

First Non-Centrosymmetric Deca-Vanadoborate with Borate Vacancies, Self-Assembled around a 1,3-Propanediammonium Cation

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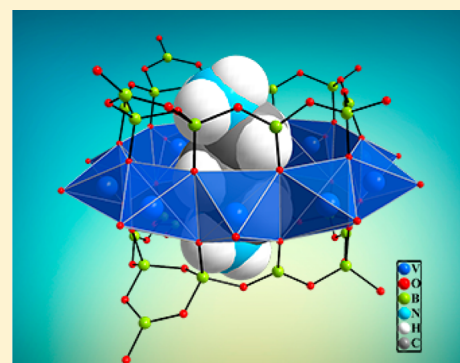
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Supporting Information

ABSTRACT: The first borate-vacant deca-vanadoborate of formula $(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_5 [(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8] \cdot 13.23\text{H}_2\text{O}$ with an occluded 1,3-propanediammonium cation, using molten methylboronic acid flux reaction is reported. This cluster lacks four borate units with respect to all known deca-vanadoborates. It crystallizes in the orthorhombic $P2_12_12$ space group which is non-centrosymmetric, leading to the first non-centrosymmetric deca-vanadoborate reported in the literature. Even though the deca-vanadoborates formed by 28 borate units have an inner space large enough to host a molecule, no examples have been reported before. The electronic properties were studied using electronic spectroscopy, corroborating a fully reduced species, due to the lack of intervalence charge transfer transitions in the 1000 to 1500 nm region. The magnetic behavior provided evidence that the studied cluster presents strong antiferromagnetism among the ten V^{IV} spin-carriers, with an $S = 0$ ground state. Using a model considering three different exchange pathways, three different J values were obtained, all of them antiferromagnetic in nature.



The structural plasticity and the high affinity for oxygen to form covalent bonds that vanadium presents in its different oxidation states allow vanadium oxide clusters better known as polyoxovanadates to be obtained. The structural self-assembly of this kind of compound has a tendency to form spherical cage-like structures, suitable to act as host systems encapsulating small ions or molecules (X) in their inner cavity; for instance, the pentadecavanadates $[\text{V}_{15}\text{O}_{36}\text{X}]^{4-}$ ($\text{X} = \text{Cl}^-$, Br^- , CO_3^{2-}),¹⁻⁴ the hexadecavanadates $[\text{V}_{16}\text{O}_{42}(\text{X})]$ ($\text{X} = \text{Cl}^-$, SO_4^{2-}),^{5,6} and the octadecavanadates $[\text{V}_{18}\text{O}_{42}(\text{X})]$ ($\text{X} = \text{H}_2\text{O}$, Cl^- , Br^- , I^- , NO_2^- , SH^- , HCOO^- , VO_4^{3-}).^{4,7} The inclusion of boron atoms to give polyoxovanadoborate clusters (VBO) enriches the structural diversity of these species.⁸ In VBO clusters, vanadium atoms always adopt square base pyramid coordination geometry $[\text{VO}_5]$, even when they present both +4 and +5 oxidation states. Within the VBO family several compounds containing 6, 10, or 12 vanadium centers, namely, the $\{\text{V}_6\text{B}_{20}\text{O}_{50}\text{H}_n\}$ ($n = 0, 6, 8, 12$),⁹⁻¹³ $\{\text{V}_6\text{B}_{22}\text{O}_{54}\text{H}_{10}\}$ ¹⁴ $\{\text{V}_6$ -type $\}$, $\{\text{V}_{10}\text{B}_{28}\text{O}_{74}\text{H}_n\}$ ($n = 4, 8$)¹⁵⁻¹⁸ $\{\text{V}_{10}$ -type $\}$, $\{\text{V}_{12}\text{B}_{16}\text{O}_{58}\text{H}_8\}$,^{19,20} $\{\text{V}_{12}\text{B}_{17}\text{O}_{58}\text{H}_8\}$ ²¹ $\{\text{V}_{12}$ -i-type $\}$, $\{\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_n\}$ ($n = 3, 6$)^{14,22-36} $\{\text{V}_{12}$ -ii-type $\}$, and

$\{\text{V}_{12}\text{B}_{32}\text{O}_{84}\text{H}_8\}$ ^{37,38} $\{\text{V}_{12}$ -iii-type $\}$ have been synthesized previously. The $\{\text{V}_6$ -type $\}$, $\{\text{V}_{12}$ -i-type $\}$, and $\{\text{V}_{12}$ -ii-type $\}$ adopt closed spherical-like structures, while the $\{\text{V}_{10}$ -type $\}$ and $\{\text{V}_{12}$ -iii-type $\}$ adopt open barrel-like structures. Usually, a water molecule is found occupying the internal cavity of these polyanions, whose crystallographic position normally matches the inversion center that is usually present in these highly symmetrical systems. Only five $\{\text{V}_{10}$ -type $\}$ structures are found in the literature,¹⁵⁻¹⁷ in which a secondary metal atom ($M = \text{Zn}, \text{Mn}$) is covalently coordinated to some oxygen atoms of the polyanion. Cao et al.¹⁶ reported a $\{\text{V}_{10}$ -type $\}$ polyanion which was magnetically characterized by EPR, with a measured g -value of 2.0527. In the present work we report a new vanadoborate containing ten vanadium centers of formula $(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_5 [(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8] \cdot 13.23\text{H}_2\text{O}$ (**1**). Compound **1** is the first VBO system whose polyanion $[\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]^{12-}$ is non-centrosym-

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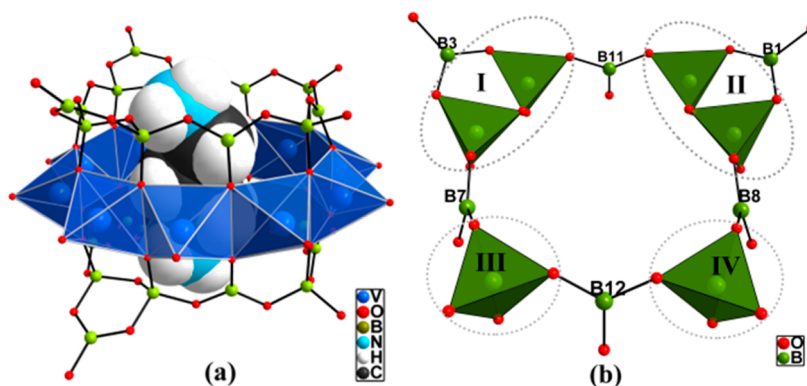


Figure 1. (a) Crystalline structure of the $[\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]^{12-}$ polyanion of **1**; pentacoordinated vanadium VO_5 units are shown as blue polyhedra, B and O atoms are represented in ball and stick fashion. (b) $[\text{B}_{12}\text{O}_{30}\text{H}_4]^{20-}$ polyborate ligand of **1**; tetrahedral boron atoms are represented as green polyhedra.

metric and is self-assembled around a protonated 1,3-propanediamine (1,3-diapH₂) molecule, which is occluded inside the polyanion cavity. This organic 1,3-diapH₂ cation acts both as a charge counterbalancing agent and as a structural directing molecule.

The green crystals of **1** were obtained under autogenous pressure, using molten methylboronic acid as a reactive flux, in the presence of V_2O_5 and 1,3-propanediamine (120 °C, 3 days; Yield: 22% based on V). The vanadoborate polyanion $[\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]^{12-}$ of **1** consists of a central decavanadate ring-like fragment ($\text{V}_{10}\text{O}_{30}$) condensed to two $[\text{B}_{12}\text{O}_{30}\text{H}_4]^{20-}$ moieties. In the central ($\text{V}_{10}\text{O}_{30}$) fragment, each of the vanadium atoms is penta-coordinated in a square base pyramid coordination geometry, with $\text{V}=\text{O}$ and $\text{V}-\text{O}$ bond distances ranging from 1.601(4) Å to 1.618(5) Å and 1.902(4) Å to 1.987(4) Å, respectively (see Supporting Information, Table S1). The VO_5 units are edge-sharing and present $\text{V}\cdots\text{V}$ distances between 2.8712(13) and 3.0880(2) Å. The $\text{O}-\text{V}-\text{O}$ angles range from 137.88(19)° to 146.73(19)°, reflecting the typical displacement from the base of the pyramid of the vanadium centers.^{39,40} As shown in Figure 1, both $[\text{B}_{12}\text{O}_{30}\text{H}_4]^{20-}$ crowns consist of six tetrahedral and six trigonal boron–oxygen units. Each $[\text{B}_{12}\text{O}_{30}\text{H}_4]^{20-}$ moiety contains two pairs of tetrahedral $[\text{BO}_4]$ units, labeled as fragment I and fragment II in Figure 1. Both fragments are linked by one trigonal $[\text{BO}_3]$ entity (B11). Between the corner-sharing $[\text{BO}_4]$ tetrahedral units which form fragments I and II, there is one $[\text{HOBO}_2]$ trigonal terminal entity (B1 and B3). The two remaining tetrahedral units, assigned as fragments III and IV, are linked together by one trigonal $[\text{BO}_3]$ entity (B12). Fragments III and IV are connected to fragments I and II by two trigonal $[\text{BO}_3]$ entities (B7 and B8), respectively, in an alternating fashion, thus forming the $[\text{B}_{12}\text{O}_{30}\text{H}_4]^{20-}$ crown. The B–O bond distances of the $[\text{BO}_4]$ and $[\text{BO}_3]$ entities are in the expected range with values between 1.343(9) and 1.501(9) Å.

A comparison of the reported $[\text{B}_{14}\text{O}_{32}\text{H}_4]^{18-}$ and $[\text{B}_{14}\text{O}_{30}(\text{OH})_2]^{20-}$ polyborates that are part of the $\{\text{V}_{10}\text{-type}\}$ systems^{15–18} with the above-described $[\text{B}_{12}\text{O}_{30}\text{H}_4]^{20-}$ fragment of **1** suggests that the latter possesses a lower degree of condensation, lacking two tetrahedral boron units (Figure 1). Therefore, **1** can be viewed as a new $\{\text{V}_{10}\text{-type}\}$ system whose crystalline structure exhibits a boron deficiency in each polyborate crown. The most amazing feature of **1** is that the $[\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]^{12-}$ anion contains a diprotonated organic molecule of 1,3-diapH₂ within its cavity (Figure 1). The

average cavity diameter is ca. 9.6 Å, measured between one of the internal vanadium atoms and the opposite one. The occluded 1,3-diapH₂ adopts a “W”-type conformation⁴¹ with a length of 5.010(9) Å ($\text{N}_5\cdots\text{N}_5'$) and a volume of 106.14 Å³. The presence of the structural directing 1,3-diammoniumpropane induces the lower degree of condensation of borate units. The use of different diamines, such as 1,2-ethylenediamine, 1,2-diaminepropane, 1,4-diaminebutane, or 1,6-diaminehexane, using methylboronic flux at 120 °C for 72 h did not produce the $[\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]$ polyanion with the corresponding occluded diammonium molecule. The size of the diamine and the position of the ammonium group in the chain apparently affects the degree of condensation of borate units generated by the decomposition of the methylboronic molecules, thus avoiding the formation of the above-mentioned non-centrosymmetric vanadoborate species. Hydrogen bond interactions between this organic molecule and different oxygen atoms of the polyborate crowns should be responsible of the stability of the new $\{\text{V}_{10}\text{-type}\}$ system (see Supporting Information, Figure S1). Unlike the previously reported vanadoborates, $[\text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]^{12-}$ does not have a center of symmetry but only axes of rotation leading to a polar unit. This is due to the bonding of a nonsymmetric polyborate fragment to a highly symmetric $\{\text{V}_{10}\text{-type}\}$ ring. Moreover this singular feature is conserved when the occluded 1,3-diapH₂ is considered. Finally, the combination of this hybrid $[(1,3\text{-diapH}_2)@ \text{V}_{10}\text{B}_{24}\text{O}_{66}\text{H}_8]^{10-}$ polyanion and the intercluster 1,3-diapH₂ cations, which are also polar molecules, results in a chiral lattice (see Supporting Information, Figure S2). The bond valence sum (BVS) average value⁴² of 4.152 obtained for **1** indicates that all the vanadium atoms are reduced, in the +4 oxidation state, each one with one unpaired electron (d^1). This is corroborated by the UV–vis spectrum which does not present absorption bands between 1000 and 1500 nm, associated with intervalence charge transfer transitions (IVCT, see Supporting Information, Figure S3). Moreover the FTIR spectrum shows a single sharp band at 974 cm^{-1} , indicating the presence of only one type of $\text{V}=\text{O}$ group in the cluster (see Supporting Information, Figure S4).

To the best of our knowledge, Cao et al.¹⁶ are the only authors that have reported magnetic properties of a deca-vanadoborate using only EPR spectroscopy. However, their deca-vanadoborate is functionalized with paramagnetic transition metals. In this work the magnetic study of a system having only V^{IV} spin carriers is reported. The magnetic behavior

of **1** as $\chi_M T(T)$ between 2 and 300 K is depicted in Figure 2, indicating a strong antiferromagnetic coupling. The magnetic

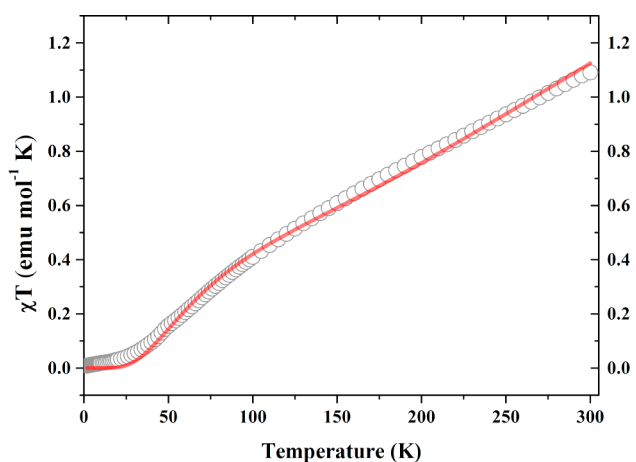


Figure 2. Temperature dependence of $\chi_M T$. Open circles represent the experimental magnetic susceptibility data ($\chi_M T$) of **1**; the red line shows the fit considering three J values.

moment (μ_{eff}) value at 300 K of $0.961 \mu_B$ per vanadium center (obtained considering an experimental g value of 1.97 from EPR measurements) is significantly lower than the expected value for one unpaired electron ($\mu_{\text{eff}} = 1.756 \mu_B$). The $\chi_M T$ decreases upon cooling reaching a value close to zero at 2 K ($\chi_M T_{(2K)} = 0.00907 \text{ emu mol}^{-1} \text{ K}$), indicating that at low temperature a $S = 0$ diamagnetic state is almost the only populated one. The fit of the experimental magnetic data of **1** (red line, Figure 2) was done using a matrix technique with the Magprop program on the DAVE code⁴³ with a fixed g value of 1.97.

Based on the values of the V–O–V angles of the structure and using the magneto-structural and theoretical study reported by Rodriguez-Fortea et al.,⁴⁴ three different exchange pathways were defined (Figure 3), where the HDVV Hamiltonian is

$$H = -J_1(S_1 \cdot S_2 + S_5 \cdot S_6 + S_7 \cdot S_8 + S_9 \cdot S_{10}) \\ - J_2(S_2 \cdot S_3 + S_4 \cdot S_5 + S_6 \cdot S_7 + S_8 \cdot S_9 + S_{10} \cdot S_1) \\ - J_3(S_3 \cdot S_4)$$

The best fit was obtained with $J_1 = -240.5 \text{ cm}^{-1}$, $J_2 = -210.2 \text{ cm}^{-1}$ and $J_3 = -9.82 \text{ cm}^{-1}$, all being antiferromagnetic.

In conclusion, the protonated diamine molecules are acting as reducing species in the synthetic procedure, as charge compensating cations in the lattice, and as structure directing agents, the reported cluster being the first one to contain an occluded organic diammonium cation. Moreover, the reported polyoxometalate is the first non-centrosymmetric decavanadoborate with a vacancy of four borate units.

A fairly good fit of the magnetic data was obtained assuming a model with three exchange pathways between the V^{IV} atoms. The antiferromagnetic interactions in **1** are strong enough to produce a $\chi_M T$ value close to zero at 2 K. The lowest obtained J value is related to the largest V–O–V angle as expected from the above-mentioned magneto-structural correlation.

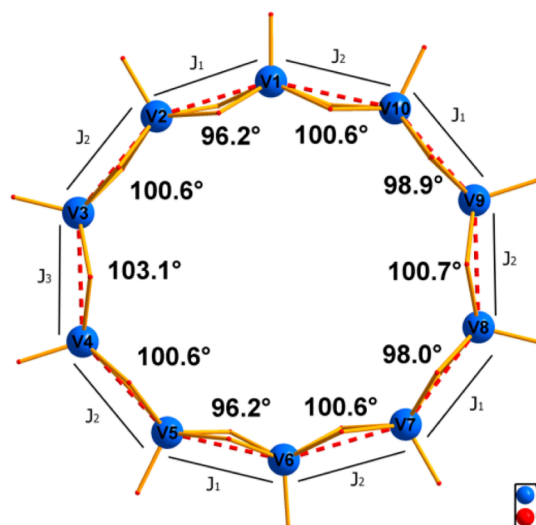


Figure 3. Graphical representation of the $(V_{10}O_{30})$ ring of the polyanion of **1**, showing three different magnetic exchange pathways (J_1 , J_2 , and J_3). The pathways were defined considering the V–O–V angle values.

■ ASSOCIATED CONTENT

📄 Supporting Information

Complete synthetic procedure and elemental analysis, crystallographic details, UV–vis absorption spectrum, FTIR spectrum, X-ray powder diffractograms (calculated and measured), and magnetic measurement details. Crystal data for **1** ($N_{12}C_{18}H_{106.46}V_{10}B_{24}O_{79.23}$): $M_r = 2528.34$, Orthorhombic, $P2_12_12_1$, $a = 16.3012(2) \text{ \AA}$, $b = 16.5873(2) \text{ \AA}$, $c = 17.1743(2) \text{ \AA}$, $V = 4643.81(10) \text{ \AA}^3$, $Z = 2$, $T = 293 \text{ K}$, $\rho = 1.798 \text{ g cm}^{-3}$, $\mu = 1.086 \text{ mm}^{-1}$, GOF = 1.051. A total of 46881 reflections were collected and 10714 reflections are unique reflections ($R_{\text{int}} = 0.0438$). The final R index was $[I \geq 2\sigma(I)] R_1 = 0.0505$ (Table S2). The structure was solved by direct methods and refined by SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. The crystallographic information file is also available from the Cambridge Crystallographic Data Center (CCDC) upon request (<http://www.ccdc.cam.ac.uk> CCDC deposition number 971731). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00102.

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Author Contributions

The manuscript was written with contributions from all the authors. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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