

Assembly of a Family of Mixed Metal {Mo:V} Polyoxometalates Templated by TeO_3^{2-} : $\{\text{Mo}_{12}\text{V}_{12}\text{Te}_3\}$, $\{\text{Mo}_{12}\text{V}_{12}\text{Te}_2\}$ and $\{\text{Mo}_{17}\text{V}_8\text{Te}\}$

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Materials

All reagents and chemicals were supplied by Sigma Aldrich Chemical Company Ltd. and Alfa Aesar. Unless stated otherwise, the materials were used without further purification.

Instrumentation

Fourier-transform infrared (FT-IR) spectroscopy: Unless stated otherwise, the materials were prepared as KBr pellets and FT-IR spectra were collected in transmission mode using a JASCO FT-IR-410 spectrometer or a JASCO FT-IR 4100 spectrometer.

Mass Spectrometry: Electrospray-ionisation mass spectrometry (ESI-MS) and coldspray-ionisation mass spectrometry (CS-MS) were performed using a Bruker micrOTOF-Q quadrupole time-of-flight mass spectrometer.

UV-Vis spectroscopy: UV-Vis spectra were collected using a JASCO V-670 spectrometer equipped with an ISV723 60mm integrating sphere in diffuse reflectance mode.

Thermogravimetric analysis (TGA): Thermogravimetric analysis was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under nitrogen or air flow at a typical heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

Flame Atomic Absorption Spectroscopy Analysis: FAAS analysis was performed at the Environmental Chemistry Section, Department of Chemistry, The University of Glasgow on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

Synthesis of $(\text{NH}_4)_9\text{K}[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_8\text{V}^{\text{IV}}_4\text{Te}^{\text{IV}}\text{O}_{69}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)_2]\cdot 27\text{H}_2\text{O}$ (1)

Ammonium molybdate tetrahydrate (0.60 g, 0.4 mmol) was dissolved in an HCl solution (37% HCl in water, 1:4 v/v, 25 mL, pH $\approx$ 0), and then solid ammonium metavanadate (0.35 g, 2.9 mmol) was added in one portion to the solution under stirring. The solid potassium tellurite hydrate (0.24 g, 0.93 mmol) was gradually added under stirring, followed by the addition of solid $\text{NH}_2\text{NH}_2\cdot 2\text{HCl}$ (0.0042 g, 0.04 mmol). Compound (1) could be synthesized within pH 2 and 4. The solution was refluxed overnight at 90 °C. The solution was then cool down at room temperature ($\sim$ 25 °C) and filtered off. The filtrate was left in an open vessel (a 100 mL beaker) at room temperature ($\sim$ 25 °C) for a week, during which time dark green rhomboid shape crystals from 1, suitable for X-ray structure analysis, were obtained. Yield 0.08 g (10 % based on V). Elemental analysis for $\text{H}_{90}\text{KMo}_{12}\text{N}_9\text{O}_{102}\text{Te}_3\text{V}_{12}$; calc: H: 2.25 %, N: 3.13 %; K: 0.97 %, Te: 9.49 %; Mo: 28.54 %, V: 15.16 %; found: H: 2.08 %; N: 3.68 %; K: 0.86 %, Te: 9.10 %; Mo: 28.84 %, V: 15.80 %. FT-IR [(KBr), cm^{-1}] 3444 (br) [$\nu(\text{O-H})$ from H_2O], 1400 (s) [$\nu(\text{NH}_4)$], 967 (s) [$\nu(\text{V=O})$], 894 (s) [$\nu(\text{Mo=O})$], 845 (s) [$\nu(\text{TeO}_3^{2-})$], 768 [$\nu(\text{TeO}_3^{2-})$].

Synthesis of $\text{K}_{14}[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_8\text{V}^{\text{IV}}_4\text{O}_{69}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)_2]\cdot 27\text{H}_2\text{O}$ (2)

Potassium molybdate dihydrate (0.67 g, 2.8 mmol) was dissolved in 25 mL of deionized water and the solid potassium metavanadate (0.6 g, 7 mmol) was added in one portion to the solution under stirring. Then, solid $\text{K}_2\text{TeO}_3\cdot x\text{H}_2\text{O}$ (0.24 g, 0.93 mmol) was gradually added under stirring; followed by (0.0042 g, 0.04 mmol) of hydrazine hydrochloride. The pH to 2.5 by addition of a 3M HCl aqueous solution and the solution was refluxed overnight at 90 °C. The solution was then cool down at room temperature ($\sim$ 25 °C) and filtered off. The filtrate was left in an open vessel (a 100 mL beaker) at room temperature ($\sim$ 25 °C) for a week, during which time green hexagonal crystals suitable for X-ray structure analysis were obtained. Yield 0.08 g (10.4 % based on Mo). Elemental analysis for $\text{H}_{54}\text{K}_{14}\text{Mo}_{12}\text{O}_{102}\text{Te}_2\text{V}_{12}$; calc: Te: 6.00 %, K: 12.78 %, Mo: 27.08 %, V: 14.38 %; found: Te: 5.74 %, K: 12.41 %, Mo: 27.61

%, V: 14.45 %. FT-IR [(KBr), cm^{-1}] 3433 (br) [$\nu(\text{O-H})$ from H_2O], 968 (s) [$\nu(\text{V=O})$], 889 (s) [$\nu(\text{Mo=O})$], 842 (s) [$\nu(\text{TeO}_3^{2-})$], 763 [$\nu(\text{TeO}_3^{2-})$].

Synthesis of $\text{K}_{10}[\text{Mo}^{\text{VI}}_{11}\text{V}^{\text{V}}_5\text{V}^{\text{IV}}_2\text{O}_{52}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)(\text{Mo}^{\text{VI}}_6\text{V}^{\text{V}}\text{O}_{22})] \cdot 15\text{H}_2\text{O}$ (3)

$\text{K}_2\text{TeO}_3 \cdot x\text{H}_2\text{O}$ (0.12 g, 0.47 mmol) were dissolved in 25 mL of deionized water and the pH of the solution was adjusted to 2 by addition of 3 M HCl solution. At this point, white precipitate appeared and the reaction was heat at 90 °C to dissolve the precipitate. Potassium molybdate dihydrate (0.67 g, 2.8 mmol) was then added to the solution under stirring, followed by the addition of solid potassium metavanadate (0.70 g, 5.1 mmol) and the pH was readjusted to 2 by addition of 3 M HCl solution. Finally, solid $\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$ (0.0042 g, 0.04 mmol) was gradually added under stirring and the solution turned from yellow to green. Compound (3) could be synthesized within the pH range 2.8-3.5. After adjusting the pH, solid KCl (2.0 g, 0.03 mol) was added under stirring. The solution was filtered off and the filtrate left in an open vessel (100 mL beaker) at room temperature (~ 25 °C) for a week, during which time dark green crystals suitable for X-ray structure analysis were obtained. Yield 0.07g (12% based on Mo). Elemental analysis for $\text{H}_{30}\text{K}_{10}\text{Mo}_{17}\text{O}_{92}\text{TeV}_8$; calc: K: 9.63 %, Te: 3.14 %, Mo: 40.18 %, V: 10.04 %; found: K: 9.10 %, Te: 3.74 %, Mo: 39.62 %, V: 10.62 %. FT-IR [(KBr), cm^{-1}] 3434 (br) [$\nu(\text{O-H})$ from H_2O], 964 (s) [$\nu(\text{V=O})$], 901 (s) [$\nu(\text{Mo=O})$], 850 (s) [$\nu(\text{TeO}_3^{2-})$], 818 [$\nu(\text{TeO}_3^{2-})$].

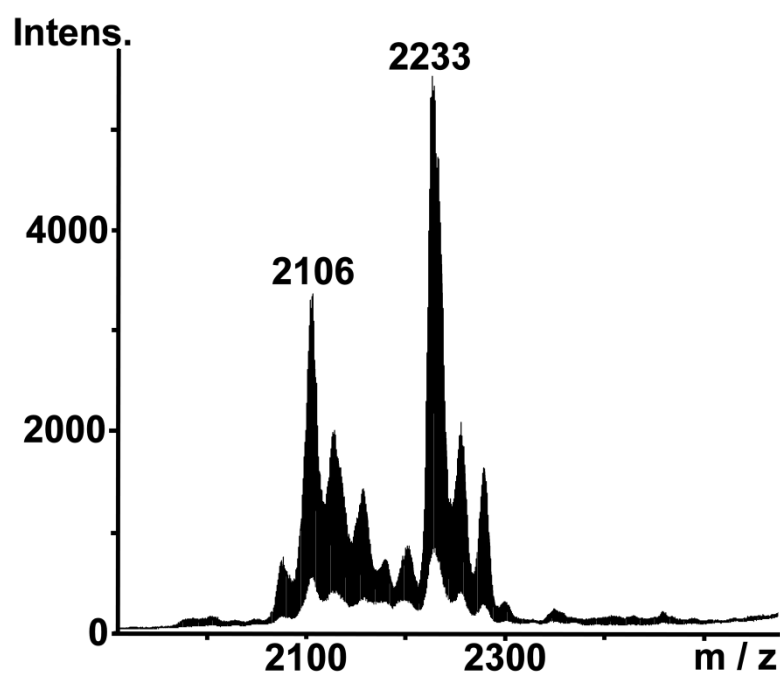
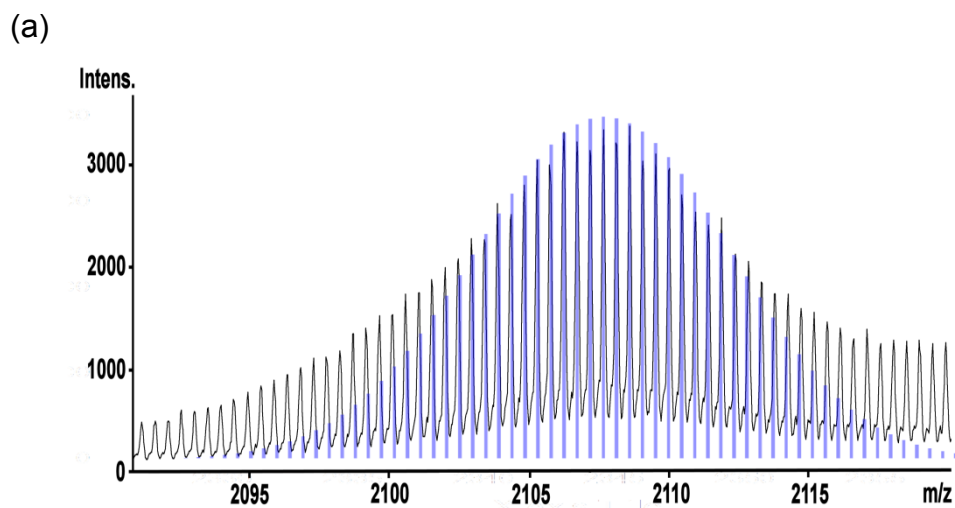
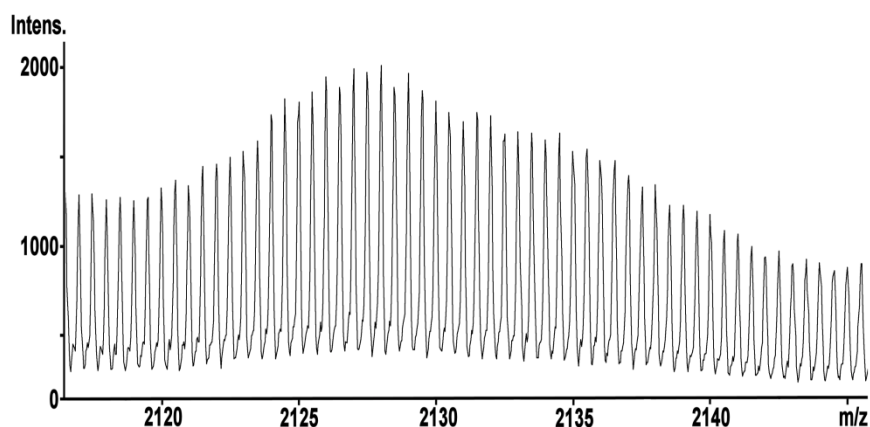


Fig. S1 Negative ion mass spectrum in acetonitrile solution of **1a**.



(b)



(c)

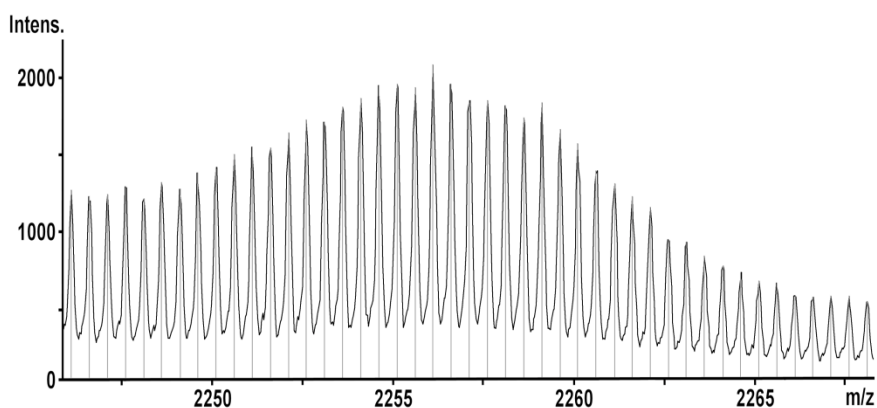


Fig. S2 Expanded MS for compound **1a**: (a) Envelope at m/z ca. 2106.48 is shown along with the calculated isotopic pattern (blue columns) and can be assigned to $\{[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_4\text{V}^{\text{IV}}_8\text{O}_{69}\text{Te}(\text{TeO}_3)_2](\text{C}_{16}\text{H}_{36}\text{N})_2\text{K}_6\text{H}_4(\text{H}_2\text{O})_8\}^{2-}$, (b) Envelope at m/z ca. 2127.98 can be assigned to $\{[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_4\text{V}^{\text{IV}}_8\text{O}_{69}\text{Te}(\text{TeO}_3)_2](\text{C}_{16}\text{H}_{36}\text{N})_2\text{K}_9\text{H}_1(\text{H}_2\text{O})_4\}^{2-}$ and (c) Envelope at m/z ca. 2255.59 can be assigned to $\{[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_4\text{V}^{\text{IV}}_8\text{O}_{69}\text{Te}(\text{TeO}_3)_2](\text{C}_{16}\text{H}_{36}\text{N})_3\text{K}_7\text{H}_2(\text{H}_2\text{O})_9\}^{2-}$.

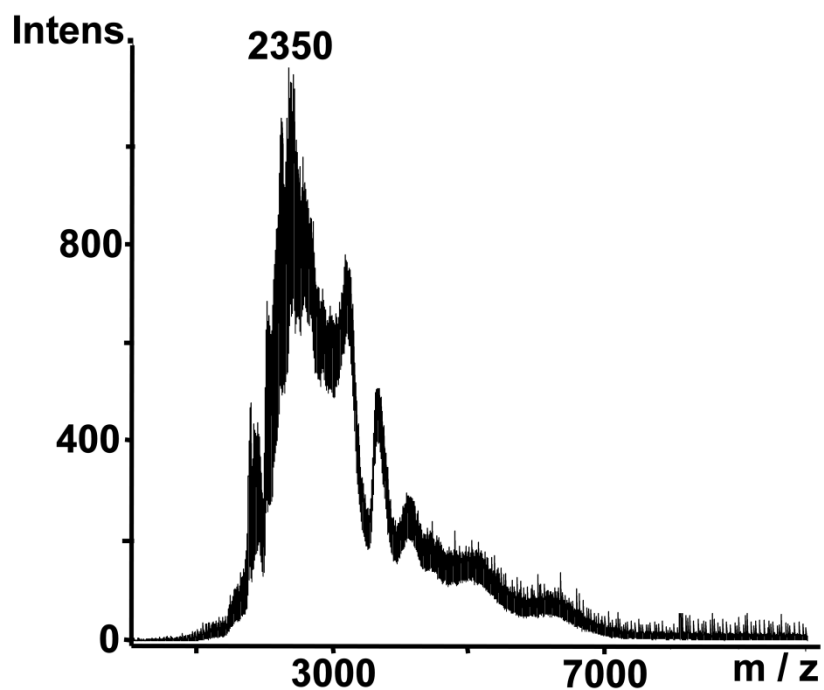


Fig. S3 Negative ion mass spectrum in aqueous medium of **2a**.

Infrared spectroscopy

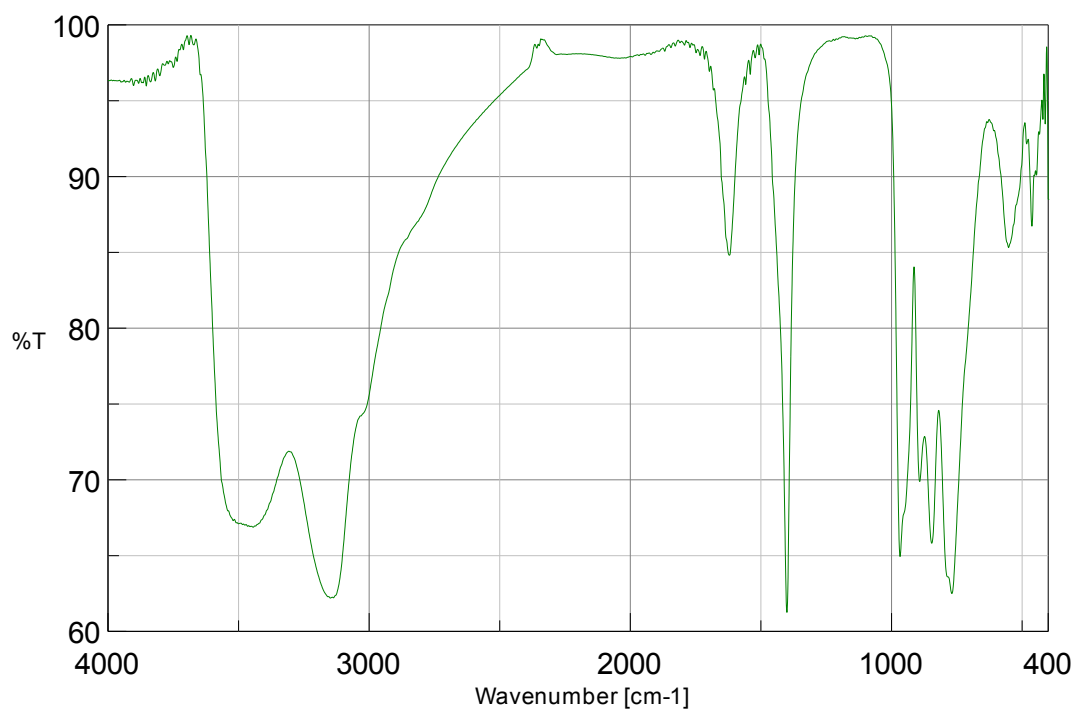


Fig. S4: Infrared spectrum of compound **1**.

UV-vis spectroscopy

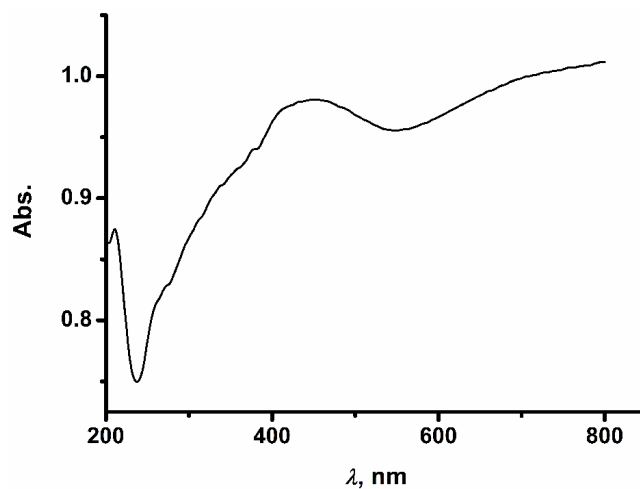


Fig. S5: UV-vis reflectance spectrum of compound **1**. A series of broad overlapping bands can be observed at 269, 339 and 447 nm respectively, assignable to O→M and IV charge transfers.¹

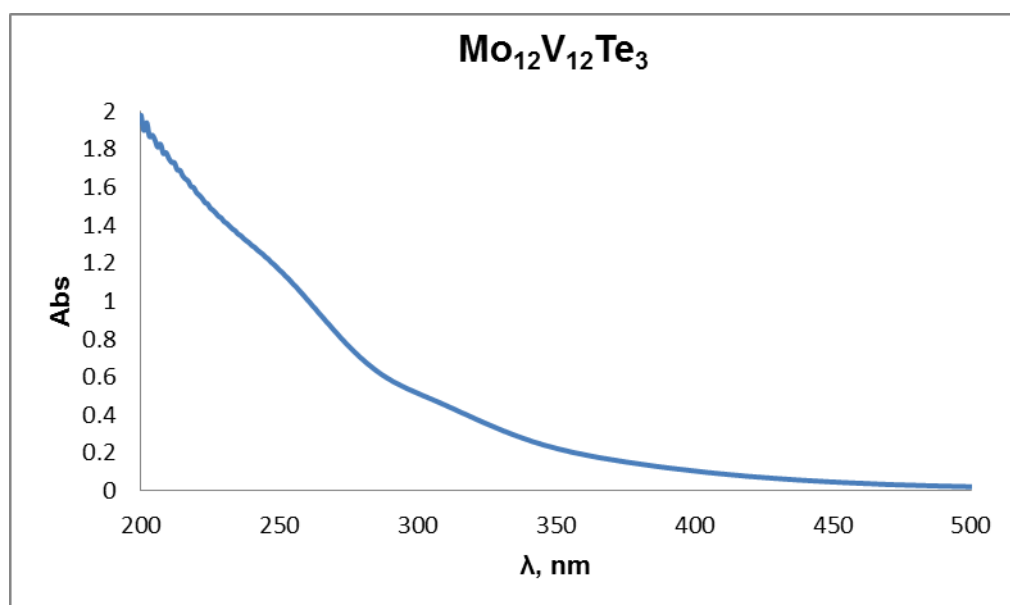


Fig. S6: UV-vis spectrum of compound **1**. The bands can be assigned to ML and IV charge transfers. λ_{max} , [nm, (dm³mol⁻¹cm⁻¹)] = 262(80578), 318(32975).¹

Thermogravimetric analysis

Weight loss between 25 – 400 °C can be assigned to approx. 27 water molecules in the crystal lattice which is overlapping the removal of 9 NH_4^+ cations as NH_3 molecules.

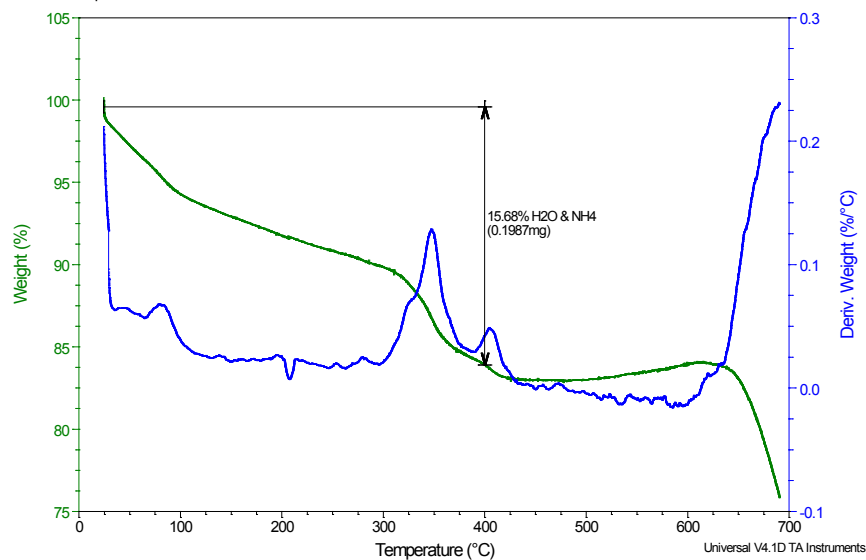


Fig. S7: Thermal gravimetric analysis of **1**, showing the loss of solvent content as well as of the NH_4^+ (RT – 400 °C)

Infrared spectroscopy

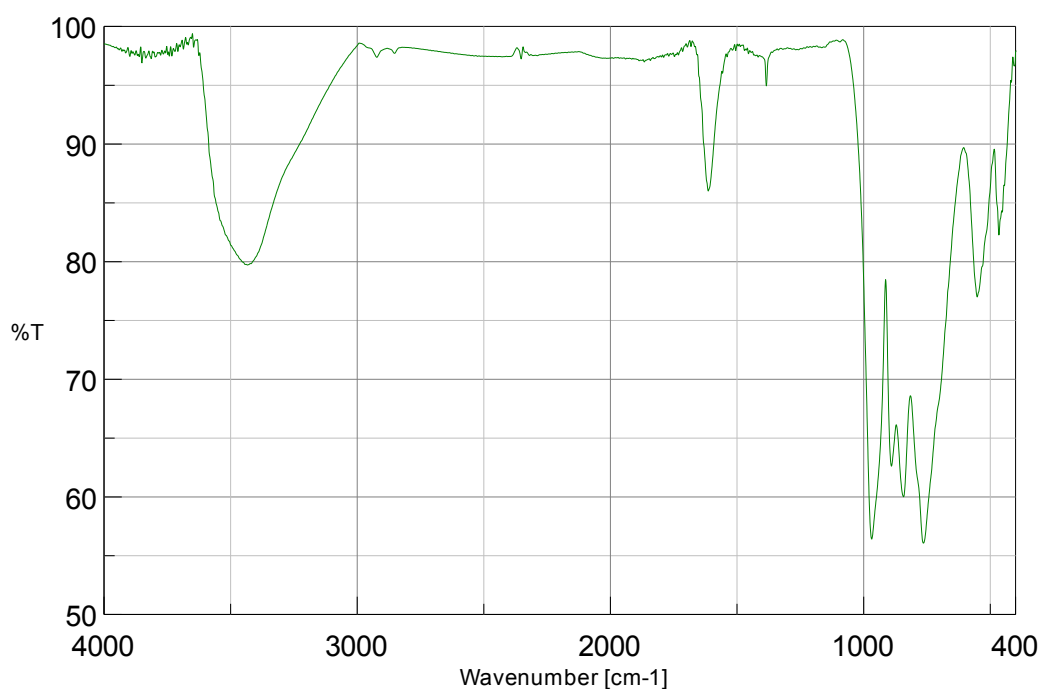


Fig. S8: Infrared spectrum of compound **2**.

UV-vis spectroscopy

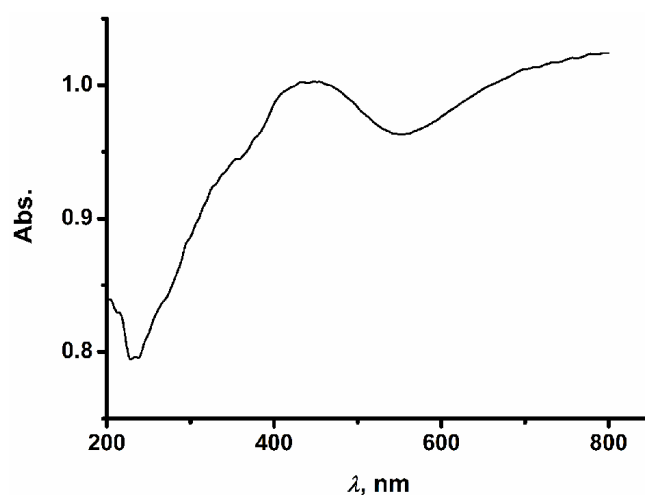


Fig. S9: Visible spectrum of compound **2**. A series of broad overlapping bands can be observed at 273, 337 and 444 nm respectively, assignable to O $\rightarrow$ M and IV charge transfers.¹

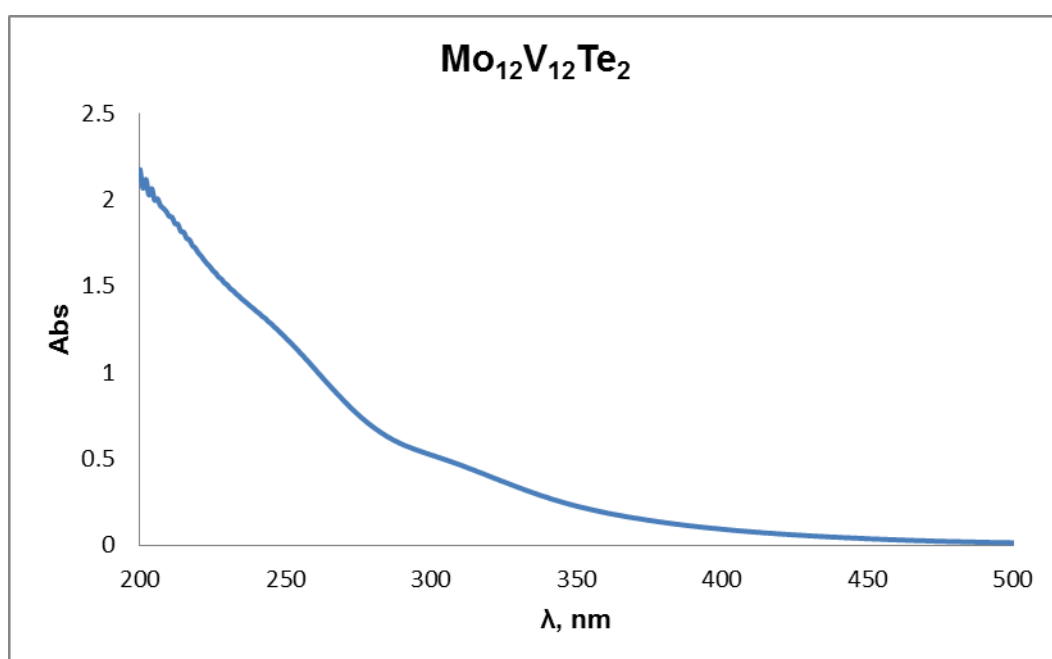


Fig. S10: UV-vis spectrum of compound **2**. The bands can be assigned to ML and IV charge transfers. λ_{max} , [nm, ($\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)] = 263(71865), 317(31791).¹

Thermogravimetric analysis

Weight loss between 0 – 200 °C can be assigned to approx. 27 water molecules in the crystal lattice. The cluster is stable up to 700 °C.

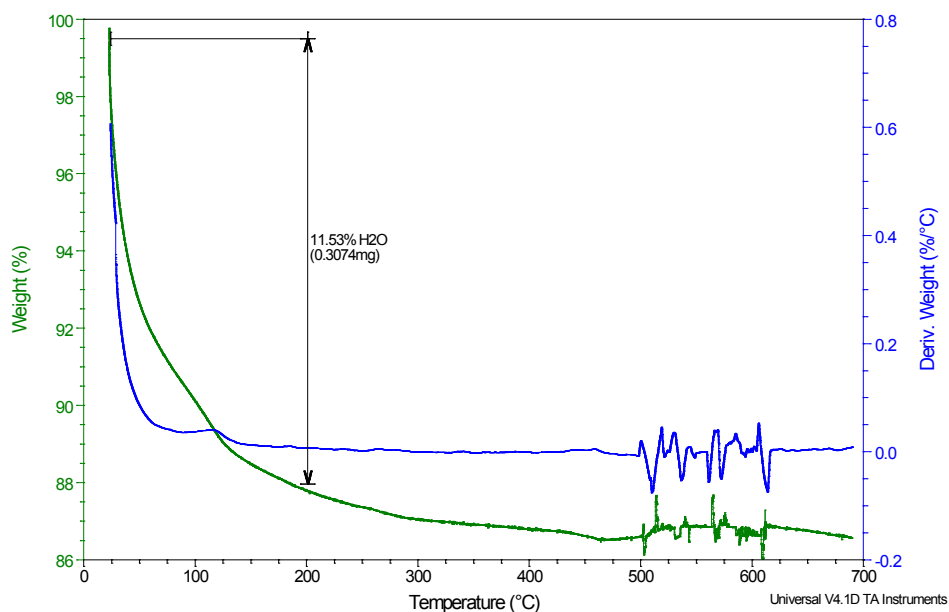


Fig. S11: Thermal gravimetric analysis of **2**, show the loss of solvent content (RT – 200 °C).

Infrared spectroscopy

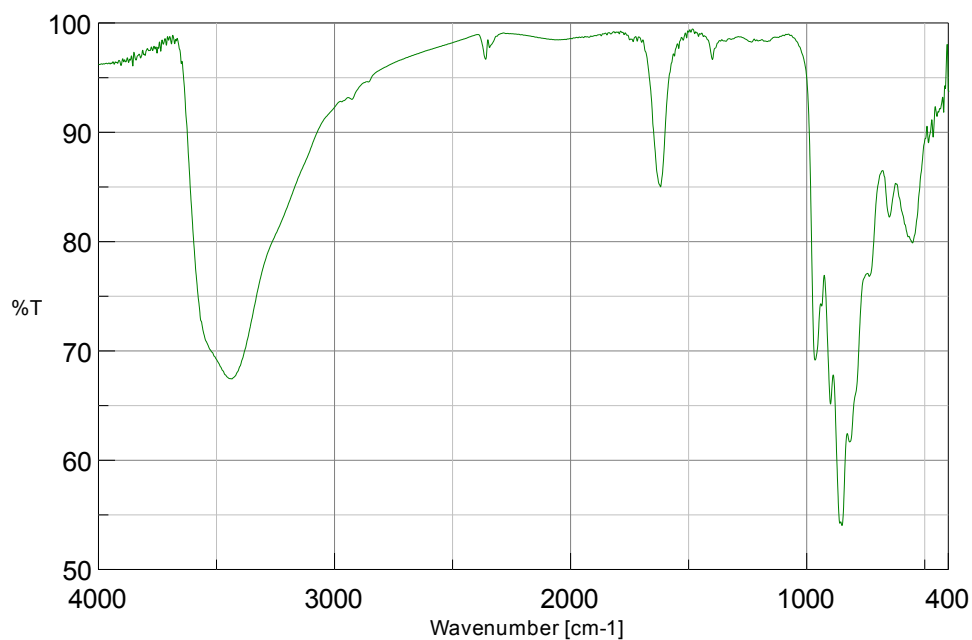


Fig. S12: Infrared spectrum of compound **3**.

Vis spectroscopy

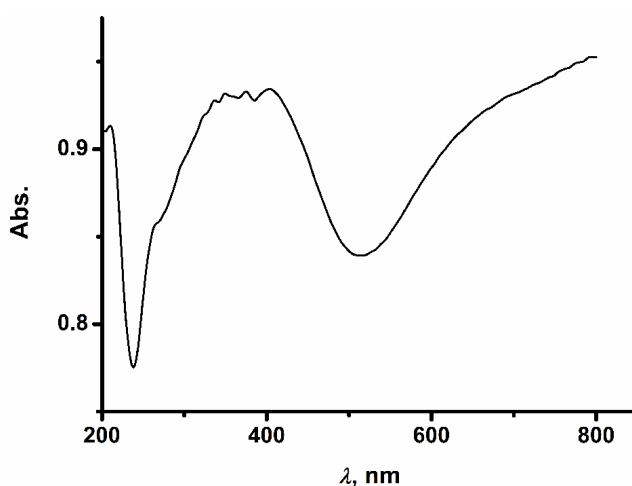


Fig. S13: Visible spectrum of compound **3**. A series of broad overlapping bands can be observed at 272, 306, 339 and 410 nm respectively, assignable to O $\rightarrow$ M and IV charge transfers.¹

Thermogravimetric analysis

Weight loss between 0 – 175 C° can be assigned to approx. 15 water molecules in the crystal lattice.

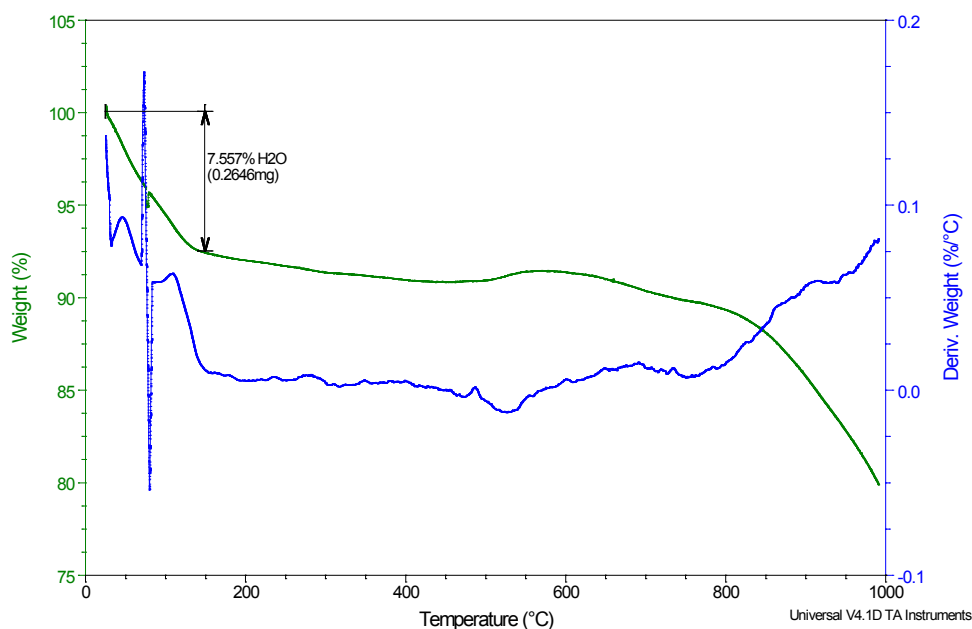
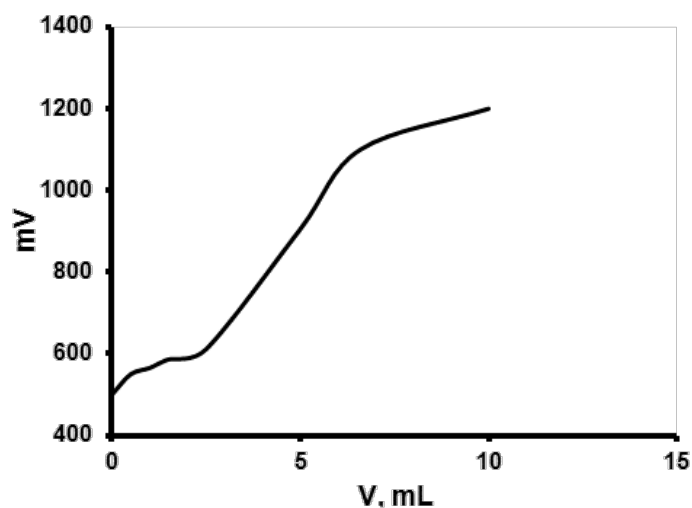


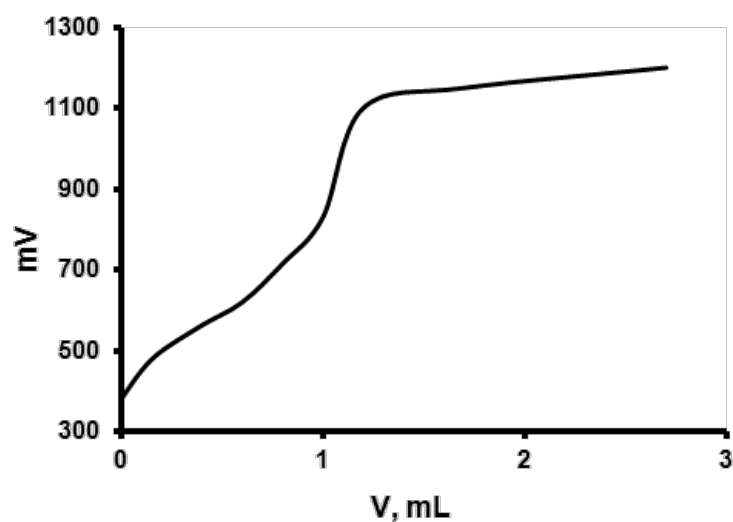
Fig. S14: Thermal gravimetric analysis of **3**, showing the loss of solvent content (RT - 175 °C). The compound is stable up until 800 °C.

Redox Titrations

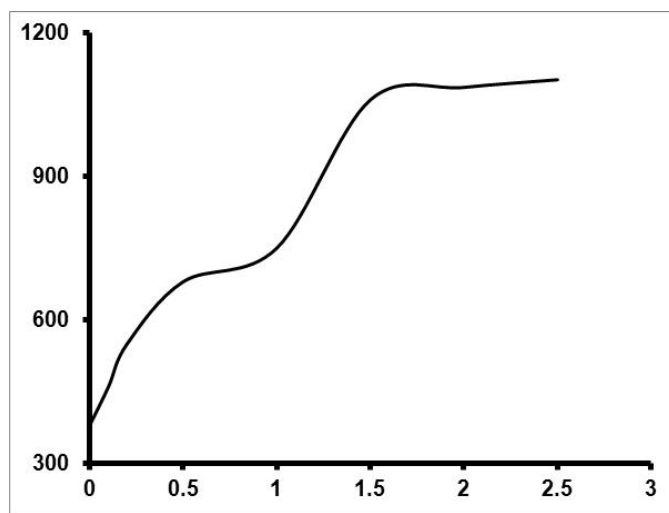
- (1) Compound **1** $(\text{NH}_4)_9\text{K}[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_8\text{V}^{\text{IV}}_4\text{Te}^{\text{IV}}\text{O}_{69}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)_2] \cdot 27\text{H}_2\text{O}$
 Mass used = 12 mg
 Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution
 Theoretical amount of oxidant for **four electron** reduced species in mL: 1.19
 Experimental amount used in mL: 1.24



- (2) Compound **2** $\text{K}_{14}[\text{Mo}^{\text{VI}}_{12}\text{V}^{\text{V}}_8\text{V}^{\text{IV}}_4\text{O}_{69}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)_2] \cdot 27\text{H}_2\text{O}$
 Mass used = 50 mg
 Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution
 Theoretical amount of oxidant for **four electron** reduced species in mL: 4.7
 Experimental amount used in mL: 4.55

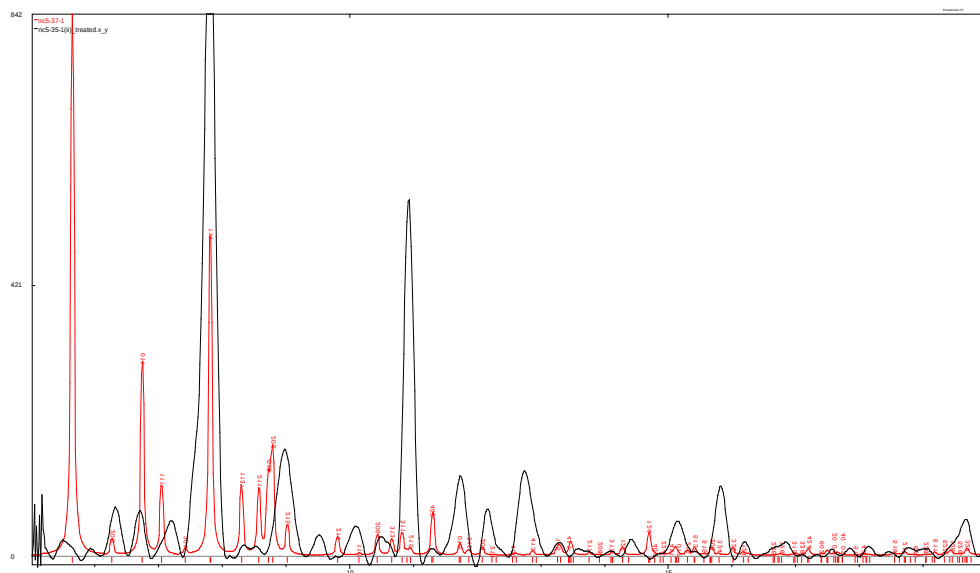


- (3) Compound **3** $\text{K}_{10}[\text{Mo}^{\text{VI}}_{11}\text{V}^{\text{V}}_5\text{V}^{\text{IV}}_2\text{O}_{52}(\mu_9\text{-Te}^{\text{IV}}\text{O}_3)(\text{Mo}^{\text{VI}}_6\text{V}^{\text{V}}\text{O}_{22})]\cdot 15\text{H}_2\text{O}$
 Mass used = 25 mg
 Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution
 Theoretical amount of oxidant for **two electron** reduced species in mL: 1.23
 Experimental amount used in mL: 1.35



Powder XRD

(A)



(B)

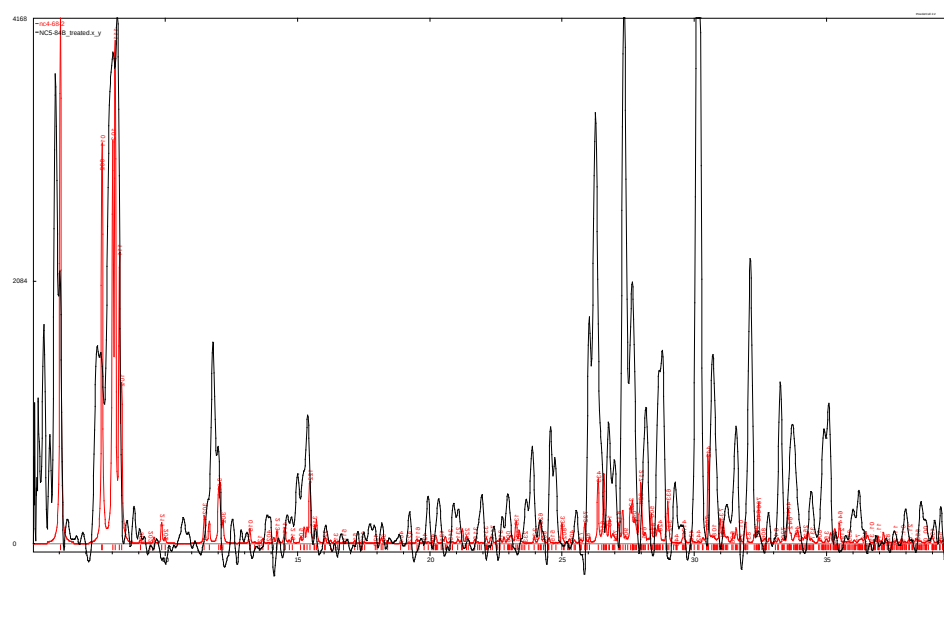


Fig. S15: Black line – experimental XRD powder diffraction pattern at room temperature. Red line – simulated XRD powder diffraction pattern from the single crystal structures at 150 K. Due to temperature difference, the corresponding peaks in the two diffraction patterns have different shifting at different index space. (a) Compound **1** and (b) compound **2**. Compound **3** becomes totally amorphous after

loss of solvent molecules and consequently no powder diffraction pattern was measured.

References

1. a) K. Nomiya, M. Miwa, R. Kobayashi and M. Aiso, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2983; b) H. So and M. T. Pope, *Inorg. Chem.*, 1972, **11**, 1441; c) H. Stratemeier, M. A. Hitchman, D. L. Kepert, B. W. Skelton, K. E. Sugars and A. H. White, *J. Chem. Soc. Dalton Trans.*, 1992, 303; d) S. A. Malik and T. J. R. Weakley, *J. Chem. Soc. A*, 1968, 2647.