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Origin of the Unusual Bending Distortion in the (μ-Oxo)divanadium(III) Complex $[V_2O(l\text{-his})_4]$: A Reinvestigation

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The title compound, $[V_2O(l\text{-his})_4]\cdot 2H_2O$ (**1**), originally reported by Kanamori et al. (*Chem. Lett.* **1993**, 1731−1734), has been reinvestigated using both X-ray crystallography and resonance Raman spectroscopy. Redetermination of the structure in the higher symmetry monoclinic space group *C*2 gives the following crystallographic parameters: $C_{24}H_{34}N_{12}O_{11}V_2$, fw = 786.5, $a = 14.583(2)$ Å $b = 14.024(2)$ Å, $c = 10.659(1)$ Å, $\beta = 129.71(1)°$, $V = 1676.9(2)$ Å^3, $Z = 2$, $R = 0.0399$ and $R_w = 0.0548$ for 249 least-squares parameters refined against 3504 unique, observed ($F > 4\sigma(F)$) data. The X-ray structure reveals two strong *intra*molecular hydrogen bonds that account for the unusually small V−O−V angle (153.9°) in this unsupporated μ-oxo divanadium complex. Resonance Raman spectroscopy in the solid-state confirms the presence of the *intra*molecular hydrogen bonding and the acute V−O−V angle. Comparison of resonance Raman spectra of **1** in solid and solution indicates that the V−O−V angle opens up to ~180° upon dissolution due to a breaking of the *intra*molecular hydrogen bonds in the solid.

Introduction

The aqueous coordination chemistry of V(III) is of some recent interest given its biological role in the blood of tunicates.[1] The tunicates, sessile marine organisms whose internal V(III) concentration can reach as high a 1 M, also contain a highly reducing, and potentially coordinating, polyphenol called tunichrome.[2] Although controversy continues as to whether tunichrome and V(III) are located in the same compartments within a cell, or even if they are in the same cell types, it seems certain that upon blood cell lysis these two components are brought into contact.[3] The observation of an intense absorption band near 450 nm in this so-called "Henze's solution" has been proposed to indicate the formation of a (μ-oxo)vanadium(III) dimer that perhaps includes tunichrome as a ligand.[4,5] Thus we, and others, have been interested in exploring the spectroscopic and magnetic properties of (μ-oxo)vanadium(III) dimers in order to better understand the fascinating chemistry of vanadium in tunicates.[6−10]

Studies of simple μ-oxo divanadium(III) complexes have identified two general classes: (1) unsupported, monobridged μ-oxo species in which the V−O−V bridging angle falls in the range 165−180°[7,8] and (2) tribridged species in which the oxo-bridge is supported by two co-bridging carboxylate or phosphate groups resulting in a bridging V−O−V angle that falls in the range 130−145°.[9,10] We were thus intrigued by the recent report by Kanamori and co-workers of the apparently unsupported dimeric complex $[V_2O(l\text{-his})_4]$ (**1**) in which the V−O−V angle, 153.9°, lies well outside the range of values for either supported or unsupported complexes.[11] Since no explanation for this extraordinary structural distortion was provided by Kanamori et al., our curiosity prompted us to analyze further the structural and spectroscopic properties of this molecule in order to learn the origin of its unusual bridging geometry. In this paper we report the redetermination of the crystal structure in a higher symmetry space group from which we confirm the previously reported bridging V−O−V angle and provide a rationale for its anomalous value. This rationale is further supported by resonance Raman spectroscopic studies which we have used to probe the differences between the solid state and solution structures of this molecule.

Experimental Section

X-ray Crystallography. The compound $[V_2O(l\text{-his})_4]\cdot 2H_2O$ was prepared using a modification of the procedure described by Kanamori et al.[11] A crystal (0.4 × 0.4 × 0.4 mm) was selected for X-ray diffraction studies and mounted on a Siemens P4 diffractometer. Unit cell constants were obtained by least-squares refinement of the angular settings of 38 well-centered reflections in the range 7−25° in 2θ.

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Table 1. Crystal Data and Structure Determination Parameters for [V_2O(*l*-his)$_4$]·$2H_2O$ (**1**)

formula	$C_{24}H_{34}N_{12}O_{11}V_2$	V, Å^3	1676.9(2)
fw	768.5	Z	2
space group	*C*2 (No. 5), monoclinic	ϱ_{calc}, g cm^{-1}	1.522
cryst dimens, mm	0.4 × 0.4 × 0.4	radiation	Mo Kα, $\lambda = 0.710\,73$ Å
temp, °C	25	μ, cm^{-1}	6.31
a, Å	14.583(2)	2θ limits, deg	7−25
b, Å	14.024(2)	R^a	0.0399
c, Å	10.659(1)	$R_w{}^b$	0.0548
β, deg	129.71(1)		

[a] $R = \Sigma(|F_o| - |F_c|)/(\Sigma|F_o|)$. [b] $R_w = (\Sigma w(|F_o| - |F_c|)/(\Sigma w|F_o|)$; $w = (\sigma^2(F_o) + 0.0008F_o{}^2)^{-1}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [V_2O(*l*-his)$_4$]·$2H_2O$ (**1**)

atom	*x*	*y*	*z*	*U*(eq)^a
V(1)	1430(1)	9110(2)	1902(1)	22(1)
O(1)	0	9399	0	24(1)
N(11)	1713(2)	8077(3)	658(3)	29(1)
N(12)	2526(3)	10084(3)	1917(3)	30(1)
N(13)	3843(3)	11194(3)	2658(4)	49(2)
N(21)	2995(3)	8566(3)	4312(3)	29(1)
N(22)	1243(3)	10011(3)	3315(4)	30(1)
N(23)	626(3)	11209(3)	3926(4)	36(2)
O(11)	4616(3)	8270(4)	1757(4)	63(2)
O(12)	3976(3)	7575(3)	2936(3)	42(1)
O(21)	782(2)	7993(3)	2400(3)	34(1)
O(22)	877(3)	7347(3)	4390(4)	53(2)
C(11)	3812(3)	8025(3)	1787(4)	35(2)
C(12)	2527(3)	8258(3)	302(4)	32(2)
C(13)	2356(3)	9279(3)	−326(4)	37(2)
C(14)	2857(3)	10019(3)	950(4)	32(2)
C(15)	3152(3)	10804(3)	2939(5)	39(2)
C(16)	3664(4)	10711(4)	1413(6)	48(2)
C(21)	1307(3)	7821(3)	3905(4)	31(2)
C(22)	2546(3)	8251(3)	5154(4)	29(2)
C(23)	2503(3)	9099(4)	6020(4)	37(1)
C(24)	1711(3)	9908(3)	4931(4)	28(1)
C(25)	584(3)	10804(3)	2756(5)	34(2)
C(26)	1333(3)	10655(4)	5309(5)	38(2)
O(1W)	0	4482(6)	0	86(3)
O(2W)^b	516(17)	2257(9)	514(21)	90(5)
O(3W)^b	5745(20)	1188(13)	878(24)	117(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Refined site occupation factors for O(2W) and O(3W) are 0.260(3) and 0.240(3), respectively (the sum of SOF[O(2W)] and SOF[O(3W)] was constrained to 0.5 during refinement).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for [V_2O(*l*-his)$_4$]·$2H_2O$ (**1**)

Bond Lengths			
V(1)−O(1)	1.794(1)	V(1)−N(22)	2.113(5)
V(1)−O(21)	2.066(5)	V(1)−N(21)	2.213(3)
V(1)−N(12)	2.095(5)	V(1)−N(11)	2.174(5)
Bond Angles			
O(1)−V(1)−N(22)	94.8(1)	O(1)−V(1)−O(21)	94.0(1)
N(22)−V(1)−O(21)	88.9(2)	O(1)−V(1)−N(21)	168.9(2)
N(22)−V(1)−N(21)	83.4(1)	O(21)−V(1)−N(21)	75.1(1)
O(1)−V(1)−N(12)	101.1(1)	N(22)−V(1)−N(12)	92.9(2)
O(21)−V(1)−N(12)	164.6(1)	N(21)−V(1)−N(12)	90.0(1)
O(1)−V(1)−N(11)	89.9(1)	N(22)−V(1)−N(11)	174.0(2)
O(21)−V(1)−N(11)	87.0(2)	N(21)−V(1)−N(11)	91.2(2)
N(12)−V(1)−N(11)	89.9(2)	V(1)−O(1)−V(1A)	153.9(2)

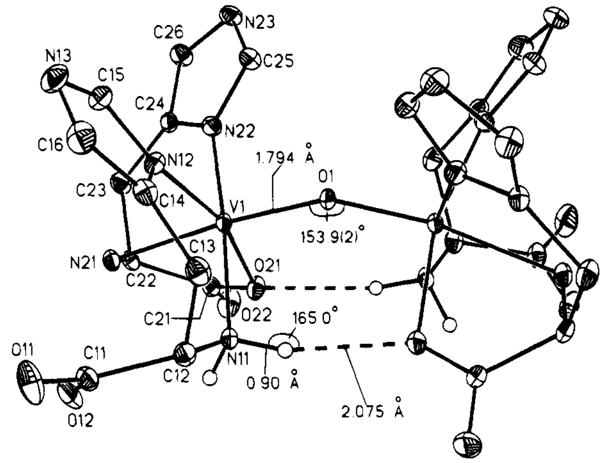

Figure 1. Thermal ellipsoid plot, viewed perpendicular to the V−O−V plane, of the metal complex in the [V_2O(*l*-his)$_4$]·$2H_2O$ structure. The hydrogen bonding responsible for the unique bending distortion of the molecule is depicted. In order to improve clarity, all other hydrogen atoms have been omitted.

Crystal data, data collection, and structure solution parameters are listed in Table 1. Structure solution and refinement in space group *C*2 were achieved using the SHELXTL crystallographic software[12] and both proceeded normally. One of the water molecules of the structure was found with 4-fold disorder and site occupancy factors were refined. All non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms were calculated to give an idealized geometry and fixed to ride on their respective bound atoms. Hydrogen atom positions were not calculated for the disordered water molecule. Common isotropic thermal paramters were refined for similar groups of hydrogen atoms. Final refinement of 240 least-squares parameters against 3504 unique, observed ($|F| > 4\sigma(F)$) reflections gives agreement factors $R = 0.0399$ and $R_w = 0.0548$ while yielding excursions between −0.47 and 0.53 e/Å^3 on the final electron density difference map. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2; bond lengths and angles for the coordination atoms are listed in Table 3. A thermal ellipsoid plot of the molecule containing the atom labeling scheme is presented in Figure 1.

Spectroscopy. Resonance Raman spectra both in the solid state (rotating KCl pellet)[13] and in solution (spinning NMR tubes)[14] were obtained under dinitrogen atmosphere at room temperature with the experimental setup previously described[15] using a 488.0 nm laser line (Coherent 90-6 Ar$^+$ ion laser) in resonance with the oxygen to vanadium charage transfer. Solution spectra (~1 mM) were measured in natural abundance water, in pure D_2O (99.9% D), and in $H_2{}^{18}O$ (98% ^{18}O; Isotec, Miamisburg, OH). Isotopic labeling for solid-state measurements were achieved by dissolving solid **1** in ~30 mL of $H_2{}^{18}O$ followed by evaporation to dryness with a stream of dry N_2 gas. Since the solid thus obtained gave a different spectrum in the 400 cm^{-1} region than the crystalline one used for X-ray analysis, an analogous solid sample was made from H_2O as a control.[16]

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(16) We attribute the differences in the internal modes of the histidine near 400 cm^{-1} between these samples to different degrees of hydration. The V−O−V bridging modes are unaffected.

Results and Discussion

Our structure of **1** agrees substantially with that reported previously with the exception that we have refined ours in the higher symmetry monoclinic space group *C*2 rather than the triclinic space Group *P*1 used initially. The previously reported triclinic cell constants can clearly be transformed to a monoclinic set since both the *a* and *b* axes and the α and β anglesd are equivalent within experimental error. Applying the appropriate transformation yields monoclinic cell constants: $a = 14.570$ Å [14.583(2)], $b = 13.991$ Å [14.024(2)], $c = 10.646$ Å [10.659(1)], $\alpha = 90.01°$, $\beta = 129.75°$ [129.71(1)], and $\gamma = 90.00°$, where our experimental values are given in brackets. The reported bond lengths and angles for the earlier structure show an equivalence (within 2σ) that is consistent with 2-fold rotation symmetry for the divanadium complex, further suggesting that the correct crystal class is monoclinic.

The present crystallographic results confirm the validity of the higher symmetry space group, e.g. agreement between equivalent monoclinic reflections in the intensity data set is excellent ($R_{\text{int}} = 0.0338$). In monoclinic *C*2 symmetry the (μ-oxo)divanadium complex formally possesses the 2-fold rotation symmetry, with the bridging oxygen on the 2-fold axis, implied by the earlier results. One of the lattice water molecules is also found on a 2-fold symmetry axis. The other lattice water molecule, however, is disordered over four sites, two of which are symmetrically inequivalent, with nearly equal weights for each site. Solution and refinement of the structure in *P*1 yields an almost identical disorder pattern for this latter water molecule and a small drop in the agreement factors (0.541 versus 0.548 in *C*2) despite an approximate doubling in the number of parameters (472 parameters and 4041 data versus 240 parameters and 3504 data in *C*2). There are no compelling reasons, such as significant violations of Laue symmetry or excessive disorder through symmetry generation, to justify adoption of the lower symmetry triclinic *P*1; hence, monoclinic *C*2 is the preferred space group.

Despite the change in space group, the details of the present structure (Table 3) agree remarkably well with those reported by Kanamori et al.[11] with reported bond lengths between the two structures within 2σ of each other and reported bond angles within 4σ. Our structure confirms the unusually acute V−O−V briding angle (153.9(2)° in both structures). However, careful examination of the present structure has also revealed a feature that accounts for this distortion. Two contacts, each between a hydrogen atom of an equatorial amine coordinated to one metal center and the oxygen atom coordinated to the neighboring metal center, indicate a substantial degree of *intra*molecular hydrogen bonding (H··O = 2.075 Å, N−H··O = 165.0°, N−H = 0.900 Å; see Figure 1). While this dimer is formally an unsupported, monobridged species, it is apparent from Figure 1 that these two hydrogen bonds effectively serve as two cobridging "ligands" in conjunction with the oxo-bridge. Clearly a compromise is reached *vis-a-vis* bending of the V−O−V angle, with its attendant reduction of π-bonding between the formally *sp*-hybridized oxygen and the V(III) ions, and the formation of two strong *intra*molecular hydrogen bonds. A similar compromise has also been observed for (μ-oxo)bis(μ-carboxylato)-vanadium(III) dimers where, as a result of the competition between optimization of backbone π-bonding and accommodation of the cobridging ligands, the observed V−O−V angles are ~10° larger than those found in other M(III) dimers.[9,10] The constraints imposed here by the hydrogen bonding are, of course, much weaker than those found with cobridging carboxylates. This, then, accounts for the intermediate value of the V−O−V bridge angle and suggests that the V(III)−O−V(III) moiety is easily deformed.

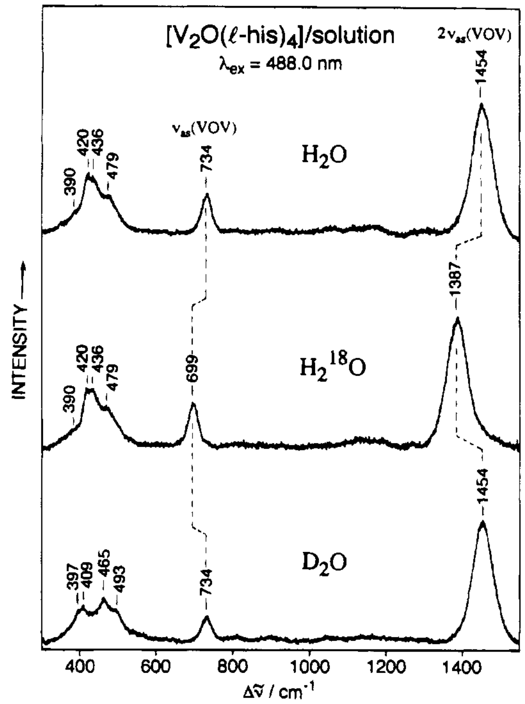

Figure 2. Solution (~1 mM) resonance Raman spectra of $[V_2O(l\text{-his})_4]$ in H_2O (top), $H_2{}^{18}O$ (middle), and D_2O (bottom) obtained via backscattering from spinning NMR tubes at room temperature using 488.0-nm laser excitation (150 mW) and 6-cm^{-1} slit widths. μ-^{18}O-sensitive bands are correlated.

As previously reported, **1** is very unstable in aerobic solution, even in the presence of excess histidine.[11] We, however, find that under a nitrogen atmosphere even relatively dilute solutions can be kept unchanged for several weeks. Figure 2 shows the resonance Raman spectra of the compound in H_2O (top), $H_2{}^{18}O$ (middle), and D_2O (bottom). The bands at 734 and 1454 cm^{-1} in H_2O and D_2O are downshifted to 699 and 1387 cm^{-1} in $H_2{}^{18}O$. The 35-cm^{-1} shift is expected for the asymmetic V−O−V stretch, ν_{as}, with a V−O−V angle of >150°. The strongly enhanced band at 1454 cm^{-1} is assigned as the first overtone of the asymmetric V−O−V stretch, $2\nu_{\text{as}}$, in agreement with Kanamori et al.[11] However, no corresponding symmetric V−O−V stretching vibration, ν_{s}, is observed (*vide infra*).

There are substantial differences between the solid state and solution frequencies of the asymmetric stretch and its first overtone, i.e. these are seen at 721 and 1437 cm^{-1} in the solid state and at 734 and 1454 cm^{-1} in solution. The assignment of the 721- and 1437-cm^{-1} bands as ν_{as} and $2\nu_{\text{as}}$ is confirmed by ~35- and ~70-cm^{-1} shifts to lower frequency upon $H_2{}^{18}O$ exchange (Figure 3). These differences are consistent with an opening up of the V−O−V angle upon dissolution caused by a loss of the *intra*molecular hydrogen bonding which stabilizes the acute V−O−V angle in the solid. The hydrogen bonding between the coordinated histidines, as shown by X-ray diffraction, is also confirmed by resonance Raman spectra of the solid. As shown in Figure 3, the ν_{as} and $2\nu_{\text{as}}$ V−O−V frequencies of a solid sample prepared from H_2O are at 721 and 1437 cm^{-1} while those for a sample prepared in D_2O are at 725 and 1446 cm^{-1}. This is consistent with a small increase in the V−O−V angle resulting from weaker deuterium bonding, as opposed to hydrogen bonding, between the histidine ligands. In solution no differences between H_2O and D_2O are noted for the bridge ν_{as} and $2\nu_{\text{as}}$ bands, suggesting a loss of the intramolecular hydrogen bonds which are presumably replaced by intermolecular hydrogen bonds between the dimer and the solvent.

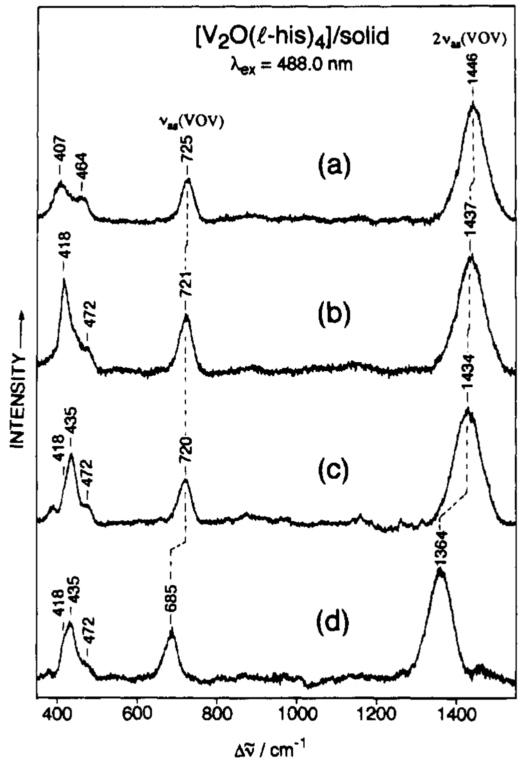

Figure 3. Solid-state resonance Raman spectra of freshly prepared [$V_2O(l\text{-his})_4$] from D_2O (a) and H_2O (b), and of solid samples obtained after evaporation of aqueous solutions (~30 mL, ~1 mM) in H_2O (c) and $H_2{}^{18}O$ (d). All spectra were obtained at room temperature via backscattering from rotating KCl pellets using 488.0-nm excitation (150 mW) and 6-cm^{-1} slit widths. The ν_{as}(VOV) and $2\nu_{as}$(VOV vibrations are correlated.

Breaking the hydrogen bonds between the histidine ligands in solution should result in a linear (μ-oxo)vanadium(III) dimer, the expected structure for an unsupported V(III)−O−V(III) bridge. To confirm this we have calculated the changes in vibrational frequencies for the ν_{as}(VOV) mode and its μ-^{18}O correspondence as a function of the V−O−V angle using a simple Y−X−Y three body harmonic model: $\nu_{as} = 1303.1\{F_{as}[\mu_V + \mu_O(1 - \cos\alpha)]\}^{1/2}$, where ν is the frequency in cm^{-1}, μ_V and μ_O are reciprocals of the massses of the V and O atoms in amu, α is the V−O−V bond angle in degrees, and F_{as} is the asymmetric stretching force constant in mdyn/Å.[17] For these calculations, graphically depicted in Figure 4, the angle α was varied from 90 to 180° and the F_{as} force constant was set to 2.2 mdyn/Å, a value derived from $\nu_{as} = 721$ cm^{-1} and $\alpha = 154°$ found experimentally in solid **1**. As expected, the ν_{as} frequency is strongly sensitive to the V−O−V bond angle while the ν_{as} ^{18}O-isotope shift is less so, showing only a small angular dependence--especially for $\alpha > 150°$. This simple normal mode calculation not only reproduces the obsered μ-^{18}O frequency shifts, but predicts that the ν_{as}(VOV) mode should occur at 735 (^{16}O) and 699 (^{18}O) cm^{-1} for $\alpha = 180°$. These frequencies are in nearly perfect agreement with those observed for ν_{as}(VOV) in H_2O and $H_2{}^{18}O$ (Figure 2), and, consequently, the V−O−V structure of **1** in aqueous solution must be very close to linear. Figure 4 also reveals that an upward shift in ν_{as} frequency from 721 (hydrogen bonded species) to 725 cm^{-1} (deuterium bonded) in the solid state corresponds to an opening of the V−O−V angle from 154° to ~160° upon H/D exchange. Finally, as compared with the solid state resonance Raman spectrum of **1** measured by Kanamori et al., our spectra have fewer bands in the low (<500 cm^{-1}) frequency region. Since none of the low frequency bands are shifted when the bridge oxygen is replaced by ^{18}O, while all of them are shifted upon deuteration, we attribute them to internal modes of the histidine itself. Therefore, the 436-cm^{-1} band in the solid spectrum reported as ν_s(VOV) by Kanamori cannot be so assigned.[18]

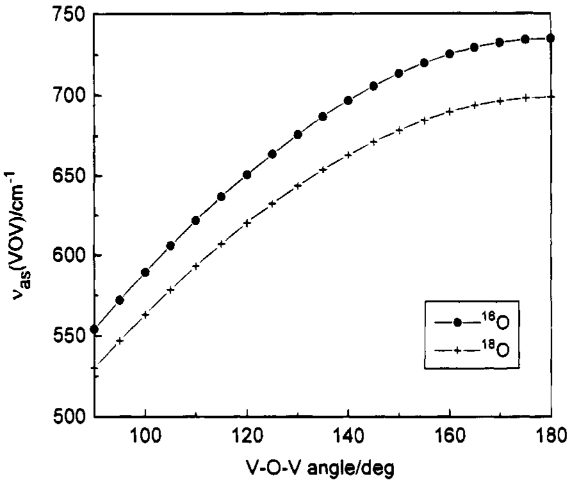

Figure 4. Variation in frequency of the ν_{as}(VOV) vibration as a function of V−O−V angle calculated from the equation described in the text using F_{as} = 2.2 mdyn/Å.

Conclusions

We have shown that the unusually acute (for an unsupported dimer) V−O−V bridge angle in [$V_2O(l\text{-his})_4$] is caused by strong *intra*molecular hydrogen bonding in the solid state which is lost in solution, resulting in a more linear V−O−V bond. Resonance Raman spectroscopy is able to detect such subtle changes and should be a useful tool in studying the chemistry of tunicate blood. Such studies are in progress.

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Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions (3 pages). Ordering information is given on any current masthead page.

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(18) Our recent studies have shown that the symmetric V−O−V stretch is strongly enhanced in the resonance Raman spectra of the tribidged complexes, however. It occurs at 536 cm^{-1} (520 cm^{-1}, μ-^{18}O) cm^{-1} in [$V_2O(O_2CCH_3)_2(HBpz_3)_2$] and 499 cm^{-1} (489 cm^{-1}, μ-^{18}O) cm^{-1} in [$V_2O(O_2P(OPh)_2)_2(HBpz_3)_2$], the V−O−V angles of which are 134 and 144°, respectively.[10b]