NO^- Anion Trapped in a Molecular Oxide Bowl

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Nitric oxide (NO) is attracting increasing interest from diverse fields ranging from biology to catalysis.[1] It has an odd number of valence electrons, and forms nitrosonium ion (NO^+) by losing one electron or nitroxyl anion (NO^-) by acquiring one electron. Although the chemistry of NO and NO^+ is well documented, that of NO^- is still sketchy due to its instability and short life under normal experimental conditions.[2] Even a simple salt like NaNO has not been isolated. During the course of studying the reactivity of molecular oxides, we have recently isolated $[(NO)V_{12}O_{32}]^{5-}$, the first example of the nitroxyl anion isolated in the solid phase. Here we report its synthesis and structural characterization.

When Et_4NVO_3[3] was reacted with NO in nitromethane, a compound that contained NO was precipitated out from the solution as a dark brown microcrystalline powder. Spectroscopic data indicated the formation of a compound that has a metal−oxygen framework similar to $[(CH_3CN)V_{12}O_{32}]^{4-}$, an inorganic inclusion compound where an acetonitrile molecule is trapped in a $V_{12}O_{32}$ bowl.[4] The result of its elemental analysis, however, was not quite right for a compound of the formula $[Et_4N]_4[(NO)V_{12}O_{32}]$.[5] We needed X-ray crystallographic data to solve the puzzle.

Much to our surprise, the X-ray crystal structural analysis, together with the result of the elemental analysis, revealed that this compound contained NO as nitroxyl anion and not as electronically neutral nitric oxide.[6] In other words, the compound obtained was $[Et_4N]_5[(NO)V_{12}O_{32}]$, not $[Et_4N]_4[(NO)V_{12}O_{32}]$. Five Et_4N^+ cations per $[(NO)V_{12}O_{32}]^{5-}$ anion were unambiguously located in the crystal structure. Reduction of the molecular vanadium oxide moiety was another possibility, but this was excluded because the compound gave three very narrow ^{51}V NMR peaks of equal intensity in nitromethane. The lengths of all V−O bonds in $[(NO)V_{12}O_{32}]^{5-}$ (Figure 1) were normal for V^V and no anomaly was observed in calculated bond valences and their sums.[7] Moreover, the N−O bond length in the current compound (1.198 Å) is significantly longer than the value reported for neutral NO molecule (1.150 Å).[8] The current compound can be most

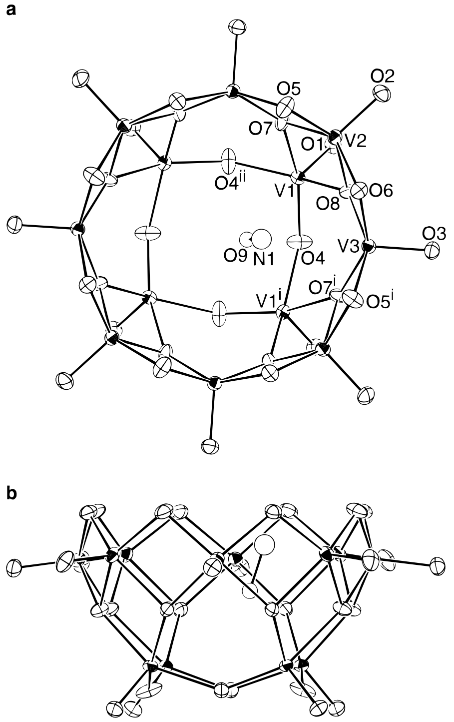

Figure 1. Structure of the $[(NO)V_{12}O_{32}]^{5-}$ anion viewed along the crystallographic 4-fold axis (a) and 90° away from the 4-fold axis (b). Ellipsoids are drawn to encompass 50% of the probability density. The symmetry operation for the atoms labeled with superscripted i and ii is *y*, −*x*, *z* and −*y*, *x*, *z*, respectively. Only one of the four possible sites for the NO units is shown for clarity. Selected distances (Å): V1−O1 1.605(2), V1−O4 1.727(2), V1−$O4^{ii}$ 1.908(2), V1−O7 2.024(2), V1−O8 1.910(1), V1−O9 2.736(6), $V1^i$−O9 2.750(6), V2−O2 1.615(2), V2−O5 1.819(2), V2−O6 1.809(2), V2−O7 1.942(2), V2−O8 1.958(2), V3−O3 1.613(2), V3−$O5^i$ 1.827(2), V3−O6 1.845(2), V3−$O7^i$ 1.911(2), V3−O8 1.925(2), V3−N1 2.750(8), N1−O9 1.198(10), N1−O8 2.959(8), O9−O4 2.785(6), O9−O7 2.756(6), O9−O8 2.861(6).

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(3) (a) Et_4NVO_3 was prepared by dissolving V_2O_5 (2.0 g, 1.1×10^{-2} mol) in a 10% aqueous solution of Et_4NOH (35 mL, 2.2×10^{-2} mol), stirring the solution for 18 h, evaporating it to dryness under vacuum, dissolving the resulting solid in 50 mL of acetonitrile, filtering off a small amount of insoluble material, adding 150 mL of diethyl ether to the filtrate, collecting the white precipitate that formed by filtration, and drying it over P_2O_5 under vacuum (4.2 g, 1.8×10^{-2} mol, 82% yield). (b) The tetraethylammonium salt of VO_3^- is hygroscopic and completely water-free material cannot be obtained. It would more appropriately be formulated as $Et_4NVO_3 \cdot xH_2O$. Since the exact amount of water is not known and can vary in different preparations, we postulate $x = 0$ for the sake of simplicity and convenience throughout the current paper.

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(5) Dark brown microcrystals of $[Et_4N]_5[(NO)V_{12}O_{32}] \cdot CH_3NO_2 \cdot 2.5H_2O$ precipitated out from solution by bubbling NO gas from a cylinder through a solution of Et_4NVO_3 (1.0 g, 4.4×10^{-3} mol) in 20 mL of nitromethane at a rate of ca. 100 mL min^{-1} for 30 min with stirring (0.18 g, 9.4×10^{-5} mol, 22% yield based on V). Anal. Calcd for $C_{41}H_{108}N_7V_{12}O_{37.5}$: C, 25.77; H, 5.70; N, 5.13; V, 32.0. Found: C, 26.07; H, 5.42; N, 5.00; V, 31.7. Infrared (Nujol mull, 1000−400 cm^{-1}): ν (cm^{-1}) 997 (sh), 980 (s), 963 (s) 844 (m), 754 (m), 704 (m), 634 (m), 542 (w), 514 (w). ^{51}V NMR (CH_3NO_2): δ (ppm) −569 (1V), −592 (1V), −600 (1V). Crystals suitable for X-ray structure determination were obtained by dissolving 0.18 g of the microcrystalline material in 4 mL of propylenecarbonate and adding 12 mL of CH_2Cl_2. Rod-shaped crystals started to appear in an hour. The crystals exhibited IR and ^{51}V NMR spectra identical with those of the microcrystalline compound.

(6) (a) Single crystals of $[Et_4N]_5[(NO)V_{12}O_{32}] \cdot 4CH_2Cl_2$ are at 125 K, tetragonal, space group *I*4, with $a = 19.3979(4)$ Å, $c = 11.3278(3)$ Å, and $Z = 2$. Diffraction data were collected on a Siemens SMART CCD diffractometer[6b] using Mo Kα radiation. 35282 reflections were collected, of which 6461 are unique ($R_{int} = 0.0308$). Structure was solved and refined using the *SHELX-97*[6c] program suite. N and O atoms of the NO^- group were refined with isotropic displacement parameters. All the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined with the riding model. Full-matrix least-squares refinement on F^2 converged to $R(F) = 0.0286$, $R_w(F^2) = 0.0745$, and GOF = 1.084 for 5959 reflections with $F_o > 4\sigma(F_o)$. The NO^- anion is located very close to the crystallographic 4-fold axis and is disordered over four equally occupied positions. The N and O atoms in the nitroxyl anion were assigned so as to give reasonable isotropic displacement parameters: U_{iso} values for O9 and N1 are 0.027(2) and 0.015(1) $Å^2$ with the current assignment; they would be 0.040(2) and 0.009(1) $Å^2$ with the interchanged assignment. (b) *SMART and SAINT: Area Detector Control and Integration Softwares*; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996. (c) Sheldrick, G. M. *SHELX-97, Program for the Analysis of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

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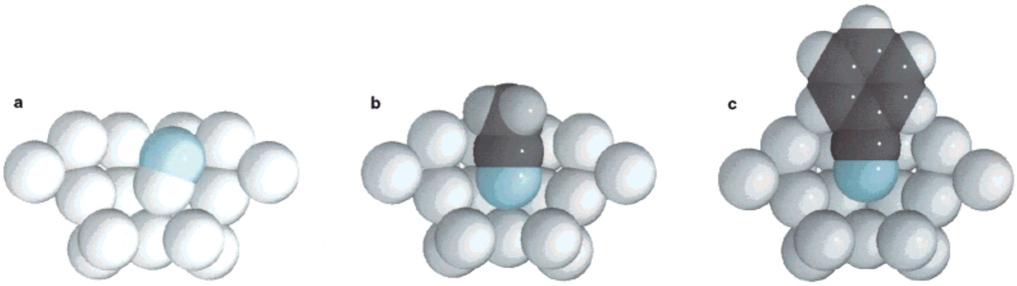

Figure 2. Space-filling cutaway views of $[(NO)V_{12}O_{32}]^{5-}$ (a), $[(CH_3CN)V_{12}O_{32}]^{4-}$ (b), and $[(C_6H_5CN)V_{12}O_{32}]^{4-}$ (c). All atoms are represented by spheres having van der Waals radii (C, 1.6 Å; H, 1.2 Å; O, 1.4 Å; N, 1.5 Å).

appropriately described as an inorganic inclusion compound where a nitroxyl anion is trapped in a bowl made of molecular oxide.[9] This is the first example of the NO^- anion isolated in the solid phase. Some very weak interactions between the NO^- anion and the bowl-shaped $V_{12}O_{32}$ are observed (O9···V1 = 2.736 Å, O9···V1^i = 2.750 Å, and N1···V3 = 2.750 Å; see Figure 1 for the symmetry code). However, these are totally different in nature from the strong metal−nitrogen interaction (<2.0 Å) found in so-called "bent metal nitrosyl" complexes where the NO ligand is *formally* considered as NO^-.[10,11]

The basic metal−oxygen framework in the current compound is the same as that of $[(CH_3CN)V_{12}O_{32}]^{4-}$ and $[(C_6H_5CN)V_{12}O_{32}]^{4-}$.[4,12] Yet one can notice some differences on a closer look. The molecular oxide bowl of the current compound is free from the elliptical distortion observed in both $[(CH_3CN)V_{12}O_{32}]^{4-}$ and $[(C_6H_5CN)V_{12}O_{32}]^{4-}$. Another, more important, difference is the penetration depth of the guest molecule. The NO^- ion penetrates much deeper into the $V_{12}O_{32}$ bowl than CH_3CN and C_6H_5CN molecules (see Figure 2). The oxygen atom of the nitroxyl anion is only 1.84 Å away from the plane defined by four basal vanadium atoms (V1). The nitrogen atom of CH_3CN in $[(CH_3CN)V_{12}O_{32}]^{4-}$ lies 2.22 Å above this basal plane and the C_6H_5CN molecule in $[(C_6H_5CN)V_{12}O_{32}]^{4-}$ locates itself much further away from the bottom of the bowl. In fact, there are several short contacts between the NO^- anion and the molecular oxide bowl that are just about the sum of the van der Waals radii (O9···O4 = 2.785 Å, O9···O7^i = 2.756 Å, O9···O8 = 2.861 Å, N1···O7^i = 2.894 Å, N1···O8 = 2.959 Å). It seems the NO^- anion is penetrating into the $V_{12}O_{32}$ bowl as deep as possible. In addition, it is sticking to the inner surface of the bowl.

Inclusion of an anionic guest into an anionic molecular oxide host might be surprising at first glance. However, such a phenomenon is not without precedence.[13] Inclusion of Cl^-,[14,15] Br^-,[14] I^-,[14] NO_3^-,[16] ClO_4^-,[17] and N_3^- [14,18] anions into anionic molecular oxides have been reported. The major difference is that the molecular oxides make a closed cage in these compounds and offer no path for the guests to come out from the cage, while the $V_{12}O_{32}$ bowl has an open structure and the guest can come out from the molecular oxide moiety. It is also interesting to note that an ab initio calculation predicts the inner part of the $V_{12}O_{32}$ bowl to be a region of charge depletion and electrophilic.[19] It is possible that the low charge density inside the $V_{12}O_{32}$ bowl is stabilizing the otherwise unstable NO^- anion. Given its open bowl-shaped structure together with the observation that formation of NO^- anion is a crucial step in the catalytic decomposition of NO over zeolite,[20] the study of the reactivity of the current inclusion compound $[(NO)V_{12}O_{32}]^{5-}$ would be a matter of great interest. Preliminary experiments showed that $[Et_4N]_5[(NO)V_{12}O_{32}]$ is relatively stable against heat. Its ^{51}V NMR and IR spectra did not change after heating at 90 °C under vacuum. The compound $[(n\text{-}Bu)_4N]_4[(CH_3CN)V_{12}O_{32}]$ loses its CH_3CN guest molecule and transforms to a compound that gives a totally different IR spectrum under similar conditions.[21] Further study on the reactivity of $[(NO)V_{12}O_{32}]^{5-}$ is in progress.

Supporting Information Available: Tables of crystal data and refinement, atomic coordinates and isotropic displacement parameters, bond length and angles, and anisotropic displacement parameters for $[Et_4N]_5[(NO)V_{12}O_{32}]\cdot 4CH_2Cl_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] The exact reaction pathway to $[(NO)V_{12}O_{32}]^{5-}$ is not currently known. Disproportionation of NO by water in the reaction mixture is one possibility ($2NO + H_2O \rightarrow HNO + HNO_2$; see ref 3b). It is also possible that the organic cation, Et_4N^+, is working as the reductant. Yet another possibility is disproportionation of NO by VO_3^-: $12VO_3^- + 8NO \rightarrow [(NO)V_{12}O_{32}]^{5-} + 4NO_2^- + 3NO^-$. Here NO is working as an oxygen abstractor.

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