

Table IV. Bond Angles (deg) in the $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2]^{4+}$ Cation

atoms	dithionate ^a	monoclinic chloride ^a	triclinic chloride ^b
Cr-O1-Cr'	101.54 (5)	99.92 (3)	100.83 (3)
O1-Cr-O1'	78.46 (4)	80.08 (3)	79.17 (3)
O1-Cr-N1	91.84 (5)	92.67 (3)	92.94 (4)
O1-Cr-N2	95.39 (6)	93.39 (3)	93.76 (4)
O1-Cr-N3	91.98 (5)	91.40 (3)	93.55 (4)
O1-Cr-N4	172.86 (9)	176.2 (3)	172.99 (3)
O1'-Cr-N1	94.17 (6)	93.25 (3)	93.46 (4)
O1'-Cr-N2	90.72 (5)	90.29 (3)	92.48 (4)
O1'-Cr-N3	170.1 (1)	171.44 (6)	172.72 (4)
O1'-Cr-N4	94.61 (5)	96.10 (3)	93.83 (4)
N1-Cr-N2	171.96 (7)	173.44 (7)	171.77 (4)
N1-Cr-N3	88.55 (6)	87.95 (3)	86.55 (4)
N1-Cr-N4	86.87 (6)	87.43 (3)	87.81 (4)
N2-Cr-N3	87.70 (6)	89.37 (4)	88.27 (4)
N2-Cr-N4	86.37 (6)	86.70 (3)	86.11 (4)
N3-Cr-N4	95.01 (5)	92.42 (3)	93.45 (4)
Cr-O1-H1	123 (2)	118 (2)	114 (1)
Cr'-O1-H1	127 (2)	120 (2)	114 (1)

^a See footnote to Table III; data from ref 5. ^b This work.

oxygen atoms of the hydrogen bridges and four ammonia nitrogen atoms. The Cr-N distances are in the range 2.068 (1)-2.081 (1) Å, which is similar to the value of 2.074 (1)-2.089 (2) Å in the monoclinic modification⁵ or those of 2.078 (2)-2.082 (2) Å in the dithionate salt.⁵ With the exception of the O1-Cr-O1' angle of 79.17 (3)° (vide infra), the angular distortions from octahedral geometry are not severe, with trans angles in the narrow range of 171.77 (4)-172.99 (3)°.

The bridging Cr₂O₂ unit is symmetric, with Cr-O1 and Cr-O1' separations of 1.974 (1) and 1.972 (1) Å, respectively. These distances are not greatly different from the average values of 1.965 and 1.974 Å in the dithionate and monoclinic chloride structures, respectively.⁵

The Cr-O1-Cr' bridging angle, ϕ , is 100.83 (3)° in the present case, which is intermediate between the values of 99.92 (3)° for the monoclinic chloride and 101.54 (5)° for the dithionate.⁵ As had been predicted by Güdel and co-workers^{11,12} on the basis of anticipated hydrogen bonding in the crystals of the cobalt analogue, the hydrogen atom on the bridging hydroxyl group is substantially out of the bridging Cr₂O₂ plane; the deviation in the present case is 0.56 (2) Å, which corresponds to a dihedral angle θ of 50 (3)°. Thus, the θ value here is substantially larger than the value of 24° in the dithionate salt and is probably significantly larger than the value of 41° in the monoclinic chloride. It is noteworthy that, in other bis(μ -hydroxo)chromium(III) complexes, θ values of less than 6° have been reported.⁶

The hydrogen bonding in the crystals is extensive, with all potential donors and acceptors apparently participating. The bridging hydroxo group forms a strong hydrogen bond to a chloride ion, and all of the ammine hydrogen atoms evidently form hydrogen bonds to chloride ions or solvent molecules. The solvent molecules also donate hydrogen bonds to the anions.

The average magnetic susceptibility and effective magnetic moment of a sample prepared by pulverizing two large triclinic crystals of the complex is shown in Figure 2. From the simple Van Vleck Hamiltonian

$$\mathcal{H} = JS_1 \cdot S_2 + g\mu_B MS'$$

the susceptibility data lead to the values $g = 1.985$ (3) and $J = 1.43$ (1) cm⁻¹. Thus, as deduced by Güdel and co-workers from optical spectroscopic measurements,^{11,12} the value of J [which corresponds to the triplet energy $E(1)$] is significantly lower than the values of 4.1 and 5.8 cm⁻¹ found in the monoclinic isomer and in the dithionate salt, respectively.⁵ On

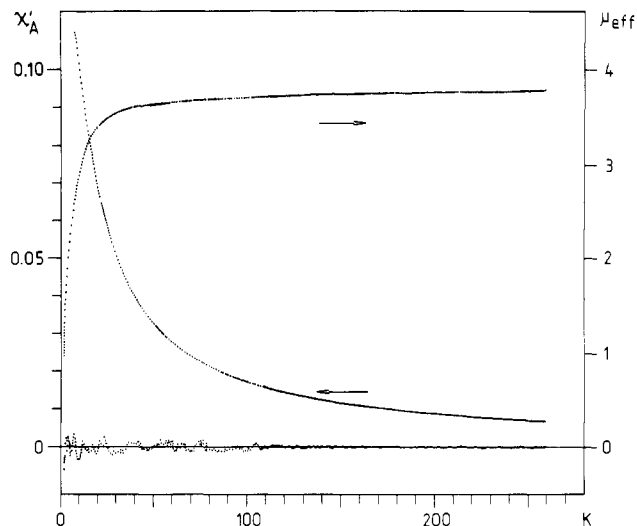


Figure 2. Magnetic susceptibility per chromium (left scale, cgsu) and effective magnetic moment (right scale, μ_B) of triclinic $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}]$. The lower almost random distribution of dots around the abscissa represents $50(\chi_{\text{obsd}} - \chi_{\text{calcd}})$ where χ_{calcd} is based on the parameters $g = 1.985$ and $J = 1.43$ cm⁻¹.

the basis of the empirical GHP model,⁶ we calculate from the observed values of R , θ , and ϕ a value of 5.89 cm⁻¹. In this parameter range, however, the model predicts that J is extremely sensitive to small changes in θ , the least precisely determined structural parameter, and for the same values of R and ϕ (1.973 Å and 100.83°, respectively) the value of J is calculated as only 1.48 cm⁻¹ if θ is increased from 50 to 60°. Such a change in θ is perfectly consistent with the crystallographic results, since it represents an increase of only 3σ in the observed value. Consequently, we must conclude that the observed results are entirely consistent with the model but that conventional X-ray diffraction methods are insufficiently precise in this parameter range to make a thorough test of the model.

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Registry No. $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}]$, 84028-63-7.

Supplementary Material Available: Tables of hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, and observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Preparation of $[\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ and $\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)(3\text{-hexyne})\text{Cl}_2$

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We have recently shown that tantalum hydride complexes of the type $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$ ($\text{R} = \text{Me}, \text{Et}$) can be prepared by treating $\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{propylene})\text{Cl}_2$ or Ta-

(η^5 -C₅Me₄R)(CH₂CMe₃)₂Cl₂ with molecular hydrogen.¹ A crystal structure of a derivative, Ta₂(η^5 -C₅Me₄Et)₂MeCl₃H₂, showed that chloride ligands are terminally bound;¹ presumably the hydride ligands bridge the Ta-Ta bond. [Ta(η^5 -C₅Me₄R)Cl₂H]₂ reacts readily with acetonitrile to give [(η^5 -C₅Me₄R)TaCl]₂(μ - η^1 -N, η^2 -C,N-NCHMe)(μ -Cl)(μ -H)-[(η^5 -C₅Me₄R)TaCl]₂ and with carbon monoxide to give Ta₂(η^5 -C₅Me₄R)₂Cl₄(μ -CHO)(μ -H).³ It was the latter reaction that generated our interest in preparing and studying an analogous niobium hydride complex. We report here the results of our attempts to do so.

Results and Discussion

A complex of the type Nb(η^5 -C₅Me₅)(olefin)Cl₂ has never been prepared by using methods that successfully yield Ta(η^5 -C₅Me₅)(propylene)Cl₂ and related species.^{4a} It also has not been possible to prepare Nb(η^5 -C₅Me₅)(CH₂CMe₃)₂Cl₂ since Nb(CH₂CMe₃)₂Cl₃^{4b} does not react smoothly with LiC₅Me₅ or TiC₅Me₅. Fortunately, NbMe₂Cl₃, prepared readily by reacting NbCl₅ with ZnMe₂ in pentane (cf. NbMe₃Cl₂⁵), does react smoothly with LiC₅Me₅ to yield Nb(η^5 -C₅Me₅)Me₂Cl₂. Furthermore, Nb(η^5 -C₅Me₅)Me₂Cl₂, unlike Ta(η^5 -C₅Me₅)Me₂Cl₂,⁶ reacts relatively rapidly with molecular hydrogen (40 psi) to give a green crystalline product that is similar to [Ta(η^5 -C₅Me₅)Cl₂H]₂ in color and form but is more soluble than [Ta(η^5 -C₅Me₅)Cl₂H]₂ in aromatic hydrocarbons and ethers.

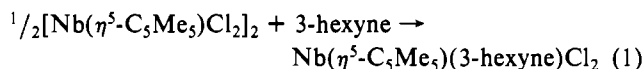
There are three pieces of evidence that suggest the niobium product is, in fact, not [Nb(η^5 -C₅Me₅)Cl₂H]₂, but [Nb(η^5 -C₅Me₅)Cl₂]₂. First, the IR spectrum of [Nb(η^5 -C₅Me₅)Cl₂]₂ shows no obvious hydride peak(s) and is identical with that of an analogous product prepared from Nb(η^5 -C₅Me₅)Me₂Cl₂ and D₂. Second, the FD mass spectrum of the product prepared in a reaction in which H₂ was used and the one in which D₂ was used each exhibits only a parent ion consistent with [Nb(η^5 -C₅Me₅)Cl₂]₂. Third, no ¹H NMR signal attributable to a hydride ligand could be found in the region +40 to -40 ppm at temperatures as low as -70 °C. These results contrast markedly with data for [Ta(η^5 -C₅Me₄R)Cl₂H]₂ where a hydride peak is observed at ~1590 cm⁻¹ in the IR spectrum and at ~10.5 ppm in the ¹H NMR spectrum, while a peak was observed for Ta(η^5 -C₅Me₄Et)Cl₂H in the mass spectrum.¹ While a peculiar set of circumstances might lead to the observed results for the Nb system, even though the complex were [Nb(η^5 -C₅Me₅)Cl₂H]₂, we prefer the more logical conclusion that it is [Nb(η^5 -C₅Me₅)Cl₂]₂. The dimer formulation is supported by the fact that the compound is diamagnetic and the fact that a molecular weight determination (cryoscopic in C₆H₆) of its η^5 -C₅Me₄Et analogue showed it to be a dimer (found 650 ± 20⁶).

The structure of [Nb(η^5 -C₅Me₅)Cl₂]₂⁷ is likely to be roughly analogous to the structures of [M(η^5 -C₅Me₅)Cl(μ -Cl)]₂ (M = Rh,⁸ Ir⁹). However, it is not unreasonable to expect a

relatively short Nb...Nb distance consistent with a significant bonding interaction (even though the Rh...Rh and Ir...Ir distances are relatively long¹⁰) since related Ta(III) dimeric molecules of the type [TaL₂Cl₂(μ -Cl)]₂ (L = a phosphine) are known to possess what amounts to approximately a Ta=Ta double bond.^{11,12}

It is interesting to note that [Ta(PMe₃)₂Cl₂(μ -Cl)]₂ adds H₂ to form [Ta(PMe₃)₂Cl₂(μ -Cl)(μ -H)]₂.¹³ We propose that [Nb(η^5 -C₅Me₅)Cl₂]₂ does not add H₂ for thermodynamic reasons, i.e., a relatively high Nb(IV)/Nb(III) redox potential compared to the analogous Ta(IV)/Ta(III) redox potential; if [Ta(η^5 -C₅Me₄R)Cl₂]₂ were to be prepared, we would expect it to add H₂ readily.

Some reactions of [Nb(η^5 -C₅Me₅)Cl₂]₂ (or lack thereof) are consistent with its formulation. For example, it does not react readily with acetonitrile or ethylene. ([Ta(η^5 -C₅Me₄R)Cl₂H]₂ reacts with styrene to give some ethylbenzene and Ta(η^5 -C₅Me₄R)(styrene)Cl₂.⁶) [Nb(η^5 -C₅Me₅)Cl₂]₂ does react readily with 3-hexyne (eq 1) to give a purple analogue of the



tantalum acetylene complexes that had been prepared by treating Ta(η^5 -C₅Me₄R)(olefin)Cl₂ complexes with the appropriate acetylene;¹⁴ as we noted above, Nb(η^5 -C₅Me₄R)(olefin)Cl₂ complexes are unavailable. The fact that both Nb and Ta benzyne complexes of the type M(η^5 -C₅Me₅)(C₆H₄)Me₂ can be prepared is consistent with these results.¹⁵ It is becoming clear that an acetylene binds strongly to a d² metal center and, in the cases where compounds have been structurally characterized,^{14,16} is apparently substantially reduced by the metal to what ultimately would be called a RC=CR dianion.

Finally, [Nb(η^5 -C₅Me₅)Cl₂]₂ does react readily with CO and PMe₃, but the products of these apparently complex reactions were not characterized.

Experimental Section

All operations, except where noted otherwise, were performed under dinitrogen either by Schlenk techniques or in a Vacuum Atmospheres drybox. Solvents were purified and dried by standard techniques. Starting materials were purchased from standard sources and used as received unless specified otherwise. Pentamethylcyclopentadiene was prepared by Bercaw's procedure.¹⁷

Preparation of Nb(η^5 -C₅Me₅)Me₂Cl₂. A pentane solution of ZnMe₂ (1.9 g, 19.9 mmol) was added dropwise to a stirred suspension of NbCl₅ (5.4 g, 20.0 mmol) in 100 mL of pentane. The mixture was stirred for 10 h at 25 °C and the ZnCl₂ removed by filtration. The solvent was removed from the filtrate in vacuo to give NbMe₂Cl₃ quantitatively (4.50 g). The NbMe₂Cl₃ was dissolved in 200 mL of diethyl ether, and LiC₅Me₅ (2.77 g, 19.5 mmol) was added slowly over 0.5 h. The mixture was stirred for 1.5 h and filtered. The filtrate was concentrated and cooled to give orange crystals, 2.13 g. The filtercake was extracted with 150 mL of toluene. The toluene solution was concentrated to 30 mL under vacuum, and pentane was added. Additional crystals were collected when the solution was cooled: total yield 4.03 g (63%); ¹H NMR (CH₂Cl₂) δ 2.00 (s, 15, C₅Me₅), 1.20 (s, 6, NbMe₂). Anal.

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Calcd for $\text{NbC}_{12}\text{H}_{21}\text{Cl}_2$: C, 43.79; H, 6.43; Cl, 21.54. Found: C, 43.81; H, 6.64; Cl, 21.40.

Preparation of $[\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$. A solution of $\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2\text{Cl}_2$ (2.3 g, 7.0 mmol) in 70 mL of toluene was added to a glass pressure vessel and stirred under H_2 (35 psi) for 14 h. The green mixture was filtered and the filtrate concentrated in vacuo. Pentane was added, and the solution was cooled to -30°C to give green crystals of $[\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$: 1.4 g (66%); $^1\text{H NMR}$ (C_6H_6) δ 2.27 (s, C_5Me_5). Anal. Calcd for $\text{NbC}_{10}\text{H}_{15}\text{Cl}_2$: C, 40.17; H, 5.37; Cl, 23.71. Found: C, 40.09; H, 5.25; Cl, 23.55.

Preparation of $\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)(3\text{-hexyne})\text{Cl}_2$. $[\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ (150 mg, 0.25 mmol) was dissolved in toluene (10 mL), and 3-hexyne (200 μL , 7.3 equiv) was added. After 15 h, the solvent was removed from the purple solution in vacuo and the residue recrystallized from minimal pentane to give $\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)(3\text{-hexyne})\text{Cl}_2$: 160 mg (83%); $^1\text{H NMR}$ (C_6D_6) δ 2.95 (q, 4, $J_{\text{HH}} = 7.5$ Hz, CH_2CH_3), 1.66 (s, 15, C_5Me_5), 1.17 (t, 6, $J_{\text{HH}} = 7.5$ Hz, CH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 217.7 (acetylenic C), 121.0 (C_5), 28.9 (C_5Me_5), 14.4 (CH_2CH_3), 11.8 (CH_2CH_3); IR (Nujol) 1725 cm^{-1} ($\nu_{\text{C}=\text{C}}$). Anal. Calcd for $\text{NbC}_{16}\text{H}_{25}\text{Cl}_2$: C, 50.42; H, 6.61; Cl, 18.60. Found: C, 50.32; H, 6.64; Cl, 19.53.

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Bis(acetylacetonato)fluorovanadium(III), $\text{VF}(\text{C}_5\text{H}_7\text{O}_2)_2$, Synthesis of a Novel Neutral Compound of Vanadium(III) from Vanadium(V)

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The tripositive state of vanadium is one of its unusual oxidation states, mainly owing to the instability of vanadium(III) compounds. Predominant among the known compounds of vanadium(III) are those derived from vanadium(III) trihalides.¹ Trivalent vanadium also forms some neutral mixed-ligand complexes of the types VL_3X_3 and VL_2X_3 , with L being a unidentate ligand and X a halide, particularly chloride. The neutral complex of V^{3+} of the type $\text{V}(\text{L-L}')_2\text{X}$, with L-L' being a bidentate mononegative ligand, does not appear to have any reported example in the literature. Moreover, reports on the syntheses of trivalent vanadium compounds from V^{5+} through chemical reduction are rather scanty. In a continuation of our studies on the synthesis and structural assessment of fluoro² and mixed fluoro^{3,4} compounds of vanadium, we have developed a method for the synthesis of a new neutral complex of vanadium(III), $\text{VF}(\text{acac})_2$, which we have achieved by a two-step electron-transfer process starting from vanadium pentoxide. In this report we present an account of the synthesis, characterization, and structural assessment of the title compound.

Experimental Section

All chemicals were of reagent grade. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method. $\text{Hg}[\text{Co}(\text{NCS})_4]$ was the calibrant.

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The mass spectra were recorded on a Varian MAT CH-5 spectrometer using a direct-insertion probe to introduce the sample directly into the ion source without any prior heating. The operation conditions were as follows: electron energy 70 eV ($1 \text{ eV} \approx 1.6 \times 10^{-19} \text{ J}$); source temperature 50, 100, and 150°C ; resolution 10000; accelerating voltage 8 kV. The mass spectrometric observations were made with the field of ionizing current being maintained sufficiently strong to trap primary ions.

Synthesis of Bis(acetylacetonato)fluorovanadium(III), $\text{VF}(\text{C}_5\text{H}_7\text{O}_2)_2$. A suspension of 2.0 g (11 mmol) of V_2O_5 in 10 cm^3 of water was treated with 2.2 cm^3 (44 mmol) of 40% hydrofluoric acid. The mixture was warmed on a steam bath with stirring for 10-15 min and then cooled followed by filtration to remove any undissolved impurity. The clear solution was cooled in an ice bath, and 99% hydrazine hydrate solution was added dropwise with occasional stirring. The solution first turned blue. The addition of hydrazine hydrate was continued until a blue crystalline compound ceased to appear, with the mother liquor becoming very faint in color. The blue compound was separated by centrifugation and dried on a filter paper and finally in vacuo. The compound was identified as $\text{N}_2\text{H}_5\text{VOF}_3$, yield 1.6 g (92%). Anal. Calcd for $\text{N}_2\text{H}_5\text{VOF}_3$: N, 17.85; H, 3.19; V, 32.47; F, 36.31. Found: N, 17.91; H, 3.14; V, 32.5; F, 36.1. Molar conductance (water): 130 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Magnetic moment (302 K): $1.51 \mu_{\text{B}}$ ($1 \mu_{\text{B}} \approx 0.927 \times 10^{-23} \text{ A m}^2$). IR: 970 ($\nu_{\text{V-O}}$), 500 cm^{-1} ($\nu_{\text{V-F}}$).

In a further experiment, starting from comparatively higher amounts of the reagents and after purging the reaction vessel with argon, the evolved gas was first passed through a dry sodium hydroxide tower and then over heated ($\sim 450^\circ\text{C}$) magnesium. The magnesium nitride thus formed was treated with water and tested for the liberation of ammonia.

The blue hydrazonium oxotrifluorovanadate(IV), $\text{N}_2\text{H}_5\text{VOF}_3$ (1.6 g, 10.2 mmol), dissolved in about 8 cm^3 of water, and acetylacetonone (10 g, 100 mmol) were placed in a small polyethylene conical flask, the neck of which was plugged with cotton wool, the whole was heated on a steam bath for ca. 1 h, and a dark blue-green solution was obtained. On cooling, blue-green crystals of bis(acetylacetonato)-fluorovanadium(III), $\text{VF}(\text{acac})_2$, were formed, which were removed from the flask and dried on a filter paper. The compound was recrystallized by dissolving in hot benzene followed by addition of petroleum ether (bp $40\text{-}60^\circ\text{C}$) until the solution was cloudy: yield of $\text{VF}(\text{C}_5\text{H}_7\text{O}_2)_2$ 2.5 g (84.7% on the basis of V_2O_5); mp $246\text{-}248^\circ\text{C}$. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{VO}_4\text{F}$: C, 44.78; H, 5.27; V, 18.99; F, 7.1. Found: C, 44.32; H, 5.6; V, 18.4; F, 6.9. Magnetic moment (302 K): $2.77 \mu_{\text{B}}$. M_r : calcd, 268; found (mass spectrum), 268.

Workup of the mother liquor, obtained after isolation of $\text{VF}(\text{acac})_2$, afforded a small amount of $\alpha,\alpha,\beta,\beta$ -tetraacetylene, $(\text{CH}_3\text{CO})_2\text{C-HCH}(\text{CH}_3\text{CO})_2$, being the oxidation product of acetylacetonone.

Elemental Analyses. Carbon, hydrogen, nitrogen, and fluoride analyses were obtained from Amel, Australian Microanalytical Service, Port Melbourne, Victoria 3207, Australia.

Vanadium was estimated volumetrically by titration with standard potassium permanganate. The compounds were first decomposed, and vanadium was oxidized to vanadium(V). A near-boiling vanadium(V) solution was treated with a stream of sulfur dioxide for ca. 10 min and then with a rapid stream of carbon dioxide to expel any excess of sulfur dioxide. The vanadium(V) solution was then cooled to ca. 80°C and titrated with standard potassium permanganate.⁵ Fluoride was also determined by precipitating as lead chloride fluoride, PbClF , and chloride was estimated by Volhard's method, from which the fluoride content was calculated.⁶

Results and Discussion

Vanadium pentoxide readily reacts with 40% hydrofluoric acid and an excess of hydrazine hydrate to yield a blue crystalline compound. The compound is soluble in water, and the results of elemental analyses suggest the atom ratio N:H:V:F as 2:5:1:3. The infrared spectrum of the compound showed a strong band at 970 cm^{-1} , indicating the presence of a V-O multiple bond, and was accordingly assigned⁷ to $\nu_{\text{V-O}}$. The band at 500 cm^{-1} has been assigned as the $\nu_{\text{V-F}}$ mode,

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