

Encapsulation of paramagnetic 3d¹-vanadium(IV) in an antiferromagnetically coupled dodecanuclear copper(II) cage†

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A mixed metal cluster $[\text{Cu}_{12}\text{VO}_5\text{L}_6]$ of a pentadentate Schiff base (H_3L) containing vanadium(IV) in a dodecanuclear copper(II) cage is prepared by vanadyl templated self assembly of dicopper(II) precursor and the structurally characterized complex shows antiferromagnetic coupling involving copper(II) centers, which leads close to diamagnetism for the $\text{Cu}(\text{II})$ cage below 40 K in the presence of an encapsulated paramagnetic 3d¹-V(IV) atom.

Encapsulation of a paramagnetic metal ion in a magnetically active polymetallic cage is of rare occurrence in the chemistry of large discrete molecular species generated by template synthesis or in a self assembly process.^{1–4} High nuclearity 3d-metal complexes with tunable magnetic properties are of importance in the development of nanomagnetic materials and single molecule magnets with potential application. Herein we report a vanadium(IV) encapsulated dodecanuclear copper(II) complex obtained from a reaction using vanadyl ion as template in the self assembly of six molecules of a dicopper(II) precursor⁵ having a pentadentate Schiff base ligand. A significant physical property of the complex is the antiferromagnetic behavior of the Cu^{II}_{12} cage which becomes essentially diamagnetic below 40 K, while the vanadium(IV) remains one-electron paramagnetic. Again, the formation of discrete high nuclearity molecular species containing an odd number of metal ions and the self assembly process in the presence of ligands with high denticity are uncommon in the chemistry of polymetallic clusters.¹

Complex $[\text{Cu}^{II}_{12}\text{V}^{\text{IV}}\text{O}_5\text{L}_6]$ (**1**) has been prepared from a reaction of $[\text{Cu}^{II}_2\text{L}(\mu\text{-Br})]$ with vanadyl sulfate hydrate in the presence of triethylamine, where H_3L is *N,N'*-(2-hydroxypropyl-1,3-diyl)bis(salicylaldehyde) (Scheme 1).[‡] The complex crystallizes as $1\cdot2\text{CHCl}_3\cdot5\text{H}_2\text{O}$ in trigonal space group $R\bar{3}c$.[§] An ORTEP view of the complex is shown in Fig. 1.^{6,7} The structure consists of a vanadium(IV) at the center of the polymetallic cage showing trigonal bipyramidal (tbp) coordination geometry with five oxo ligands linking vanadium(IV) to the copper(II) atoms that are bound to the pentadentate Schiff base ligands retaining the essential structural features of the dimeric unit of the precursor (Fig. 2). The vanadium sits along the crystallographic three-fold axis with two μ_4 -oxo atoms showing tetrahedral geometry and the remaining three μ_3 -oxo in a trigonal plane. The polymetallic core consists of six metallacyclic rings fused to each other keeping vanadium at the center. Each of these six membered rings consists of two oxo, one alkoxo, two copper and the vanadium atoms. The three-fold

axis of the metallacyclic core has led to a propeller shape of the core.

The polymetallic cluster consists of six $\{\text{Cu}_2\text{L}\}^+$ units that are linked to the vanadium atom through oxo bridges. The dicopper(II) units are linked to each other through the oxo oxygen atoms in forming the cage structure. While the oxo atom having tetrahedral geometry links three dicopper(II) units, the

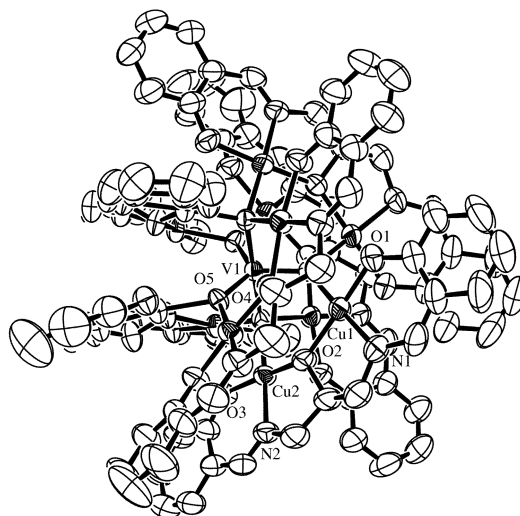
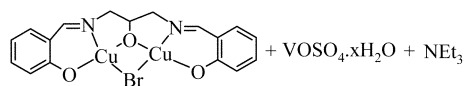


Fig. 1 An ORTEP view of $[\text{Cu}_{12}\text{VO}_5\text{L}_6]$ in $1\cdot2\text{CHCl}_3\cdot5\text{H}_2\text{O}$ showing 50% probability thermal ellipsoids and atom numbering scheme. Selected bond distances (Å) and angles (°) are: Cu(1)–O(1) 1.905(4), Cu(1)–O(2) 1.943(4), Cu(1)–O(5)#1 1.940(3), Cu(1)–N(1) 1.902(5), Cu(2)–N(2) 1.934(5), Cu(2)–O(2) 2.008(4), Cu(2)–O(3) 1.937(4), Cu(2)–O(3)#2 2.332(6), Cu(2)–O(4) 1.963(3), V(1)–O(4) 1.994(6), V(1)–O(5) 1.697(5), Cu(1)–O(2)–Cu(2) 135.4(2), Cu(1)#2–O(5)–Cu(1)#4 104.5(2), Cu(2)#1–O(4)–Cu(2) 103.3(2), V(1)–O(5)–Cu(1)#2 127.76(11), Cu(2)–O(4)–V(1) 115.13(17), O(5)–V(1)–O(4) 90.0, O(4)#3–V(1)–O(4) 180.0, O(5)–V(1)–O(5)#1 120.0. Symmetry transformations used to generate equivalent atoms are: #1 $-x + y + 1, -x + 1, z$; #2 $-y + 1, x - y, z$; #3 $y + 1/3, x - 1/3, -z + 1/6$; #4 $x - y + 1/3, -y + 2/3, -z + 1/6$.



Scheme 1 (i) MeCN–MeOH–CHCl₃, reflux 90 min

† Electronic supplementary information (ESI) available: magnetic susceptibility data for compound **1**. See <http://www.rsc.org/suppdata/cc/b3/b310521k/>

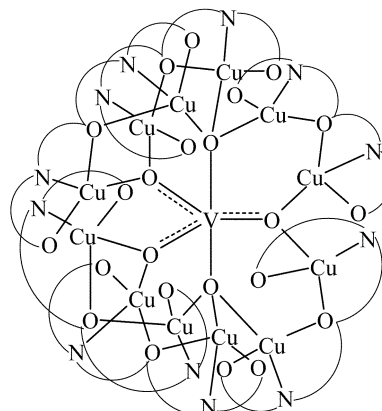


Fig. 2 The structure of **1** showing encapsulation of vanadium(IV) in the dodecanuclear copper(II) cage.

planar oxo atom bridges two dicopper(II) units. The dicopper(II) cores resemble an asymmetrically bridged unit having a monoatomic bridging alkoxo and a triatomic bridging O–V–O group. The coordination environments at the copper(II) centers Cu(1) and Cu(2) are square planar and square pyramidal (4 + 1), respectively. The Cu–N and Cu–O distances are similar to those observed for dimeric copper(II) complexes containing pentadentate Schiff base ligand.^{5,8}

In the tbp geometry of the vanadium atom, the equatorial V–O distance of 1.697(5) Å is significantly shorter than the axial V–O distance of 1.994(6) Å. The axially bound oxygen atom O(4), bonded to three coppers and the vanadium ion, is tetrahedral with a V–O single bond. The equatorial oxygen atom O(5), bonded to two coppers and vanadium, is planar and has a V–O double bond character.⁹ The distances between V and Cu atoms of > 3.26 Å preclude any direct interaction between the metal centers.

The self-assembly of the dicopper(II) units to the cage structure has a significant effect on the magnetic property of the complex. The complex is thermally stable up to 250 °C. The variation of the magnetic susceptibility in the temperature range 450 to 17 K is shown in Fig. 3. The precursor complex [Cu₂L(μ-Br)] is known to show a magnetic moment of 1.80 μ_B per copper at 300 K and 0.68 μ_B at 18 K.¹⁰ Complex 1·2CHCl₃·5H₂O displays an overall antiferromagnetic (AF) behavior. The μ_{eff} values per cluster unit at 450, 300 and 18 K are 5.77, 4.90 and 1.77 μ_B, respectively. The data suggest that the Cu₁₂ cage becomes essentially diamagnetic below 40 K with a magnetic moment that corresponds to the one-electron paramagnetic vanadium(IV). The copper(II) centers in the Cu₁₂ cage with μ_{eff} value of 1.59 and 1.32 μ_B (per copper) at 450 and 300 K, respectively, are significantly paramagnetic in the presence of a non-interacting vanadium(IV) ion with a magnetic moment value of 1.74 μ_B (calculated excluding the TIP values for the copper(II) atoms). The dicopper(II) units in 1 with a Cu(1)–O(2)–Cu(2) angle of 135° are likely to promote strong antiferromagnetic interaction between the copper centers. The oxo-bridging atom having a tetrahedral geometry is unlikely to mediate any superexchange interaction between the copper and vanadium or between two copper centers. The Cu–O–Cu bridge having a planar oxo atom could mediate significant interdimer intracluster interaction between two copper centers. The magnetic interaction between the vanadium and copper centers involving the planar-oxo atom bridge is, however, expected to be weak considering the involvement of different magnetic orbitals for the 3d⁹-Cu(II) and 3d¹-V(IV) atoms. This leaves the vanadium(IV) atom as an essentially uncoupled one-electron paramagnetic center. Such a situation makes this complex unique in having an isolated trapped single spin center in a magnetically active Cu₁₂ cage whose property varies from

weak AF coupled paramagnetic at higher temperatures to essentially diamagnetic below 40 K.

In summary, the self assembly process using vanadyl ion as a template has generated a 3d¹ vanadium(IV) encapsulated in a Cu₁₂ cluster cage exemplifying a novel discrete polymetallic molecular species. The Cu₁₂ cage is antiferromagnetically coupled at all temperatures and acts as an essentially diamagnetic “host” below ca. 40 K in the presence of the encapsulated paramagnetic vanadium(IV) atom. Complex 1 exemplifies a rare cluster with 13 transition metal ions in a discrete molecular species in the presence of a polydentate ligand.

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Notes and references

‡ Preparation of [Cu₁₂VO₅L₆] (1). The complex was prepared by reacting [Cu₂L(μ-Br)] (0.24 g, 0.47 mmol) in MeCN (10 cm³) with triethylamine (0.15 cm³, 1.1 mmol) whilst stirring followed by addition of vanadyl sulfate hydrate (0.07 g, 0.42 mmol) taken in methanol (5 cm³). The mixture was refluxed for 15 min and CHCl₃ (5 cm³) was added to it for dissolving any suspended solid. The solution was refluxed further for a period of 90 min. It was then cooled to an ambient temperature and filtered. The product as a dark green crystalline mass was obtained on slow evaporation of the solvent. The solid was separated, washed with ethanol and dried in vacuum over fused CaCl₂. Single crystals of composition 1·2CHCl₃·5H₂O for X-ray diffraction and analytical studies were grown by slow evaporation of the mother liquor at 25 °C. Yield: ~57% (0.12 g). Found: C, 41.5; H, 3.2; N, 5.5. Calc. for C₁₀₂H₉₀N₁₂O₂₃Cu₁₂V·2CHCl₃·5H₂O: C, 41.8; H, 3.3; N, 5.6%. Electronic spectral data in MeOH [λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹): 630 (1.4 × 10³), 365 (5.5 × 10⁴), 270 (1.55 × 10⁴), 242 (2.3 × 10⁴), 227 (2.4 × 10⁴). FT-IR (KBr phase, cm⁻¹): 3419br, 2906w, 1637vs, 1599m, 1537m, 1469m, 1449s, 1396w, 1343w, 1319m, 1193m, 1149m, 1125w, 1058w, 1028w, 892w, 836m, 752m, 691m, 584w, 540w, 458w, 420w (s, strong; m, medium; w, weak; br, broad). χ_M^{corr} for 1·2CHCl₃·5H₂O: 9.23 × 10⁻³ cm³ mol⁻¹ at 450 K; 22.80 × 10⁻³ cm³ mol⁻¹ at 17 K (TIP for 12 copper(II) = 720 × 10⁻⁶ cm³ mol⁻¹; χ_{dia} = 1685 × 10⁻⁶ cm³ mol⁻¹). § Crystal data for 1·2CHCl₃·5H₂O: C₁₀₄H₁₀₂Cu₁₂VN₁₂O₂₈Cl₆, *M* = 2994.1, trigonal, space group *R*3c (no. 167), *a* = 16.001(3), *b* = 16.001(3), *c* = 79.15(4) Å, *U* = 17552(9) Å³, *Z* = 6, *D*_c = 1.7 g cm⁻³, *T* = 293(2) K, 1.54 ≤ θ ≤ 27.56°, μ = 24.21 cm⁻¹, *F*(000) = 9042, *R*1 = 0.0729, *wR*2 = 0.2191 for 3121 reflections with *I* > 2σ(*I*) and 239 parameters [*R*1 (*F*²) = 0.0964 (all data)]. Weighing scheme: *w* = 1/[σ²(*F*_o²) + (0.1561*P*)² + 49.27*P*], where *P* = [*F*_o² + 2*F*_c²]/3. X-ray data were from Bruker SMART APEX CCD diffractometer and the structure was solved by the heavy atom method and refined using SHELX system of programs.⁶ CCDC 219239. See <http://www.rsc.org/suppdata/cc/b3/b310521k/> for crystallographic data in .cif or other electronic format.

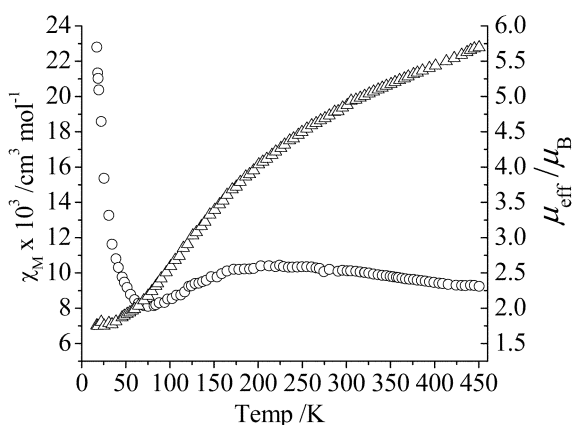


Fig. 3 Plots showing the variation of χ_M, O (per cluster) and μ_{eff}, Δ (per cluster) vs. temperature for complex 1.

- R. E. P. Winpenny, *Adv. Inorg. Chem.*, 2001, **52**, 1.
- V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf and A. Barwinski, *Prog. Inorg. Chem.*, 1997, **45**, 83.
- J.-M. Lehn, *Supramolecular Chemistry – Concepts and Properties*, VCH, Weinheim, Germany, 1995; G. B. Deacon, T. Feng, D. C. R. Hockless, P. C. Junk, B. W. Skelton and A. H. White, *Chem. Commun.*, 1997, 341.
- A. Müller, L. Toma, H. Bögge, M. Schmidtman and P. Kögerler, *Chem. Commun.*, 2003, 2000.
- W. Mazurek, K. J. Berry, K. S. Murray, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Inorg. Chem.*, 1982, **21**, 3071.
- G. M. Sheldrick, *SHELX-97, Program for crystal structure solution and refinement*, University of Göttingen, Göttingen, Germany, 1997.
- C. K. Johnson, *ORTEP, III Report ORNL-5138*, Oak Ridge National Laboratory, Oak Ridge, TN.
- Y. Nishida and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1986, 2633; A. Mukherjee, I. Rudra, M. Nethaji, S. Ramasesha and A. R. Chakravarty, *Inorg. Chem.*, 2003, **42**, 463.
- Y. Zhang, J. R. D. DeBord, C. J. O'Connor, R. C. Haushalter, A. Clearfield and J. Zubietta, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 989; X.-M. Zhang, M.-L. Tong and X.-M. Chen, *Chem. Commun.*, 2000, 1817.
- A. Mukherjee, S. G. Naik, I. Rudra, M. Nethaji, S. Ramasesha and A. R. Chakravarty, *Inorg. Chem.*, 2003, **42**, 5660.