Supporting Information File

A Mixed Valent Dodecanuclear Vanadium Cluster Encapsulating Chloride Anions and its Reaction to form a "Bowl" Shaped Cluster

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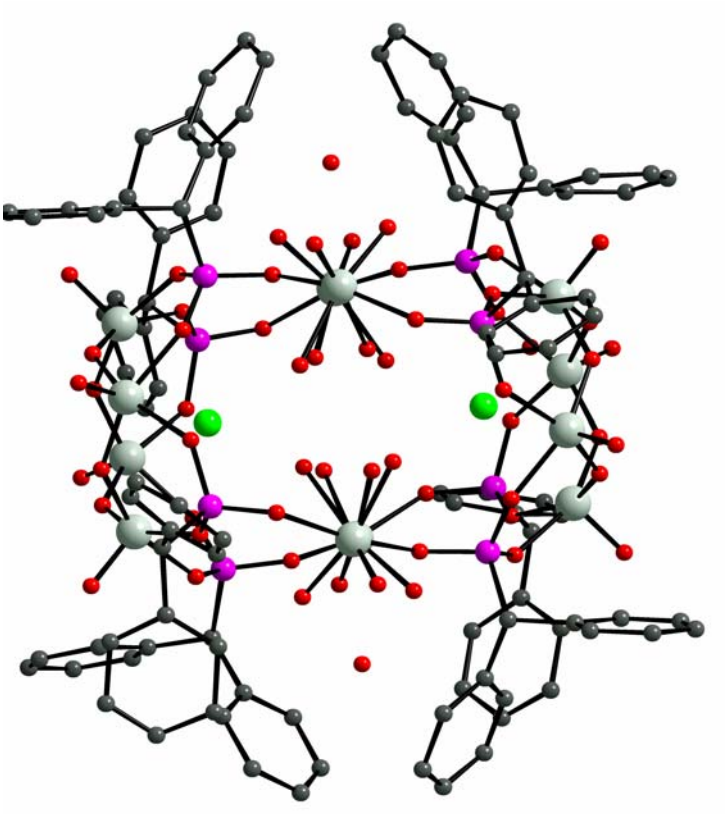

Figure S1. Molecular structure of **1**. Color Code: red, oxygen; dark-grey, carbon; pink, phosphorus; light-grey, V; green, chloride. Hydrogen atoms are removed for clarity.

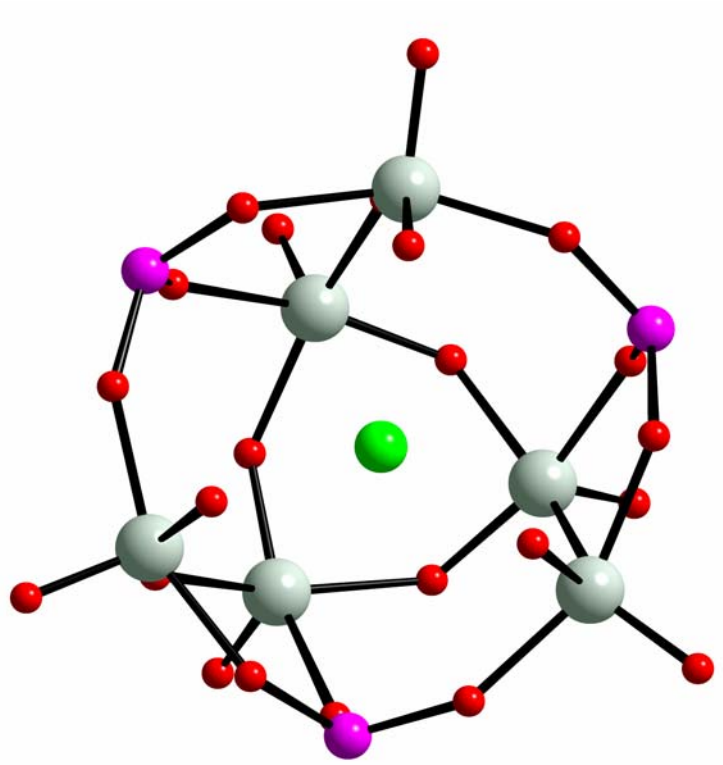

Figure S2. Core structure of hexavanadyl subunit of **2** along *b* axis, illustrating the location of encapsulated chloride anion. Color Code: red, oxygen; pink, phosphorus; light-grey, V; green, chloride.

Table S1. Bond Valance Sum Calculation for **1** and **2.**

1			**2**		
V Site	**BVS**	**Assigned Oxidation State**	**V Site**	**BVS**	**Assigned Oxidation State**
V1	5.37	5	V1	5.46	5
V2	5.13	5	V2	5.44	5
V3	5.21	5			
V4	4.07	4			
V5	4.14	4			
V6	4.14	4			
V7	5.27	5			
V8	5.18	5			
V9	5.22	5			
V10	4.13	4			
V11	5.21	5			
V12	5.26	5			

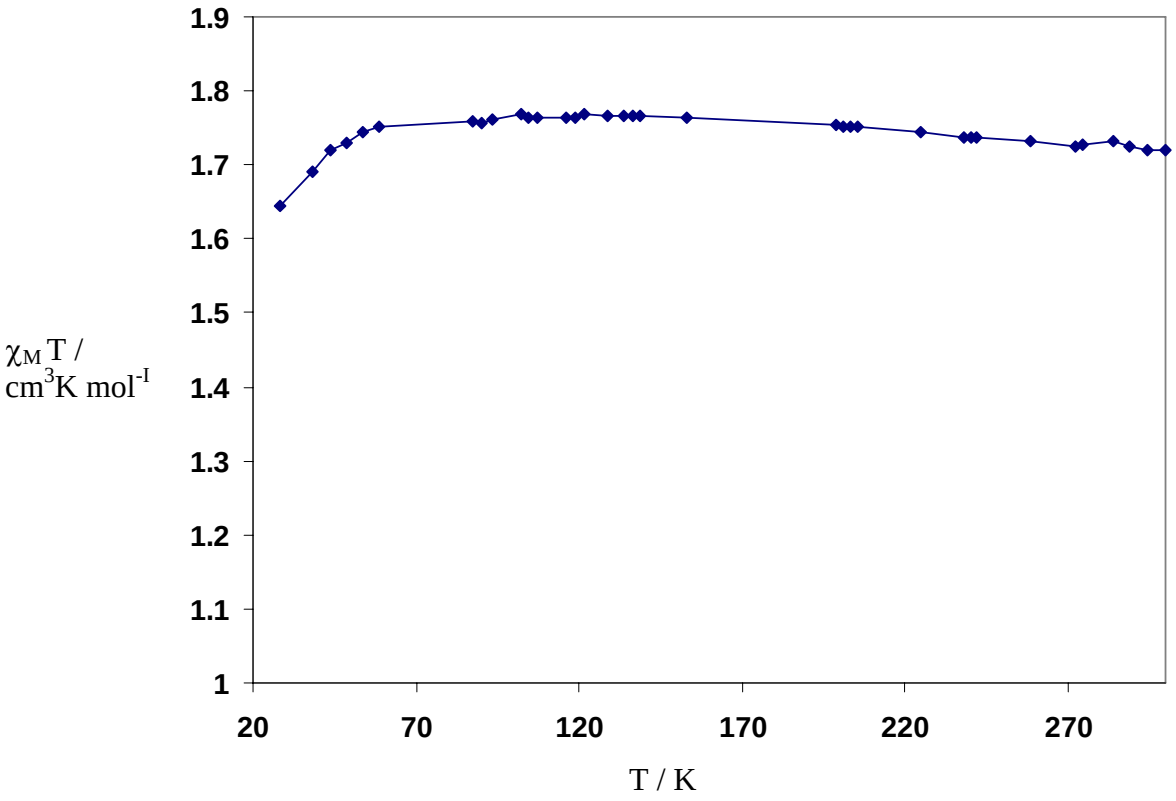

Figure S3. a) Temperature dependence of $\chi_M T$ for a powder sample of **1** in the temperature range 20-300K.

The room temperature $\chi_M T$ value of the compound is 1.71 which is close to the calculated value 1.5(g=2) for four isolated vanadium(IV) centers. This confirms the mixed valent (+5 and +4) nature of the compound.

Compound 2 is diamagnetic and this confirms the +5 oxidation state of both of the vanadiums.