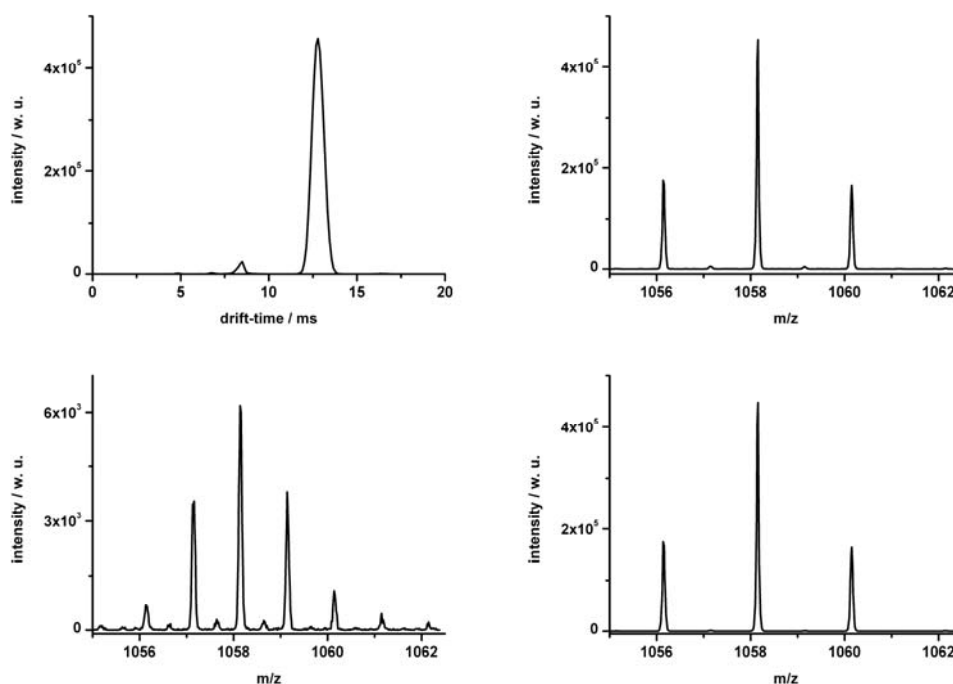


Figure 4. Top left: drift – time chromatogram of compound **1** in the  $m/z$  range from 1055 to 1062 Da. Top right: unresolved peak envelope, bottom left: resolved peak envelope for  $\{(Ag_2[V_9O_{24}])_2\}$  and bottom right: resolved peak envelope for  $(Ag_2[V_9O_{24}])$ .

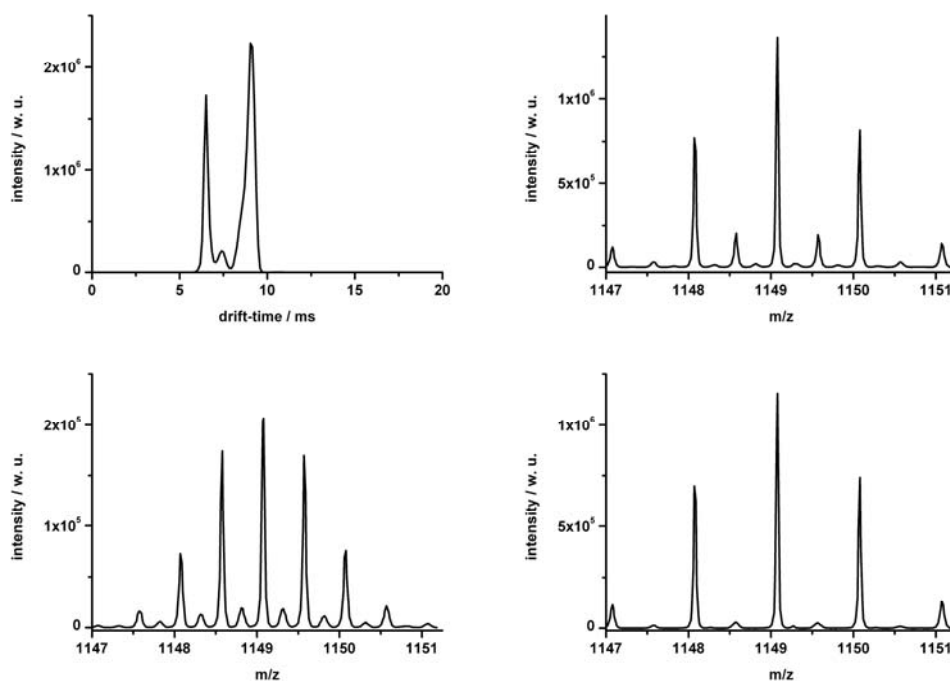


Figure 5. Top left: drift – time chromatogram of compound **1** in the  $m/z$  range from 1147 to 1152 Da. Top right: unresolved peak envelope, bottom left: resolved peak envelope for  $\{(Ag_4[V_{10}O_{28}][V_{10}O_{25}])_2\}$  and bottom right: resolved peak envelope for  $(Ag_4[V_{10}O_{28}][V_{10}O_{25}])$ .

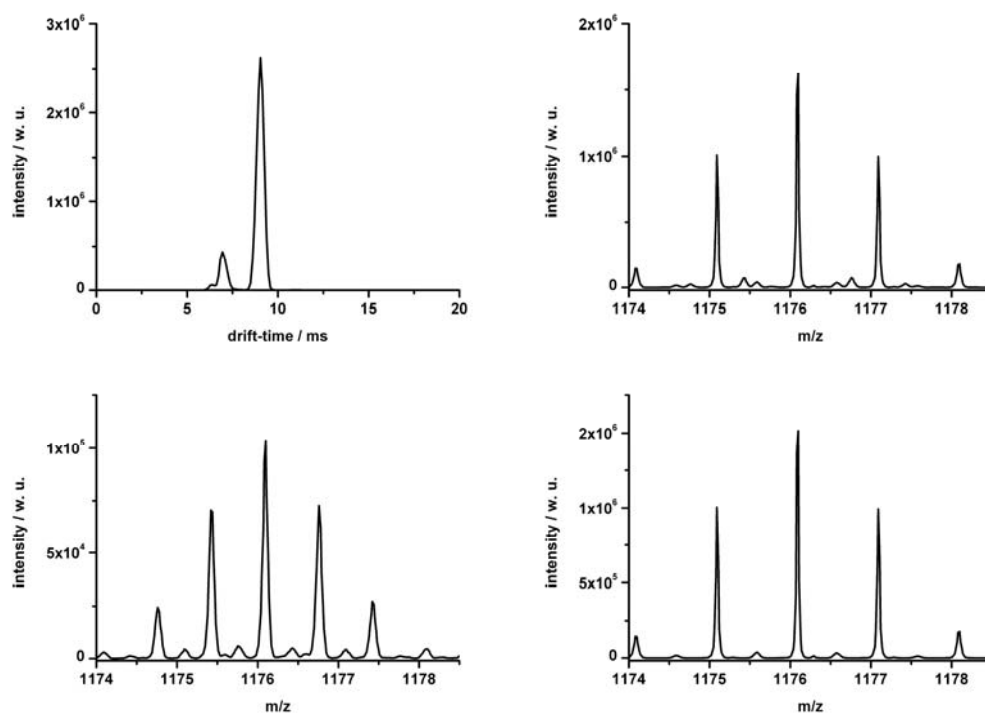


Figure 6. Top left: drift – time chromatogram of compound **1** in the  $m/z$  range from 1174 to 1179 Da. Top right: unresolved peak envelope, bottom left: resolved peak envelope for  $(\text{H}_9\text{Ag}_6[\text{V}_{10}\text{O}_{28}]_3)^{3-}$  and bottom right: resolved peak envelope for  $(\text{H}_6\text{Ag}_4[\text{V}_{10}\text{O}_{28}]_2)^{2-}$ .

## References

1. W. G. Klemperer and O. M. Yaghi, *Inorganic Syntheses*, John Wiley & Sons, 1990, **27**.
2. G. M. Sheldrick, *Acta Cryst., Sect. A: Found. Cryst.*, 2008, **64**, 112-122.
3. L. J. Farrugia, *J. App. Cryst.*, 1999, **32**, 837-838.