Preparation and Properties of a Closo Nitride Cluster, the Cubane $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$

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Summary: Reduction of $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2$ with sodium amalgam in toluene gave the diamagnetic cubane $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$, which was characterized by spectroscopy, chemical analysis, and X-ray crystallography. The cluster has short V-V and V-N distances (2.674(8) and 1.87(2) Å, respectively), indicative of a strong V-N bond. It can be reversibly reduced electrochemically to $\{[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4\}^-$.

Clusters containing main-group atoms which are three-coordinated to the triangular faces of transition-metal arrays are common for the elements of groups 16 and 17 but very rare for group 15. Dahl and co-workers prepared the cubanes $[Co(CO)_3(\mu_3\text{-}Sb)]_4$[1] and $[(\eta\text{-}C_5H_5)Co(\mu_3\text{-}P)]_4$[2] and discussed possible routes to similar compounds containing nitrogen.[3] Roesky and co-workers prepared $[(\eta\text{-}C_5Me_5)Ti(\mu_2\text{-}NH)]_3(\mu_3\text{-}N)$,[4] and during the writing of this paper, Mena and co-workers obtained $[(\eta\text{-}C_5Me_5)Ti(\mu_3\text{-}N)]_4$ by treatment of $(\eta\text{-}C_5Me_5)Ti(NMe_2)_3$ with NH_3.[5] We communicate here the rational synthesis of the nitride cubane $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$, by reduction of $[(\eta\text{-}C_5Me_5)VCl(\mu_2\text{-}N)]_2$.

Reduction of $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2$[6] with sodium amalgam in toluene, or with lithium nitride or magnesium in tetrahydrofuran, gave golden brown $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ (equation 1).[7] The reaction appeared to proceed

$$2[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2 + 4Na \rightarrow [(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4 + 4NaCl \quad (1)$$

quantitatively, although workup was complicated by the presence of colloidal sodium, lithium, or magnesium, chloride.

Diamagnetic $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ was characterized by NMR spectroscopy in $C(^2H_1)Cl_3$ solution (^1H, 1.75 ppm, singlet; ^{13}C, 114.3 ppm, singlet, $C_5(CH_3)_5$ and 12.6 ppm, singlet, $C_5(CH_3)_5$; ^{51}V, 19.2 ppm, singlet), high-resolution mass spectrometry (found *m/e* 800.2513, calculated for $C_{40}H_{60}V_4N_4$ 800.2578), low-resolution mass spectrometry (all $(C_5Me_5)_nV_4N_4$ fragments for $n = 4-2$), infrared spectroscopy (intense absorption band at 441 cm^{-1}, assigned to the antitranslational mode of the $[V(\mu_3\text{-}N)]_4$ core[8]), elemental analysis (Anal. Found: C, 59.2 H, 7.5; N, 7.4. Calcd for $C_{40}H_{60}N_4V_4$: C, 60.0; H, 7.6; N, 7.0), and X-ray crystallography[9] (Figure 1). The results prove that the product was the desired cubane.

The cluster was moderately sensitive to O_2 but very sensitive to hydrolysis. It could be reduced electrochemically (tetrahydrofuran solution, $Bu^t{}_4NBF_4$ as supporting electrolyte) with a reversible reduction wave at +0.16 V.

In $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ the V-V and V-N distances average 2.674(8,48) and 1.87(2,12) Å, respectively.[12] Both distances are very similar to those in $[(\eta\text{-}C_5Me_5)$-

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(7) Experimental details: a solution of $[(\eta\text{-}C_5Me_5)VCl(\mu_2\text{-}N)]_2$[5] (1.51 g, 3.20 mmol) in toluene (100 cm^3) was added to sodium amalgam (0.74 g (32 mmol) of Na in 15 cm^3 of Hg). The resultant mixture was stirred vigorously for 12 h. During the first 1 h, the color of the solution changed from green-blue to very dark brown. The solution was decanted from the mercury layer and then set aside for 24 h before filtering twice through Celite to remove sodium chloride. The solution was reduced in volume to 20 cm^3 under vacuum, and then hexane (80 cm^3) was distilled onto it. The mixture was set aside at −25 °C for 12 h, after which the brown precipitate was collected by filtration. It was recrystallized by extraction with warm (60 °C) toluene (100 cm^3), reduction of the volume to 20 cm^3, and addition of hexane (80 cm^3) as before. Yield of $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$: 0.58 g, 45%. An analytically pure sample was obtained by sublimation of the recrystallized product at 160 °C and 0.02 Torr for 12 h, followed by recrystallization from toluene/hexane.

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(9) Very small crystals of $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ were obtained by recrystallization from toluene/ether. Because of the size of the crystal (0.06 × 0.15 × 0.22 mm), all diffraction experiments were performed with a rotating copper anode (Cu Kα, $\lambda = 1.5418$ Å). Initially, the structure was determined in the triclinic space group $P\bar{1}$: $a = 18.147(6)$ Å, $b = 10.888(6)$ Å, $c = 10.906(5)$ Å, $\alpha = 66.89(4)°$ $\beta = 83.79(4)°$, $\gamma = 83.98(4)°$, $V = 1965.8$ $Å^3$, $Z = 2$ (of $C_{40}H_{60}V_4N_4$). This cell is very similar to those of $[(\eta\text{-}C_5Me_5)Ti(\mu_3\text{-}N)]_4$,[5] $[(\eta\text{-}C_5Me_5)Cr(\mu_3\text{-}O)]_4$,[8] and $[(\eta\text{-}C_5Me_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti,[10] V[11]). The intensities of 5850 reflections to $2\theta = 120°$ were measured on a Rigaku AFC5R diffractometer at 296 K. Refinement using 1723 reflections with $I > 3.0\sigma(I)$ gave $R = 0.187$, with all atoms isotropic. Although the determination clearly showed the cubane structure of $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ (average V-V distance 2.66(1) Å, V-N = 1.86(4) Å, V-N-V 90.5(22)°, N-V-N = 89.4(20)°), the *R* value could not be reduced further, and many of the thermal parameters of C and N were unreasonable. Inspection of photographs and of the diffraction sphere on the diffractometer revealed the presence of significant reflections which arose from a doubling of the *a* dimension of the cell. A new data set of 11 708 reflections was collected from the cell: $a = 36.285(6)$ Å, $b = 10.877(3)$ Å, $c = 10.918(3)$ Å, $\alpha = 66.89(2)°$, $\beta = 83.68(2)°$, $\gamma = 83.88(2)°$, $V = 3929.7$ $Å^3$, $Z = 4$. Refinement on F^2 using 11 568 reflections gave $R1 = 0.099$ and $wR2 = 0.250$. The V atoms were refined anisotropically (426 parameters, GOF = 2.02). The average distances and angles in the two independent molecules of $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ (which do not differ significantly) are given in the caption to Figure 1; they are not significantly different from those derived from the data obtained from the smaller cell. The N and C atoms could not be refined anisotropically. This fact, combined with the observation of some reflections which could not be indexed with the present cell, suggests that a yet larger supercell is present. This possibility is being investigated. However, the metrical parameters of $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}N)]_4$ will not be significantly affected by refinement in the new cell.

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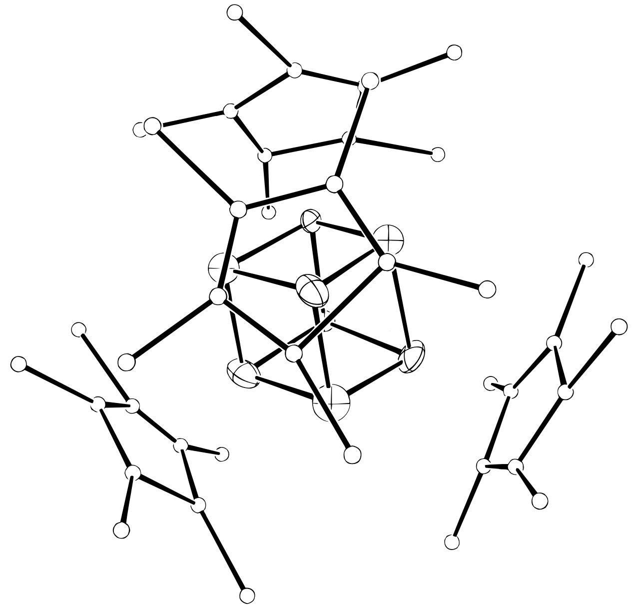

Figure 1. Structure of [(η-C_5Me_5)V(μ_3-N)]$_4$, as determined by X-ray diffraction. Important average distances (Å) and angles (deg) in the two independent molecules are as follows: V-V, 2.674(8,48); V-N, 1.87(2,67); V-Cp, 2.01(2,4); V-N-V, 91.1(9,67); N-V-N, 88.8(9,72).

Ti(μ_3-N)]$_4$, (Ti-Ti = 2.788 Å, Ti-N = 1.939 Å[5]) when the difference in radii of Ti and V is taken into account. The average V-N distance is longer than that in [(η-C_5Me_5)-VCl(μ_2-N)]$_2$ (1.771(2) Å[6]). This is expected because [(η-C_5Me_5)V(μ_3-N)]$_4$ contains μ_3-N, whereas [(η-C_5Me_5)VCl-(μ_2-N)]$_2$ contains μ_2-N. However, the observation that the V-V and V-N distances are considerably shorter than the Cr-Cr and Cr-O distances in [(η-C_5Me_5)Cr(μ_3-O)]$_4$ (2.834(2) and 1.945(5) Å, respectively[8]) is unexpected. Regardless of whether the clusters are considered as containing $V^{IV}-N^{-III}$ and $Cr^{III}-O^{-II}$ or as containing neutral atoms, the vanadium nitride is expected to be larger than the chromium oxide cluster. There are four cluster electrons in [(η-C_5Me_5)V(μ_3-N)]$_4$, which occupy the e orbitals shown in Figure 2.[13,14] This e orbital is completely nonbonding. In [(η-C_5Me_5)Cr(μ_3-O)]$_4$ there are 12 cluster electrons, which occupy the e, 1t$_2$, and a$_1$ orbitals (Figure 2). The 1t$_2$ orbital is antibonding by symmetry, and the a$_1$ is bonding, but the overlap integrals for all of the e, 1t$_2$, and a$_1$ orbitals are very small. Thus, the reduction in the average M-M distance on going from [(η-C_5Me_5)Cr(μ_3-O)]$_4$ to [(η-C_5Me_5)V(μ_3-N)]$_4$ is not due to the number or configuration of the cluster electrons. The position of the ^{51}V signal in the NMR spectrum (+19.2 ppm relative to V(O)Cl_3) is indicative of a low electron density at the vanadium atoms.[15] Thus, the spectroscopic, diffraction, and molecular orbital results suggest that the size of the [V(μ_3-N)]$_4$ core is a reflection of a very strong V-N σ-bond in [(η-C_5Me_5)V(μ_3-N)]$_4$.

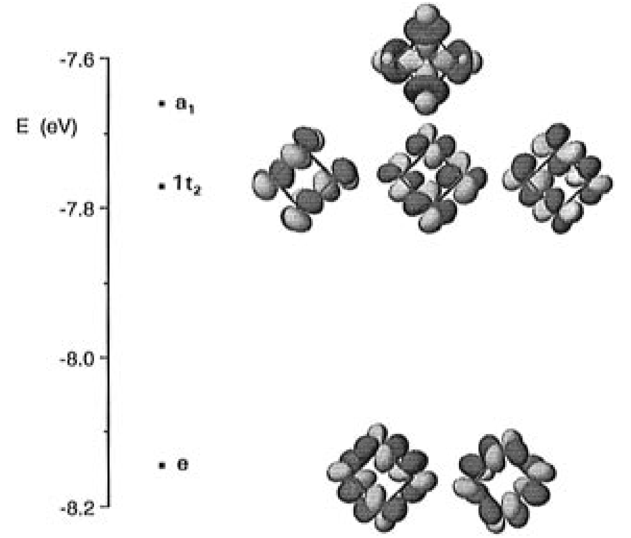

Figure 2. The six cluster orbitals of lowest energy in a [(η-C_5R_5)M(μ_3-A)]$_4$ cluster. In [(η-C_5Me_5)V(μ_3-N)]$_4$, the e orbital is fully occupied; the others are unoccupied. In [(η-C_5Me_5)Cr(μ_3-O)]$_4$ all six orbitals are occupied.

We are exploring the reduction of (η-C_5R_5)MCl(A) complexes as a general route to [(η-C_5R_5)M]$_m$(μ_3-A)$_n$ clusters. Preliminary spectroscopic and crystallographic results show that reduction of [(η-C_5Me_5)TaCl(μ_2-N)]$_3$[16] with Na/Hg gives [(η-C_5Me_5)Ta(μ_3-N)]$_4$, reduction of (η-C_5Me_5)VCl_2(O)[17] gives [(η-C_5Me_5)V(μ_3-O)]$_4$, reduction of (η-C_5Me_5)MoCl_2(O)[18] gives [(η-C_5Me_5)MoO]$_4$ (which is not a cubane), and reduction of [(η-C_5Me_5)MoCl(O)]$_2$(μ_2-O)[18] gives [(η-C_5Me_5)Mo]$_4$(μ_2-O)$_6$.

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, bond lengths and angles, and crystal data and refinement details and figures showing atom labeling for the title compound (26 pages). Ordering information is given on any current masthead page.

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(12) The first numeral in brackets is the mean estimated standard deviation; the second numeral is the maximum deviation from the mean.

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