# Structural Characterization of [VO(salicylhydroximate)($CH_3OH$)]$_3$: Applications to the Biological Chemistry of Vanadium(V)

VINCENT L. PECORARO

*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, U.S.A.*

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The biological chemistry of vanadium has garnered increased attention due to the recent isolation of vanadium enzymes capable of nitrogenase [1] and bromoperoxidase [2, 3] activities. The latter enzymes, isolated from marine algae, contain a mononuclear V(V) active site [4] that does not appear to require redox chemistry in the catalytic mechanism. It is well established that bacteria and algae often produce low molecular weight chelating agents (siderophores) which will sequester metal ions and facilitate the transport of these nutrients into the cell [5]. The two major classes of siderophores are based on catecholate and hydroxamate metal ligands [6]. Because vanadium bromoperoxidase is isolated from algae and bacteria, we felt that it would be interesting to examine the coordination chemistry of vanadium with hydroxamate ligands that might form the basis of vanadium sequestering agents for these organisms. In the process of our studies, we have isolated an intriguing trinuclear cluster composed of $VO^{3+}$ and salicylhydroxamic acid and report herein the structure and solution chemistry of this molecule.

[VO(salicylhydroximate)($CH_3OH$)]$_3$ (**1**) can be prepared in 70% yield by the room temperature reaction of one equivalent of VO(acetylacetonate)$_2$ or $VCl_3$ with salicylhydroxamic acid and three equivalents of $NaOCH_3$ or NaOH in methanol. Air acts as the oxidant to form deep blue solutions of **1**. Slow evaporation of a methanol solution gave deep blue blocks which were suitable for X-ray crystallographic analysis. Crystallographic data for **1**: monoclinic, space group $P2_1/c$, $a = 11.006(3)$, $b = 15.722(7)$, $c = 21.240(6)$ Å; $\beta = 111.40(2)°$; $V = 3422(2)$ Å$^3$, $Z = 4$; $\lambda$(Mo K$\alpha$) = 0.7107 Å; crystal dimensions $0.42 \times 0.49 \times 0.52$ mm$^3$; $\mu = 8.19$ cm$^{-1}$. The intensities of 4504 reflections were measured at room temperature ($0 \leqslant 2\theta \leqslant 45°$) on a $P2_1$ diffractometer using Mo K$\alpha$ radiation. The structure was solved using the SHELX-86 program. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were located, but not refined, and placed at fixed distances (0.95 Å) from bonded carbon atoms. All calculations were carried out using the SHELX-86 program. For 2567 unique observed reflections [$(I) > 3\sigma(I)$], the final $R = 0.058$; $R_w = 0.053$.

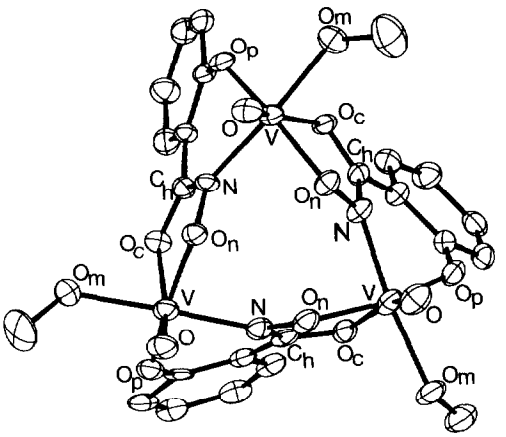


Fig. 1. An ORTEP diagram of **1** with thermal ellipsoids at 30% probability. Selected mean bond lengths (Å) and angles (°) for chemically equivalent bonds with range in parentheses: V=O, 1.59 (1.582–1.602); V–$O_p$, 1.85 (1.842–1.861); V–$O_m$, 2.08 (2.061–2.096); V–$O_c$, 2.12 (2.090–2.143); V–$O_n$, 1.86 (1.858–1.868); V–N, 2.02 (2.014–2.030); $O_n$–N, 1.37 (1.362–1.376); $C_h$–N, 1.33 (1.318–1.339); $C_h$–O, 1.26 (1.260–1.275); V–V, 4.66 (4.652–4.671); O=V–$O_m$, 91 (88.1–92.7); O=V–$O_p$, 108 (107.5–108.6); O=V–$O_n$, 94 (93.8–94.7); O=V–N, 98 (97.0–98.1); O=V–$O_c$, 165 (163.1–166.7); V–N–$O_n$, 120 (119.5–120.6); N–$O_n$–V, 120 (119.4–120.2).

Figure 1 illustrates the structure of **1** and provides important bond lengths and angles for the cluster. All of the vanadium ions are in the +5 oxidation state as the $VO^{3+}$ unit and are related by a pseudo-three-fold axis. The salicylhydroxamic acid is triply deprotonated; therefore, this trianionic ligand is coordinated as a salicylhydroximate rather than the doubly deprotonated salicylhydroxamate. Although all four oxygen and nitrogen atoms are bound to vanadium, an individual ligand donates only two heteroatoms to each independent vanadium(V). The deprotonated hydroximate nitrogen and phenolate oxygen bind to one vanadium while the two remaining oxygen atoms bind to the second vanadium. This bonding repeats throughout the cluster forming a triangular unit with a [–V–N–O–]$_3$ core. A methanol occupies the sixth coordination site in a position *cis* to the vanadyl oxygen. The average $C_H$–N* distance (1.33 Å) in **1** is significantly shorter than C–N single bonds (1.43–1.45 Å) [7] and slightly longer than the C=N of

*The nomenclature used in the text for carbon and oxygen atoms is as follows: $O_c$ = carbonyl oxygen of the hydroximate group; $O_n$ = oxime oxygen of hydroximate group; $O_p$ = phenolate oxygen; $O_m$ = methanol oxygen; $C_h$ = carbonyl carbon of hydroximate.

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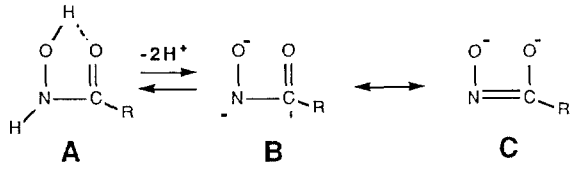


Scheme 1.

ethylbenzohydroximic acid (1.27 Å) [8] and tris-(benzohydroximato)Cr(III) [9] (1.30 Å), illustrating that the dominant resonance form is given as **C** in Scheme 1; however, there is a greater proportion of form **B** in **1** compared to other hydroximato complexes due to the donation of negative charge to the metal through the V–N bond. The metal atoms are separated by 4.66 Å.

The structure of **1** contains a variety of interesting structural features which have not previously been observed in vanadium chemistry. These include the description of a non-polyoxo anion $VO^{3+}$ phenolate cluster, an example of a neutral solvent molecule coordinated in a position *cis* to the vanadyl oxygen of the $VO^{3+}$ unit; a hydroximate nitrogen–metal bond; and an intriguing core composed of $[-V-N-O-]_3$ units that provide structural stability for the molecule. The only previous example of a structurally characterized [10, 11] $VO^{3+}$ complex containing organic ligands is $VO(SALEN)^+$. Evidence for the existence of $VO(EHPG)^-$, VO(EHGS) and $VO(SHED)^{2+}$ * from solution studies has been presented [13–16]; however, structural studies have been ruled out because these molecules rapidly oxidize the coordinated ligands. Transition metal–hydroxamato nitrogen bonds are very rare, with the only previous example being the square-planar bis(glycinohydroxamato)nickel(II) [12]. Although strong hydrogen bonds and coordination to alkali countercations by hydroximate nitrogens are known [9], direct coordination of a hydroximate nitrogen to a transition metal or as part of a discrete molecular compound has not previously been observed.

Additional chemical characterization supports the structural and oxidation state assignments of **1**. The blue crystals are diamagnetic at room temperature and EPR silent, illustrating the $d^0$ electronic configuration of V(V). The strong ligand-to-metal charge-transfer excitation at 602 nm ($\epsilon$ = 3300) is a hallmark of mono-oxovanadium(V) phenolates [13–16]. The V=O stretch (970 $cm^{-1}$) is also in the range for other $VO^{3+}$ complexes [13–16]. The cluster is stable for long periods in dry acetonitrile, but decomposes rapidly in water or DMF. Compound **1** displays a completely irreversible reduction at −10 mV (*versus* SCE) which rapidly passivates the electrode. Further characterization of the reactivity of this material will be presented separately.

A comparison of the visible spectra of the known $VO^{3+}$ phenolates, which all have strong charge-transfer transitions at ≈600 nm, and the vanadium bromoperoxidase [4], which shows no appreciable visible absorptions, clearly rules out a formulation for this enzyme's active site which includes both the mono-oxovanadium unit and a coordinated phenolate. In addition, the isolation of **1** illustrates that V(V) has a strong affinity for hydroxamate and *N*-oxide type ligands. The *N*-oxide group has precedent in the biological chemistry of vanadium as an important metal binding ligand in amavadin [17, 18]. In this light, it will be interesting to see whether vanadium siderophores are isolable from the organisms that express the vanadium bromoperoxidase.

*Abbreviations used: SALEN = *N,N'*-bis(salicylideneaminato)ethylene; EHPG = ethylene-bis(*o*-hydroxyphenylglycine); EHGS = ethylene-*N*-(salicylideneaminato)-*N'*-(*o*-hydroxyphenylglycine); SHED = *N*-(salicylideneaminato)-*N'*-(2-hydroxyethyl)ethylenediamine.

## Supplementary Material

Tables 1–6 provide fractional atomic coordinates for all non-hydrogen atoms (Table 1); fractional atomic coordinates for all hydrogen atoms (Table 2); anisotropic thermal parameters for all non-hydrogen atoms (Table 3); bond distances (Table 4); bond angles (Table 5); and observed and calculated structure factors for **1** (Table 6). Ordering information is given on any current masthead page.

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