

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
SIMON FRASER UNIVERSITY, BURNABY 2, BRITISH COLUMBIA, CANADA**Crystal and Molecular Structure and Vibrational Spectrum of the Vanadium(V) Oxide Trinitrate-Acetonitrile Complex, $\text{VO}(\text{NO}_3)_3 \cdot \text{CH}_3\text{CN}$**

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The crystal and molecular structure and vibrational spectrum of the vanadium oxide trinitrate-acetonitrile complex $\text{VO}(\text{NO}_3)_3 \cdot \text{CH}_3\text{CN}$ have been determined. The compound crystallizes in the orthorhombic space group *Pbca* with eight monomeric molecules in a unit cell of dimensions $a = 11.14$ (3), $b = 12.88$ (3), $c = 13.93$ (4) Å. The calculated density is 1.95 (3) g cm^{-3} and the measured density 1.9 (1) g cm^{-3} . Full-matrix least-squares refinement of 548 observed three-dimensional X-ray counter measured intensities led to a final conventional *R* index of 0.095. The configuration about the vanadium atom is that of a pentagonal bipyramid. The equatorial pentagon of five oxygen atoms is formed by the coordination of two bidentate nitrate groups and one unidentate nitrate group, with the vanadyl oxygen atom and the nitrogen of the acetonitrile group forming the apices. The vanadium atom is displaced 0.27 Å out of the plane toward the vanadyl oxygen atom. The V-O bond length to the unidentate nitrate group is 1.92 (2) Å; the lengths of the V-O bonds to the bidentate nitrate groups range from 2.02 (2) to 2.07 (2) Å. The V=O bond length is 1.55 (2) Å and acetonitrile is coordinated by a somewhat long V-N bond of 2.24 (3) Å. Infrared and Raman spectra for the complex have been measured and assignments aided by recording Raman spectra on the complex prepared with isotopically substituted (^2H and ^{15}N) acetonitrile. Bands which arise from the bidentate and unidentate nitrate groups have been distinguished.

Introduction

Vanadium(V) oxide trinitrate, a yellow liquid first reported by Schmeisser,¹ is believed on the basis of infrared and Raman spectroscopy to have a molecular structure in which all three nitrate groups are bidentate ligands and the vanadium is seven-coordinate.² Such a structure is consistent with the identification of bidentate coordination as a recurring property of several nitrates of both transition and nontransition metals in high oxidation states, e.g., $\text{Ti}(\text{NO}_3)_4$,³ $\text{Co}(\text{NO}_3)_3$,⁴ and $\text{Sn}(\text{NO}_3)_4$.⁵ The reaction with simple aliphatic nitriles proceeds smoothly, unlike most organic compounds which are vigorously oxidized or nitrated. In the case of acetonitrile a stable crystalline 1:1 adduct is readily isolated. Interest therefore centers on the possibilities for the molecular structure of such an adduct. One consideration is that the reaction is a simple addition to yield an eight-coordinate complex; alternatively one can visualize that the coordination of the base might induce some relaxation in the coordination of one or more of the oxygen atoms in one or more of the nitrate groups, as a result of competition between the ligands.

This single-crystal X-ray diffraction study shows conclusively that relaxation of nitrate coordination does occur. The structure consists of two bidentate nitrate ligands and one unidentate nitrate group, the seven-coordinate of vanadium being completed by the oxide and acetonitrile groups. The Raman and infrared spectra are correspondingly more complicated than those of $\text{VO}(\text{NO}_3)_3$ and bands assignable to the single unidentate nitrate group can be identified. In addition, spectra of the complex synthesized using ^{15}N - and ^2H -labeled

CH_3CN have been measured in an attempt to determine the position of the metal-nitrogen stretching frequency.

Experimental Section

Preparation of the Complex.—Pale yellow vanadium oxide trinitrate (3 g), prepared by allowing V_2O_5 to react with N_2O_5 and distilling,¹ was added slowly under dry nitrogen gas to about 30 ml of stirred anhydrous acetonitrile (freshly distilled from P_2O_{10}). Excess acetonitrile was then removed carefully under vacuum from the pale yellow solution until the solid complex crystallized as a yellow-orange mass. This was then pumped for a further 30 min. The crude product could be purified by recrystallization from a hot solution in dry carbon tetrachloride, with which it does not react, or by sublimation at room temperature under a low pressure of 10^{-4} mm onto a cold finger held at 10° . Complexes with $\text{CH}_3\text{C}^{15}\text{N}$ (96.1% ^{15}N purchased from Isotopes Inc., Chicago, Ill.) and CD_3CN were prepared by adding the parent nitrate to CCl_4 solutions containing a small excess of the nitrile. The complex does undergo appreciable dissociation into its components when pumped continuously for several hours, and so care was taken to prevent contamination of the crystals with droplets of $\text{VO}(\text{NO}_3)_3$ which could also condense out under these conditions. We found the best procedure was to avoid prolonged pumping of the product after removing excess acetonitrile, to evacuate the system for about 10 min before cooling the cold finger, and to close the system from the pump for the greater part of the sublimation. The pale yellow crystals produced by either method gave identical X-ray powder photographs, analyses, and spectra. The crystals (mp 72°) are extremely sensitive to small traces of moisture, becoming rapidly opaque and orange, and were handled in an efficient drybox.

Analyses.—The complex was analyzed for C, H, and N in the usual way and for vanadium by reduction to vanadium(IV) with ferrous ion and back-titration with permanganate. Corrections were made for the interference of nitrate ion by comparison with standards having similar nitrate activity. Confirmation of the 1:1 complex was made by comparison of the integrated CH_3 resonance in the nmr spectra of equimolar solutions of the complex and of pure acetonitrile in carbon tetrachloride. *Anal.* Calcd for $\text{VO}(\text{NO}_3)_3 \cdot \text{CH}_3\text{CN}$: C, 8.2; H, 1.0; N, 19.1; V, 17.3. Found: C, 8.2; H, 1.2; N, 18.9; V, 17.3.

Spectra.—Infrared spectra were recorded in the range 4000–350 cm^{-1} using the Beckman Model IR-12 for the solid complex as (a) mulls in Nujol, hexachlorobutadiene, and Fluoroube between silver chloride plates, (b) a sublimed film on a silver chlo-

(1) M. Schmeisser, *Angew. Chem.*, **67**, 493 (1955).(2) C. C. Addison, D. W. Amos, D. Sutton, and W. H. H. Hoyle, *J. Chem. Soc. A*, 808 (1967).(3) C. D. Garner and S. C. Wallwork, *ibid.*, **A**, 1496 (1966).(4) J. Hilton and S. C. Wallwork, *Chem. Commun.*, 871 (1968).(5) C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc. A*, 1949 (1967).

ride plate held at about 100°K in a specially designed cold cell provided with cesium bromide external windows, and (c) solutions in carbon tetrachloride. The complex reacted rapidly with Nujol to produce a complicated spectrum of products^{6,7} which was not studied further. Attempts were also made to obtain the spectrum below 350 cm⁻¹ of a sample sublimed onto a polyethylene plate, but these were not successful since we were never able to obtain a satisfactory deposit of sublimate under these conditions. We also attempted to obtain infrared spectra for solutions in acetonitrile, but rapid decomposition of the solutions was apparently promoted by contact with the silver chloride cells (Beckman "extrocells"), with the formation of an intense orange coloration.

Raman spectra were measured using the Cary Model 81 with 70 mW He-Ne laser excitation for crystals and solutions in acetonitrile at room temperature. The solid-phase Raman spectrum is an excellent example of the high-quality spectra obtainable from laser excitation of crystalline materials. The spectrum quoted was obtained on a sample which was freshly vacuum sublimed directly into a glass bulb at 10° and is identical with (but of better quality than) spectra recorded on crystals sealed in glass tubes. Solutions in carbon tetrachloride could not be obtained at sufficient concentration to yield Raman lines other than those of the solvent. Depolarization measurements were recorded for coaxial viewing and are corrected with reference to the known degree of depolarization of the lines due to the uncoordinated acetonitrile solvent. Frequency calibrations were carried out using rare gas emission lines. Reported intensities are not corrected for wavelength dependence of detector sensitivity. Nmr spectra were recorded using a Varian A-60 60-Mcps spectrometer and solutions in carbon tetrachloride. Samples were run at room temperature using cyclohexane as internal reference. The single peak due to the methyl protons appeared shifted slightly downfield from free CH₃CN, but the shift was exceedingly small (~1 cps) and of doubtful significance.

Collection and Refinement of X-Ray Data

A single crystal of the complex prepared by sublimation was carefully chosen and sealed in a Lindemann glass capillary. This single crystal yielded the entire diffraction results (collected over a period of 6 weeks); during this time no significant decomposition was detected. However, after a period of 6 months the crystal had completely disappeared leaving an amber yellow liquid.

Weissenberg photographs of the zones $hk0$ - $hk6$ using Cr K α radiation together with precession photographs of the $h0l$ and $0kl$ zones using Mo K α radiation showed systematic absences for $hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$. This combined with the Laue group indicated unambiguously the space group $Pbca$.

Crystal Data.—VO(NO₃)₃·CH₃CN, formula weight 294, crystallizes in the orthorhombic space group $Pbca$: $a = 11.14$ (3), $b = 12.88$ (3), $c = 13.93$ (4) Å; λ 0.7107 Å for Mo K α radiation; $V = 1999$ Å³; $d_m = 1.9$ (1) g cm⁻³, $Z = 8$, $d_x = 1.95$ (3) g cm⁻³, $F(000) = 1168$; μ (Mo K α) = 11.0 cm⁻¹.

All data were collected using a crystal of dimensions 0.24 × 0.28 × 0.35 mm mounted with its longest edge (c axis) parallel to Φ . Cell dimensions were obtained from accurate counter measurements at 22° of a number of reflections.

Reflection intensities for the unique set of data were

(6) Reaction with saturated aliphatic hydrocarbons is a well-known property of compounds containing bidentate nitrate groups. See, for example, ref 7.

(7) C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

measured on a Picker manual four-circle diffractometer using zirconium-filtered Mo K α radiation and a scintillation detector with pulse height analysis. Measurements were made at a scan rate of 2°/min using a 1.2° takeoff angle with a symmetrical θ - 2θ scan of 2° width. The detector was positioned 23 cm from the crystal. Examination of a number of reflection profiles indicated that reflections throughout the reciprocal lattice showed somewhat broad but uniform profiles indicating isotropic mosaicity.

The background intensity was examined in a number of different directions in reciprocal space and a curve as a function of θ alone satisfactorily described the results. Accordingly each reflection was corrected for background and those reflections which counted above 1.5 times the estimated background were regarded as observed. The remainder were given a value of half the scan count and coded as unobserved. Of the 931 intensities recorded in the range $0^\circ < 2\theta < 40^\circ$, 548 were observed. Three standard reflections were measured at 3-hr intervals and retained a constancy of $\pm 1.6\%$ over the entire data collection. Coincidence losses were carefully checked for the most intense reflections by remeasuring them with a substantially lower beam intensity; no correction was found to be necessary. Lorentz and polarization factors were applied and the structure factors were calculated in the usual manner. No correction for absorption was made; the maximum error that this would introduce is 6% between extreme values of F^2 .

Solution and Refinement of the Structure

A three-dimensional Patterson function showed seven large peaks at $1/2, 0, 0$; $0, 1/2, 0$; $0, 0, 1/2$; $1/2, 1/2, 0$; $1/2, 0, 1/2$; $0, 1/2, 1/2$; and $1/2, 1/2, 1/2$. This could be fitted in two ways: either the two crystallographically non-equivalent special positions (each with a center of symmetry) could be occupied by vanadium atoms or the vanadium atoms themselves could be accidentally arranged to give a subcell halved in each direction (a , b , and c). Chemical considerations allowed us to reject the two crystallographically different, centrosymmetric vanadium atom arrangement. A careful examination of both the three-dimensional Patterson map and the difference Patterson map provided evidence for a slight displacement of the vanadium atom from a subcell position, particularly along the z axis.

The structure was solved in stages since the data showed an extreme distribution of intensity in the following way. (a) Reflections with h , k , and l all even exhibited approximately double the average $|F_o|$ (accounting for one-eighth of the total data); (b) for reflections with either $h + k$ even, l even, or $h + k + l$ even, the average $|F_o|$ for observed reflections were approximately 50% greater than for the corresponding odd parity groups. These parity alternations required the presence of pseudo mmm point symmetry about the vanadium atom. A symbolic addition procedure⁸ on

(8) F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, "N.R.C. Crystallographic Programs for the I.B.M./360 Systems. World List of Computer Programs," 2nd ed, Appendix, 1966, p 52.

TABLE I
 FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
V(1)	0.4984 (5)	0.2446 (3)	0.5145 (3)	<i>b</i>
N(2)	0.5966 (20)	0.2282 (16)	0.6758 (15)	3.63 (48)
O(3)	0.5176 (18)	0.1667 (13)	0.6430 (11)	3.89 (40)
O(4)	0.6164 (16)	0.3006 (12)	0.6138 (11)	3.05 (36)
O(5)	0.6409 (17)	0.2230 (13)	0.7525 (15)	5.16 (43)
N(6)	0.4673 (19)	0.3863 (16)	0.3969 (14)	3.07 (45)
O(7)	0.4025 (17)	0.3065 (13)	0.4006 (11)	3.43 (38)
O(8)	0.5444 (15)	0.3871 (13)	0.4656 (12)	3.46 (39)
O(9)	0.4562 (18)	0.4570 (15)	0.3430 (13)	4.93 (49)
N(10)	0.3629 (22)	0.0737 (16)	0.4309 (16)	3.75 (49)
O(11)	0.3682 (15)	0.1466 (12)	0.5105 (11)	3.30 (36)
O(12)	0.4179 (21)	0.0865 (17)	0.3589 (16)	6.41 (58)
O(13)	0.2824 (18)	0.0101 (16)	0.4501 (13)	5.60 (49)
O(14)	0.5946 (16)	0.1866 (13)	0.4555 (11)	3.61 (39)
N(15)	0.3715 (21)	0.3416 (16)	0.6013 (14)	3.67 (48)
C(16)	0.3094 (23)	0.3999 (19)	0.6422 (17)	2.96 (57)
C(17)	0.2311 (24)	0.4742 (17)	0.6901 (16)	2.84 (54)

^a Estimated standard deviations in the least significant figures are given in parentheses. ^b Anisotropic vibration tensor components U_{ij} (Å²) for the expression $T = \exp[-2\pi(U_{11}a^2h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$ are $U_{11} = 0.00403$ (30), $U_{22} = 0.00252$ (20), $U_{33} = 0.00298$ (24), $U_{23} = -0.00039$ (24), $U_{13} = 0.00020$ (30), $U_{12} = 0.00031$ (32).

the reflections $h + k$ even was applied and a Fourier map based upon 154 independent signed structure factors was calculated. Of these, 15 proved subsequently to be incorrect. Structure factors were calculated for a variety of models involving the vanadium atom displaced from its special position together with the inclusion of both full and partial oxygen atoms in the peaks surrounding it. The best agreement achieved at this stage was an *R* index of 0.28 for the $h + k$ even reflections only.

At this point it was not possible to visualize the structure from its superimposed mirror image. Since the $h + k$ odd parity groups were specially weak, we believed that if the reflections with the highest *E*'s could be interrelated, we could then use them to destroy the remaining mirror plane. We selected the 70 largest *E*'s among the $h + k$ even and were able to assign symbols and then signs to 25 of the $h + k$ odd reflections. An electron density map based on these 25 reflections together with 125 of the $h + k$ even reflections gave evidence for a shift in the *y* direction of the vanadium atom and tentative positions for 15 of the light atoms. The overall agreement for all observed data after two cycles of full-matrix least-squares refinement varying all positional and isotropic thermal parameters and a scale factor was 0.26.

After careful examination of various drawings of this model, two light atoms were interchanged (in terms of a pseudo mirror plane) and a third was introduced. This model refined from an initial *R* of 0.17 to 0.106 in two cycles of full-matrix refinement. An electron density difference map showed as its largest feature peaks which indicated that the vanadium atom was moving anisotropically.

Refinement was completed on this basis and the final *R* index was 0.095. For the vanadium atom the rms components of vibration along the principal axes of the

 TABLE II
 INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)^a

(a) Intramolecular Bonded Contacts			
V(1)-O(3)	2.06 (2)	N(6)-O(7)	1.26 (3)
-O(4)	2.04 (2)	-O(8)	1.29 (3)
-O(7)	2.07 (2)	-O(9)	1.19 (3)
-O(8)	2.02 (2)	N(10)-O(11)	1.45 (3)
-O(11)	1.92 (2)	-O(12)	1.19 (3)
-O(14)	1.55 (2)	-O(13)	1.24 (3)
-N(15)	2.24 (3)	N(15)-C(16)	1.17 (3)
N(2)-O(3)	1.27 (3)	C(16)-C(17)	1.46 (4)
-O(4)	1.29 (3)		
-O(5)	1.18 (3)		
(b) Intramolecular Nonbonded Contacts			
V(1)-O(12)	3.12 (3)	O(7)-O(8)	2.09 (3)
-O(13)	3.98 (3)	-O(11)	2.60 (3)
O(3)-O(4)	2.08 (3)	-O(14)	2.75 (3)
-O(11)	2.50 (3)	O(8)-O(14)	2.65 (3)
-O(14)	2.76 (3)	O(11)-O(14)	2.70 (3)
O(4)-O(8)	2.48 (3)		
-O(14)	2.66 (3)		
(c) Interatomic Angles Selected from Bonded Contacts			
O(3)-V(1)-O(4)	61.1 (7)	O(8)-V(1)-O(11)	140.9 (7)
-O(7)	154.8 (8)	-O(14)	94.8 (8)
-O(8)	135.0 (7)	-N(15)	80.6 (7)
-O(11)	77.5 (7)	O(11)-V(1)-O(14)	101.0 (8)
-O(14)	98.9 (8)	-N(15)	84.6 (7)
-N(15)	82.5 (7)	O(14)-V(1)-N(15)	174.4 (10)
O(4)-V(1)-O(7)	135.7 (6)	O(3)-N(2)-O(4)	109.2 (19)
-O(8)	75.2 (7)	-O(5)	125.6 (22)
-O(11)	137.5 (7)	O(4)-N(2)-O(5)	125.2 (23)
-O(14)	94.8 (8)	O(7)-N(6)-O(8)	111.0 (19)
-N(15)	81.0 (7)	-O(9)	126.5 (23)
O(7)-V(1)-O(8)	61.6 (7)	O(8)-N(6)-O(9)	122.3 (22)
-O(11)	80.9 (7)	O(11)-N(10)-O(12)	122.2 (23)
-O(14)	97.8 (8)	-O(13)	107.0 (20)
-N(15)	82.7 (7)	O(12)-N(10)-O(13)	130.2 (25)
		N(15)-C(16)-C(17)	178.1 (27)
(d) Intermolecular Contacts Shorter than 3.3 Å			
O(3)-O(9)	3.28 (2) (1) ^b	O(9)-O(13)	3.11 (3) (5) ^b
O(4)-O(9)	3.28 (3) (2)	-C(16)	3.20 (3) (2)
-N(10)	3.26 (3) (3)	-C(17)	3.11 (3) (6)
-O(13)	3.19 (3) (3)	O(12)-C(16)	3.26 (3) (7)
O(5)-N(6)	3.12 (3) (1)	-C(17)	3.23 (4) (7)
-O(14)	3.10 (3) (1)	O(13)-O(14)	3.16 (3) (8)
-C(16)	3.30 (3) (4)	-C(16)	3.20 (3) (9)
N(6)-O(13)	3.29 (3) (5)	O(14)-N(15)	3.19 (3) (3)
O(8)-O(8)	3.22 (3) (2)	-C(16)	2.98 (3) (3)
-O(13)	3.19 (3) (3)	-C(17)	3.28 (3) (3)

^a Esd's in the least significant figures are given in parentheses.

^b Figures in this column refer to the following symmetry transformations with respect to atoms in column two: (1) $x, 1/2 - y, 1/2 + z$; (2) $1 - x, 1 - y, 1 - z$; (3) $1/2 + x, 1/2 - y, 1 - z$; (4) $1/2 + x, y, 1/2 - z$; (5) $1/2 - x, 1/2 + y, z$; (6) $1/2 - x, 1 - y, -1/2 + z$; (7) $x, 1/2 - y, -1/2 + z$; (8) $1 - x, -y, 1 - z$; (9) $1/2 - x, -1/2 + y, z$.

thermal ellipsoid are 0.15, 0.18, and 0.21 Å with the directions of greatest motion lying in the plane of the adjacent nitrate oxygen atoms. An electron density difference map based on the final structure parameters given in Table I did not show any peaks higher than 0.7 e⁻/Å³. There was an ill-defined electron density region near the methyl carbon atom which could have been due to the methyl hydrogen atoms. It should be noted that while significant correlation between atomic coordinates of different atoms was observed, it was not nearly as severe as the coincidences in the Patterson might have led one to expect.

The weighting scheme used throughout the refinement employed unit weights for all observed reflections. Unobserved reflections were omitted from the least-squares refinement procedure. Analysis of Δ^2 ($\Delta = |F_o - F_c|$) as a function of either $\sin \theta_1 |F_o|$, or the

TABLE III^a
MEAN PLANES AS $Ax + By + Cz + D = 0$

Plane	Atoms in plane	A	B	C	D	χ^2 ^b	Dist of V(l) from plane, Å	Max dev, Å
1	N(2), O(3), O(4), O(5)	0.7305	-0.5585	-0.3931	0.5036	0.75	0.018	0.016
2	N(6), O(7), O(8), O(9)	0.6482	-0.4545	-0.6109	2.2914	2.17	0.079	0.027
3	N(10), O(11), O(12), O(13)	-0.7108	0.5762	-0.4035	4.7026	5.14	0.320	0.046
4	O(3), O(4), O(7), O(8), O(11)	0.6580	-0.5296	-0.5353	2.1200	2.19	0.268	0.017

^a Equations, expressed in Å, refer to axes x, y, z , parallel to a, b, c , respectively. ^b $\chi^2 = \sum_{i=1}^N (P_i^2 / \sigma^2(P_i))$ where N is the number of atoms in the plane and $\sigma^2(P_i) = A\sigma^2(x_i) + B\sigma^2(y_i) + C\sigma^2(z_i)$. $\sigma(x_i)$ is the estimated standard deviation in the x direction of atom i and P_i is the distance of the atom from the plane.

TABLE IV
OBSERVED AND CALCULATED STRUCTURE FACTORS^a

h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc
0	0	0	1.000	1.000	1	0	0	0.129	-0.129	1	0	0	0.129	-0.129
1	0	0	0.129	-0.129	2	0	0	0.258	-0.258	2	0	0	0.258	-0.258
3	0	0	0.387	-0.387	3	0	0	0.574	-0.574	3	0	0	0.574	-0.574
4	0	0	0.514	-0.514	4	0	0	0.742	-0.742	4	0	0	0.742	-0.742
5	0	0	0.641	-0.641	5	0	0	0.869	-0.869	5	0	0	0.869	-0.869
6	0	0	0.768	-0.768	6	0	0	0.996	-0.996	6	0	0	0.996	-0.996
7	0	0	0.895	-0.895	7	0	0	1.123	-1.123	7	0	0	1.123	-1.123
8	0	0	1.022	-1.022	8	0	0	1.250	-1.250	8	0	0	1.250	-1.250
9	0	0	1.149	-1.149	9	0	0	1.377	-1.377	9	0	0	1.377	-1.377
10	0	0	1.276	-1.276	10	0	0	1.504	-1.504	10	0	0	1.504	-1.504
11	0	0	1.403	-1.403	11	0	0	1.631	-1.631	11	0	0	1.631	-1.631
12	0	0	1.530	-1.530	12	0	0	1.758	-1.758	12	0	0	1.758	-1.758
13	0	0	1.657	-1.657	13	0	0	1.885	-1.885	13	0	0	1.885	-1.885
14	0	0	1.784	-1.784	14	0	0	2.012	-2.012	14	0	0	2.012	-2.012
15	0	0	1.911	-1.911	15	0	0	2.139	-2.139	15	0	0	2.139	-2.139
16	0	0	2.038	-2.038	16	0	0	2.266	-2.266	16	0	0	2.266	-2.266
17	0	0	2.165	-2.165	17	0	0	2.393	-2.393	17	0	0	2.393	-2.393
18	0	0	2.292	-2.292	18	0	0	2.520	-2.520	18	0	0	2.520	-2.520
19	0	0	2.419	-2.419	19	0	0	2.647	-2.647	19	0	0	2.647	-2.647
20	0	0	2.546	-2.546	20	0	0	2.774	-2.774	20	0	0	2.774	-2.774
21	0	0	2.673	-2.673	21	0	0	2.901	-2.901	21	0	0	2.901	-2.901
22	0	0	2.800	-2.800	22	0	0	3.028	-3.028	22	0	0	3.028	-3.028
23	0	0	2.927	-2.927	23	0	0	3.155	-3.155	23	0	0	3.155	-3.155
24	0	0	3.054	-3.054	24	0	0	3.282	-3.282	24	0	0	3.282	-3.282
25	0	0	3.181	-3.181	25	0	0	3.409	-3.409	25	0	0	3.409	-3.409
26	0	0	3.308	-3.308	26	0	0	3.536	-3.536	26	0	0	3.536	-3.536
27	0	0	3.435	-3.435	27	0	0	3.663	-3.663	27	0	0	3.663	-3.663
28	0	0	3.562	-3.562	28	0	0	3.790	-3.790	28	0	0	3.790	-3.790
29	0	0	3.689	-3.689	29	0	0	3.917	-3.917	29	0	0	3.917	-3.917
30	0	0	3.816	-3.816	30	0	0	4.044	-4.044	30	0	0	4.044	-4.044
31	0	0	3.943	-3.943	31	0	0	4.171	-4.171	31	0	0	4.171	-4.171
32	0	0	4.070	-4.070	32	0	0	4.298	-4.298	32	0	0	4.298	-4.298
33	0	0	4.197	-4.197	33	0	0	4.425	-4.425	33	0	0	4.425	-4.425
34	0	0	4.324	-4.324	34	0	0	4.552	-4.552	34	0	0	4.552	-4.552
35	0	0	4.451	-4.451	35	0	0	4.679	-4.679	35	0	0	4.679	-4.679
36	0	0	4.578	-4.578	36	0	0	4.806	-4.806	36	0	0	4.806	-4.806
37	0	0	4.705	-4.705	37	0	0	4.933	-4.933	37	0	0	4.933	-4.933
38	0	0	4.832	-4.832	38	0	0	5.060	-5.060	38	0	0	5.060	-5.060
39	0	0	4.959	-4.959	39	0	0	5.187	-5.187	39	0	0	5.187	-5.187
40	0	0	5.086	-5.086	40	0	0	5.314	-5.314	40	0	0	5.314	-5.314
41	0	0	5.213	-5.213	41	0	0	5.441	-5.441	41	0	0	5.441	-5.441
42	0	0	5.340	-5.340	42	0	0	5.568	-5.568	42	0	0	5.568	-5.568
43	0	0	5.467	-5.467	43	0	0	5.695	-5.695	43	0	0	5.695	-5.695
44	0	0	5.594	-5.594	44	0	0	5.822	-5.822	44	0	0	5.822	-5.822
45	0	0	5.721	-5.721	45	0	0	5.949	-5.949	45	0	0	5.949	-5.949
46	0	0	5.848	-5.848	46	0	0	6.076	-6.076	46	0	0	6.076	-6.076
47	0	0	5.975	-5.975	47	0	0	6.203	-6.203	47	0	0	6.203	-6.203
48	0	0	6.102	-6.102	48	0	0	6.330	-6.330	48	0	0	6.330	-6.330
49	0	0	6.229	-6.229	49	0	0	6.457	-6.457	49	0	0	6.457	-6.457
50	0	0	6.356	-6.356	50	0	0	6.584	-6.584	50	0	0	6.584	-6.584
51	0	0	6.483	-6.483	51	0	0	6.711	-6.711	51	0	0	6.711	-6.711
52	0	0	6.610	-6.610	52	0	0	6.838	-6.838	52	0	0	6.838	-6.838
53	0	0	6.737	-6.737	53	0	0	6.965	-6.965	53	0	0	6.965	-6.965
54	0	0	6.864	-6.864	54	0	0	7.092	-7.092	54	0	0	7.092	-7.092
55	0	0	6.991	-6.991	55	0	0	7.219	-7.219	55	0	0	7.219	-7.219
56	0	0	7.118	-7.118	56	0	0	7.346	-7.346	56	0	0	7.346	-7.346
57	0	0	7.245	-7.245	57	0	0	7.473	-7.473	57	0	0	7.473	-7.473
58	0	0	7.372	-7.372	58	0	0	7.600	-7.600	58	0	0	7.600	-7.600
59	0	0	7.499	-7.499	59	0	0	7.727	-7.727	59	0	0	7.727	-7.727
60	0	0	7.626	-7.626	60	0	0	7.854	-7.854	60	0	0	7.854	-7.854
61	0	0	7.753	-7.753	61	0	0	7.981	-7.981	61	0	0	7.981	-7.981
62	0	0	7.880	-7.880	62	0	0	8.108	-8.108	62	0	0	8.108	-8.108
63	0	0	8.007	-8.007	63	0	0	8.235	-8.235	63	0	0	8.235	-8.235
64	0	0	8.134	-8.134	64	0	0	8.362	-8.362	64	0	0	8.362	-8.362
65	0	0	8.261	-8.261	65	0	0	8.489	-8.489	65	0	0	8.489	-8.489
66	0	0	8.388	-8.388	66	0	0	8.616	-8.616	66	0	0	8.616	-8.616
67	0	0	8.515	-8.515	67	0	0	8.743	-8.743	67	0	0	8.743	-8.743
68	0	0	8.642	-8.642	68	0	0	8.870	-8.870	68	0	0	8.870	-8.870
69	0	0	8.769	-8.769	69	0	0	9.000	-9.000	69	0	0	9.000	-9.000
70	0	0	8.896	-8.896	70	0	0	9.127	-9.127	70	0	0	9.127	-9.127
71	0	0	9.023	-9.023	71	0	0	9.254	-9.254	71	0	0	9.254	-9.254
72	0	0	9.150	-9.150	72	0	0	9.381	-9.381	72	0	0	9.381	-9.381
73	0	0	9.277	-9.277	73	0	0	9.508	-9.508	73	0	0	9.508	-9.508
74	0	0	9.404	-9.404	74	0	0	9.635	-9.635	74	0	0	9.635	-9.635
75	0	0	9.531	-9.531	75	0	0	9.762	-9.762	75	0	0	9.762	-9.762
76	0	0	9.658	-9.658	76	0	0	9.889	-9.889	76	0	0	9.889	-9.889
77	0	0	9.785	-9.785	77	0	0	10.016	-10.016	77	0	0	10.016	-10.016
78	0	0	9.912	-9.912	78	0	0	10.143	-10.143	78	0	0	10.143	-10.143
79	0	0	10.039	-10.039	79	0	0	10.270	-10.270	79	0	0	10.270	-10.270
80	0	0	10.166	-10.166	80	0	0	10.397	-10.397	80	0	0	10.397	-10.397
81	0	0	10.293	-10.293	81									

of molecules in the unit cell is shown in the projection in Figure 2.

Description and Discussion of the Structure

The structure of the complex consists of discrete, monomeric $\text{VO}(\text{NO}_3)_3\text{CH}_3\text{CN}$ molecules, with the vanadium atom situated in a pentagonal-bipyramidal seven-coordinate environment. The vanadium atom is coordinated in the equatorial plane to five oxygen atoms from one unidentate and two bidentate nitrate groups; the nitrogen atom of CH_3CN and a single oxygen atom form the two apices. A result of the shorter distances between the chelating oxygen atoms within each of the

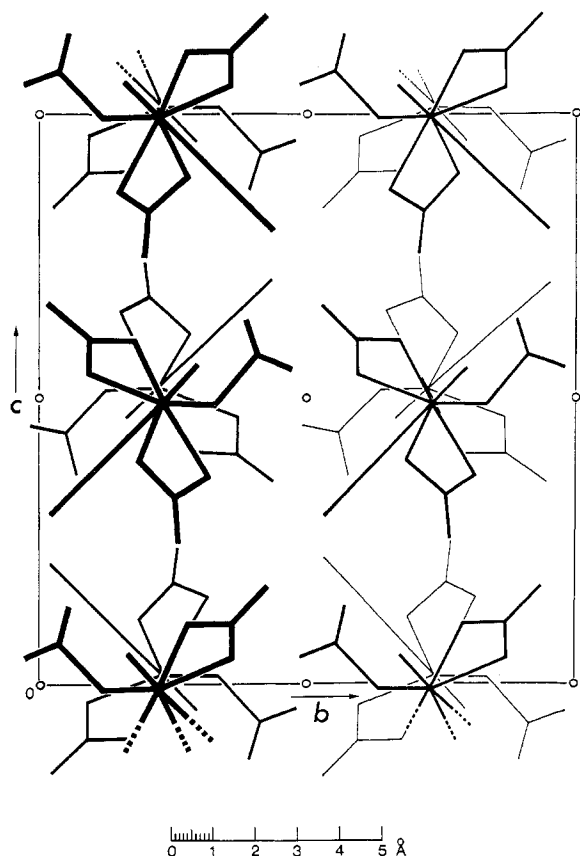


Figure 2.—The unit cell viewed down the a axis. Three different line thicknesses are used to distinguish molecules in three separate layers based on vanadium atoms separated by $\sim 0.5a$. Note the false symmetry (approximate C centering).

two equivalent bidentate nitrate groups (2.08 \AA), compared with the longer distances found either between the adjacent oxygens from the two bidentate nitrates (2.48 \AA) or between the unidentate nitrate and either bidentate nitrate (2.75 \AA), is that the pentagon of oxygens is not regular. However, the two bidentate nitrate groups are clearly seen to be symmetrically placed with respect to the oxygen of the unidentate nitrate group. This symmetry is reflected in the dimensions of the two equivalent nitrate groups also. Atoms O(3) and O(7) form V–O bonds which are on the average 0.03 \AA longer and N–O bonds which are on the average 0.02 \AA shorter than those involving atoms O(4) and O(8). While the

actual differences are of questionable significance, the trend is exactly the expected one. The very short terminal N–O bond length (1.18 \AA) is a familiar feature of bidentate nitrate groups^{3–4} and is responsible² for characteristic properties of the infrared and Raman spectra reported below.

The vanadium atom is not coplanar with the surrounding oxygen pentagon but is displaced 0.27 \AA toward the vanadyl oxygen O(14). Distortions of this type are commonly found in oxovanadium(V)⁹ and oxovanadium(IV) complexes¹⁰ and are attributed to vanadium–oxygen π bonding. This conclusion is supported by the short oxygen–vanadium bond length. It is difficult, because of varying uncertainties among the different structural determinations, to draw any definite bond length correlations, but it does seem, as expected, that the vanadyl oxygen may be more tightly bound in this vanadium(V) compound [$\text{V}=\text{O} = 1.55 (2) \text{ \AA}$] than in some vanadium(IV) compounds¹⁰ [e.g., $\text{VO}(\text{acen})$, $1.585 (7)$; $\text{VO}(\text{acac})_2$, $1.571 (10)$; $\text{VO}(\text{bzac})_2$, $1.612 (10) \text{ \AA}$]. Estimated oxygen–vanadium bond lengths in some other vanadium(V) compounds (with, unfortunately, rather large standard errors) are $1.51 (5)$ and $1.58 (4) \text{ \AA}$ in $\text{VO}(\text{OCH}_3)_3$ ⁹ and $1.56 (4) \text{ \AA}$ in VOCl_3 .¹¹

The dimensions of the coordinated acetonitrile group agree with the results of other recent studies in which no significant differences from those of acetonitrile itself were found.^{12–14} The reorganization of the acetonitrile group brought about by coordination to the vanadium atom is therefore not detectable in bond length changes within the accuracy of this determination.¹⁵ The acetonitrile is coordinated to the vanadium atom by means of a somewhat long V–N bond ($2.24 (3) \text{ \AA}$). This may be compared with values of 1.96 and 1.97 \AA reported by Willett and Rundle¹⁶ for copper(II) complexes $\text{Cu}_2\text{Cl}_4(\text{CH}_3\text{CN})_2$ and $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$ and $1.93 (6)$ and $1.91 (5) \text{ \AA}$ reported by Duffin¹⁷ for $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{CN}$. Furthermore, it is almost as long as the Re–N bond in the ion $\text{ReOBr}_4(\text{CH}_3\text{CN})^-$ which has a value¹⁴ of $2.31 (6) \text{ \AA}$. In the latter compound the acetonitrile was considered to be only weakly attached and must be judged similarly in the present compound, especially after differences in the covalent radii of vanadium and rhenium are taken into account.

The shortest intermolecular contact is between the nitrile carbon atom (C(16)) and the vanadyl oxygen atom (O(14)), consistent with the expected direction of greatest polarity in the molecule.

Although the molecular structures of many complexes

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involving bidentate,^{8,4,18,19} bridging,^{17,18} and unidentate^{18,20,21} coordination of the nitrate group are now known, this is, to our knowledge, the first instance in which a complex has been established definitely to contain both unidentate and bidentate nitrate groups. It provides a unique opportunity for a comparison of the structural features of the two types of coordination. We observe that the unidentate group is bonded to vanadium by a distinctly shorter (at least 0.1 Å), and presumably stronger, bond than either bidentate group. The N-O(11) bond, which is expected to be long, is, nevertheless, surprisingly so (1.45 (3) Å) compared with 1.34 (4) Å in Au(NO₃)₄⁻²⁰ and 1.32 (1) Å in Pd(NO₃)₂·2(CH₃)₂SO.²¹ A further feature is the possibly significant difference in the N-O(12) and N-O(13) bond lengths. A similar inequality observed²⁰ in the case of the ion Au(NO₃)₄⁻ was interpreted in terms of a weak interaction with the metal atom: the apparently longer N-O bond length involved the uncoordinated oxygen atom having the shortest Au---O contact (2.87 Å). In the present structure we find the opposite to be the case: the nonbonded contacts are V---O(12), 3.12 Å, and V---O(13), 3.98 Å, whereas the corresponding N-O lengths are N-O(12), 1.19 (3) Å, and N-O(13), 1.24 (3) Å; these N-O values are likely to represent significant differences in view of the correlation with the angles about N(10). This result, coupled with the belief that the vanadium-oxygen distances are too large to be responsible for measurable differences within the nitrate group, leads us to the conclusion that the effect is a simple and direct result of the mode of coordination of the single oxygen atom to the metal in the present case and probably in the case of Au(NO₃)₄⁻ also. It is quite feasible that the inequivalence of the two "uncoordinated" N-O bonds is merely a manifestation of the lack of any symmetry element equating the oxygen atoms in the MONO₂ group; in other words, the electrical asymmetry introduced into the nitrate group as a result of the nonlinear M-O-N bond may be transmitted also to the uncoordinated N-O bonds.

Finally, we turn to a discussion of the coordination number of vanadium in this complex. As far as the number of bonded nearest-neighbor atoms is concerned the complex is seven-coordinate and may be viewed then not so much as an addition compound of VO(NO₃)₃ but rather as a derivative from seven-coordinate VO(NO₃)₃ by severing the V-O bond to one bidentate nitrate group and replacing that coordination site by an acetonitrile, thereby retaining the overall seven-coordination with some probable rearrangement of the coordination sphere. An alternative view is that VO(NO₃)₃ is a formally pseudotetrahedral four-coordinate molecule, each bidentate nitrate group bonding with one coordination site (or vacant sd³ hybrid) by means of a three-center bond. The acetonitrile complex may then be viewed as

an addition compound in which the coordination number has been increased to 5. On this basis a description of the molecule could be that of a distorted trigonal bipyramid with nitrate groups occupying equatorial positions with apical oxygen and acetonitrile. Possibly, then, bidentate bonding of all three equatorial nitrate groups cannot occur because of steric crowding. If this description is adopted, then the angles about vanadium defined by O(11), N(2), and N(6) should approximate to 120°. The values are: N(2)-N(6), 136°; N(2)-O(11), 109°; N(6)-O(11), 112°.

A closely analogous structure occurs in the ion W₂O₁₁·2H₂O²⁻. The tungsten atoms are in a pentagonal-bipyramidal environment in which the pentagonal plane is made up of two peroxo groups and an oxygen bridge, with the neutral atom displaced out of the plane toward an apical oxo group. A water molecule is weakly bonded in the apical seventh position.²² In this example, also, similar arguments as to whether each peroxo group occupies one or two coordination positions can be made.

Infrared and Raman Spectra

An analysis of the vibrational spectra of this complex is potentially rewarding in several ways. First, there is the possibility of identifying differences in the spectra of the two types of nitrate ligand and, incidentally, providing added support for the proposed structure of the parent nitrate by a comparison of the spectra. Second, there is the opportunity for making an assignment of the metal-nitrogen stretching frequency in acetonitrile complexes.

Spectrum of Solid VO(NO₃)₃·CH₃CN.—Infrared and Raman spectra of the solid complex are included in Table V. Spectra for the adduct (Figure 3) reproduce many of the features of the spectrum of VO(NO₃)₃, for which all NO₃ groups are bidentate. Many bands exhibit small, if any, differences in band position and these are therefore assigned to vibrations associated with the bidentate nitrate groups in the complex. In addition, however, extra bands are present, and we now attempt to clarify those which arise from vibrations of unidentate nitrate, coordinated acetonitrile, or metal-ligand bonds. The principal bands observed in the Raman spectra of isotopically substituted CH₃CN are listed in Table VI.

Apart from the band at 1365 cm⁻¹ which is clearly assigned to ν₃ for coordinated acetonitrile (see below), the region 1100–1700 cm⁻¹ contains only bands associated with the coordinated nitrate groups. As a result of the expected difference in the intensities, positions, and Raman polarization properties² of the bands arising from the unidentate and bidentate nitrate groups, we assign the bands at about 1566 and 1260 cm⁻¹, respectively, to ν_{as}(NO*₂) and ν_s(NO*₂) of the unidentate nitrate group and the remaining bands at 1215–1230 and 1602–1637 cm⁻¹, respectively, as ν_{as}(NO₂) and ν_s

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TABLE V
 INFRARED AND RAMAN SPECTRA OF $\text{VO}(\text{NO}_3)_3\text{CH}_3\text{CN}$ AND RELATED COMPOUNDS

$\text{VO}(\text{NO}_3)_3\text{-CH}_3\text{C}^{14}\text{N}$ Raman ^g	$\text{VO}(\text{NO}_3)_3\text{-CD}_3\text{C}^{14}\text{N}$ Raman ^g	$\text{VO}(\text{NO}_3)_3\text{CH}_3\text{C}^{14}\text{N}$			$\text{VO}(\text{NO}_3)_3$ ^d		Assignment
		Raman ^a	Raman ^b	Ir ^c	Raman ^e	Ir ^f	
118 m	118 m	119 m	~120 sh		76 vb, d ⁱ		Metal-ligand def
171 m	171 m	171 m			157 m, d		
203 m	199 m	203 m					$\nu(\text{VO}_2)$ or $\delta(\text{VO}_2)$ bidentate NO_3
235 m	234 m	235 m	237 m, p		236 m, p		
265 vs	266 vs	265 vs	269 vs, p				$\nu(\text{VO})$ unidentate NO_3
		287 w			285 m, d		$\nu_s(\text{VO}_2)$ bidentate NO_3
299 m	300 m	300 m	290 m, p		303 m, p		
			313 m, p				$\nu_8(\text{CCN})$ bend) or $\nu(\text{V-N})$
351 vs	351 vs	351 vs	354 vs, p	355 m	358 s, p	379 m	
402 m	374 m	407 m	404 m, p				$\nu_{as}(\text{VO}_2)$ bidentate NO_3
436 s	436 s	436 s	446 s, d	446 s	455 m, d	452 s	$\delta(\text{ONO}^*)$ bidentate NO_3
677 w	678 w	677 w	675 sh	677 vw		682 w	
689 w	689 w	689 w	693 w, p	689 vw	687 w, p	690 w	$\delta_s(\text{NO}^*_2)$ unidentate NO_3
745 m	746 m	745 m	753 m, p	753 sh, m			
				775 s	777 w	775 s, b	VO_2N ring def, bidentate NO_3
782 s	782 m	782 s	788 s, p	785 s	787 m, p		
888 m	887 m	888 m	890 m, d	901 m			$\nu_4(\text{C-C str})$
				916 sh			
936 w	851 m	945 w	942 m, p	945 vw, sh			$\nu_8(\text{NO}_2)$ bidentate NO_3^+
				968 m	965 w, d	962 s	$\nu_8(\text{NO})$ unidentate NO_3^+
				997 s		995 s	
1009 vs	1009 vs	1010 vs	1013 s, p	1010 s	1007 w, d	1007 m	$\nu(\text{V=O})$
					1015 m, p	1014 s	
				1035 w			$\nu_{as}(\text{NO}_2)$ bidentate NO_3
1215 m	1215 m	1215 m	1217 m, d	1213 vs, b	1191 m, d	1196 m, sh	
					1210 m, d	1209 m	$\nu_s(\text{NO}^*_2)$ unidentate NO_3
1230 w	1231 w	1230 w	1232 w, d			1216 s	
1259 s	1260 s	1260 s	1270 s, p	1270 s			$\nu_8(\text{CH}_3 \text{ sym bend})$
				1308 m		1305 w	
1364 m	[1100 ^h]	1365 m		1373 w			$\nu_7 + \nu_8$
				1410 w			
				1443 w			$\nu_8(\text{CH}_3 \text{ antisym bend})$
						1550 w	
1564 m	1564 m	1566 m	1584 m, d	1568 s			$\nu_{as}(\text{NO}^*_2)$ unidentate NO_3
1601 m	1601 m	1602 m		(1600-1650) vs, b			
1624 s	1624 s	1625 s			1612 w, d	1615 vs	$\nu(\text{NO}^*)$ bidentate NO_3
1637 m, sh	1637 m, sh	1637 m, sh	1638 s, b, p		1660 m, p	1635 vs	
				1885 w			$\nu_2(\text{C-N str})$
2266 m	2304 m	2289 m	2292 m, p	2294 w			
2302 w		2316 m	2314 m, p	2309 w			$\nu_3 + \nu_4$
				2640 vw			
				2720 vw			$\nu_1(\text{CH}_3 \text{ or } \text{CD}_3 \text{ sym str})$
2903 m ^o	2902 m ^o						
2950 m	2117 m	2948 m		2950 w			$\nu_5(\text{CH}_3 \text{ antisym str})$
				3010 w			

^a Solid at room temperature. ^b Solution in CH_3CN ; bands due to solvent are not included. ^c Solid sublimed film at 100°K . ^d Values from ref 2. ^e Pure liquid at room temperature; p = polarized, d = depolarized. ^f Solution in CCl_4 or pure liquid at room temperature. ^g This sharp, medium band at 2902 cm^{-1} is presumably due to impurity, or grating ghost, as the band was absent in the starting $\text{CH}_3\text{C}^{15}\text{N}$ and $\text{CD}_3\text{C}^{14}\text{N}$. ^h Expected position; band unobserved in our spectrum. ⁱ Seen resolved at 85 cm^{-1} in our spectrum.

(N-O*) of the bidentate nitrate group.²³ Thus, the 1260-cm^{-1} band is quite strong and polarized in a region where the $\nu_{as}(\text{NO}_2)$ gives depolarized and rather less intense bands. The depolarized 1566-cm^{-1} band is far too strong to be identified with the ($2 \times 782 \text{ cm}^{-1}$) overtone. Such an overtone appears of medium strength

(23) In order to simplify the description of the normal modes the uncoordinated oxygen atoms in the unidentate and bidentate nitrate groups are signified by an asterisk.

in the infrared spectra of $\text{VO}(\text{NO}_3)_3$, $\text{Ti}(\text{NO}_3)_4$, and $\text{Sn}(\text{NO}_3)_4$ in this region² but is invariably absent from the Raman spectra.

In the region $900\text{--}1100 \text{ cm}^{-1}$ we expect to observe bands due to $\nu_4(\text{CH}_3\text{CN})$, $\nu_8(\text{N-O})$, and $\nu_8(\text{NO}_2)$ for the coordinated oxygen atoms of the unidentate and bidentate nitrate groups and $\nu(\text{V=O})$ of the vanadyl group. The band at 945 cm^{-1} is identified as ν_4 of co-

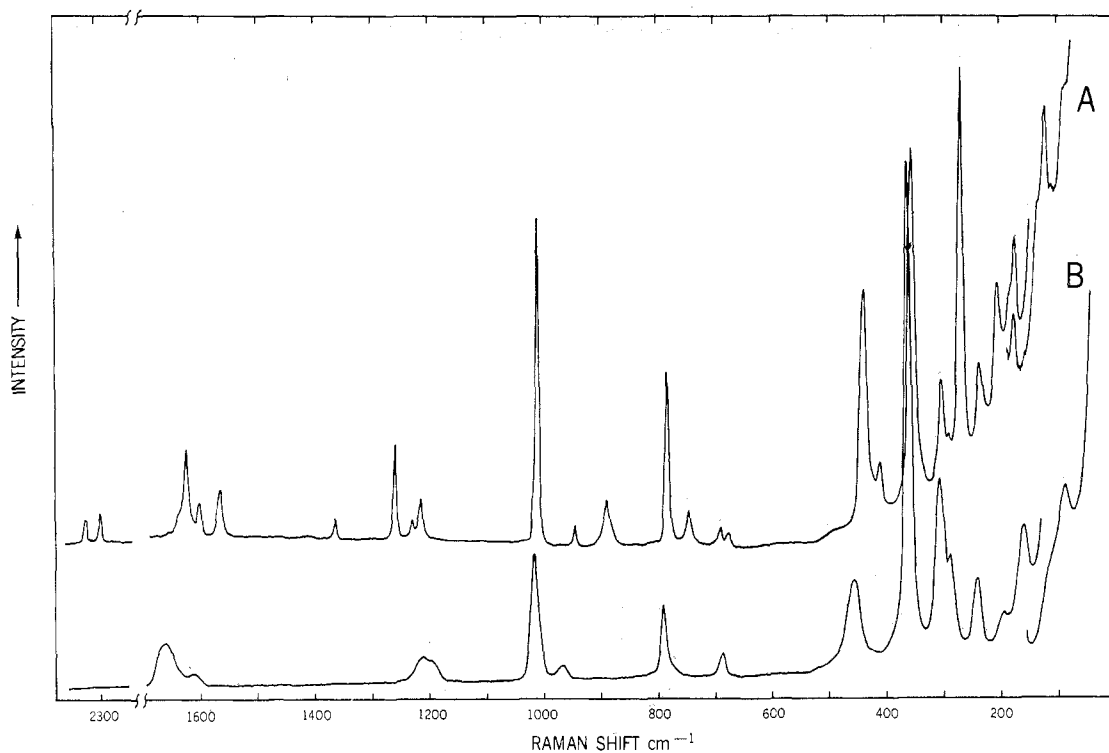


Figure 3.—Raman spectra for $\text{VO}(\text{NO}_3)_3\text{CH}_3\text{C}^{14}\text{N}$ (trace A, sublimed crystals) and $\text{VO}(\text{NO}_3)_3$ (trace B, pure liquid).

TABLE VI
PRINCIPAL BANDS IN THE RAMAN SPECTRA
OF $\text{CH}_3\text{C}^{14}\text{N}$, $\text{CD}_3\text{C}^{14}\text{N}$, AND $\text{CH}_3\text{C}^{15}\text{N}$

$\text{CH}_3\text{C}^{14}\text{N}$	$\text{CH}_3\text{C}^{15}\text{N}$	$\text{CD}_3\text{C}^{14}\text{N}$	Assignment
379 vs, d	378 vs	349 s	$\nu_8(\text{C}-\text{C}-\text{N}$ bend)
749 w, d	745 w	698 w	$2\nu_8$
918 vs, p	911 vs	833 s	$\nu_4(\text{C}-\text{C}$ str)
1375 m, p	1374 m	1103 w	$\nu_3(\text{CH}_3$ sym bend)
~1420 w	~1410 w		$\nu_7 + \nu_8$
1443 m, d	1445 w	1043 w	$\nu_6(\text{CH}_3$ antisym bend)
2252 vs, p	2227 vs	2262 s	$\nu_2(\text{C}-\text{N}$ str)
2291 m, p	2286 w		$\nu_3 + \nu_4$
2732 w, p		2214 w	$2\nu_8$
2885 w, d		2060 w	$2\nu_8$
2944 s, p	2945 s	2117 vs	$\nu_1(\text{CH}_3$ sym str)
3002 w, d		~2250 w, sh	$\nu_6(\text{CH}_3$ antisym str)

ordinated CH_3CN by isotopic substitution (see below). The only other Raman band is the intense 1010-cm^{-1} band. This is surprising in view of the several symmetric modes expected in this region. Extensive intramolecular coupling of these modes undoubtedly complicates this problem but we would have expected several of the resulting modes to be Raman active in view of the low molecular symmetry. Consequently, as in the example of $\text{VO}(\text{NO}_3)_3$,² it has not been possible to give detailed assignments. However we point out some observations. The ir bands at 968 and 997 cm^{-1} have close counterparts in the ir spectrum of $\text{VO}(\text{NO}_3)_3$, so that these bands probably do not arise from the unidentate nitrate group. We have been unsuccessful in attempts to separate the 1010-cm^{-1} Raman band into components under high resolution. This band is probably due mainly to $\nu(\text{V}=\text{O})$ but may be accidentally degenerate with one or more nitrate modes.

The bands at about 677 and 689 cm^{-1} in the nitrate

bending region are likely (by comparison with $\text{VO}(\text{NO}_3)_3$) to be associated with the bidentate nitrate groups, and we assign the new band at about 745 cm^{-1} to the symmetric deformation mode of the unidentate group. The depolarized band at 890 cm^{-1} may be due to the corresponding antisymmetric NO_2^* bend, but if this is the case, it represents an unusually high value and an exceptionally large separation of the symmetric and antisymmetric modes.

The vibrations of coordinated acetonitrile have been determined by comparison with those of the free ligand and by ^{15}N and ^2H substitution. Generally, the fundamental modes of CH_3CN are observed in the complex also. There is, however, some doubt about the assignment of the $\text{C}-\text{C}-\text{N}$ deformation (ν_8). This occurs at 379 cm^{-1} in CH_3CN and is expected to occur just below 400 cm^{-1} in the CH_3CN complex by comparison with other examples.^{18,24} This suggests that the band we observe at 407 cm^{-1} should be assigned to ν_8 . While this may be the case and in agreement the band exhibits the expected shift of about 30 cm^{-1} in the deuterated complex, there is some evidence to indicate that this assignment may not be correct but that the band is instead due to $\nu(\text{V}-\text{N})$. Thus, whereas the position of ν_8 in pure acetonitrile was found to be insensitive to ^{15}N substitution, the Raman band at 407 cm^{-1} in the complex shifted to 402 cm^{-1} upon ^{15}N substitution. This is the expected order of shift for $\nu(\text{V}-\text{N})$ based upon a simple mass calculation. In addition, the band is polarized in the solution spectrum as expected for $\nu(\text{V}-\text{N})$ but not ν_8 . Other CH_3CN bands exhibit expected isotopic shifts. The $\text{C}\equiv\text{N}$ stretch of acetonitrile (ν_2 ,

(24) C. C. Addison, D. W. Amos, and D. Sutton, *J. Chem. Soc. A*, 2285 (1968); M. Farona and J. G. Grasselli, *Inorg. Chem.*, 6, 1675 (1967).

2252 cm^{-1}) is shifted to higher frequency by some 37 cm^{-1} in the complex (39 cm^{-1} from 2227 to 2266 cm^{-1} , in the case of $\text{CH}_3\text{C}^{15}\text{N}$). The C—C stretch (ν_4) shifts from 918 to 945 cm^{-1} in the complex and, in the case of $\text{CH}_3\text{C}^{15}\text{N}$, from 911 to 936 cm^{-1} in the complex. The nitrogen mass dependence of ν_4 incidentally provides added support for the assignment of the combination band ($\nu_4 + \nu_3$) in the 2290- cm^{-1} region of acetonitrile itself,²⁴ since ν_3 remains stationary upon ^{15}N substitution and the shift in the ν_4 fundamental is reproduced almost exactly in the shift of the combination band. This is reflected again in the complexes where there is a shift of about 9 cm^{-1} in "coordinated ν_4 " from 945 (^{14}N) to 936 cm^{-1} (^{15}N) and a similar shift of the combination band from 2316 (^{14}N) to 2302 cm^{-1} (^{15}N). Different proximities of the overtone and ν_2 and hence changes in the degree of Fermi resonance between these modes will contribute to the small differences observed in these relative shifts.

A large number of bands occur below 500 cm^{-1} which might be attributable to V—O and V—N stretching modes or deformations. By analogy with $\text{VO}(\text{NO}_3)_3$, the bands at 436, 351, 300, 235, and 156 cm^{-1} are assigned to vibrations of the metal-bidentate nitrate linkage. Bands at 407, 265, 203, 171, and 119 cm^{-1} , therefore, remain to be assigned to metal-unidentate nitrate or metal-nitrogen modes. Careful examination of this region using the ^{15}N -substituted complex revealed that only one band exhibited a shift in excess of 1 cm^{-1} ; the band at 407 cm^{-1} (^{14}N) shifted to 402 cm^{-1} (^{15}N), and as mentioned earlier, this band is therefore assigned as the V—NCCH₃ stretch. Although the infrared and Raman spectra of a number of nitrile complexes have been reported, frequently it has not been possible to identify bands due to M—N stretching modes;²⁵ in other instances assignments of $\nu(\text{M—N})$ have been disputed.^{26,27} Reported values for $\nu(\text{M—N})$ vary over an unusually wide range, from 174 cm^{-1} claimed²⁸ for $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$ to as high as 490–552 cm^{-1} for $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$).²⁹ A recent study¹³ of *cis*- $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$ places $\nu(\text{Sn—N})$ at 219 and 206 cm^{-1} . Difficulty is sometimes experienced in observing the Raman spectra of single bonds adjacent to triple bonds,^{30,31} and indeed the intensity of the 407- cm^{-1} band is rather low for a symmetrical mode and it is absent from the infrared spectrum. While we do not believe our assignment of $\nu(\text{V—N})$ to be beyond dispute,

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we can find no evidence for assigning any other low-energy band in our spectra to this mode. However, the value does seem to be high in view of the length of the V—N bond. Finally, we tentatively assign the band at 265 cm^{-1} to the V—O stretch of the unidentate nitrate group and the bands at 203, 171, and 119 cm^{-1} to various metal-nitrate deformation modes. A more complete assignment of this region is hindered by the unavailability of sufficiently low-frequency infrared spectra.

Spectra of $\text{VO}(\text{NO}_3)_3 \cdot \text{CH}_3\text{CN}$ in Solution.—Exact comparison of solution spectra is made difficult by some conflicting sampling problems. Solutions in acetonitrile gave excellent Raman spectra; however, infrared spectra could not be obtained with these solutions due to reaction with the silver chloride cell as explained earlier. Conversely, solutions in CCl_4 or hexachlorobutadiene did not react with silver chloride so that ir spectra were obtained, but in these cases solutions could not be made sufficiently concentrated for Raman spectroscopy. Ir spectra on mulls in Fluolube and hexachlorobutadiene were closely similar to that of the complex at 100°K, but hexachlorobutadiene mulls (in which the complex is somewhat soluble) indicated some dissociation by the appearance of very weak absorption in the "free ν_2 " region for CH_3CN ($\sim 2250 \text{ cm}^{-1}$). Actual solutions in CCl_4 and hexachlorobutadiene, obtained by gently warming the complex without visible signs of decomposition, confirmed that partial dissociation does occur in the solutions; there was now near equality in the intensities of bands due to free and coordinated CH_3CN and changes in the relative intensities of bands due to unidentate and bidentate nitrate groups.

Raman spectra for acetonitrile solutions were studied in detail in order to distinguish the bands due to the complex from those of the solvent, and depolarization ratios were determined so as to assist in the assignments of the bands. The presence of excess ligand presumably prevents dissociation of the complex, but it is not clear whether or not additional solvent molecules do become coordinated. However, the basic features of the spectrum are closely similar to those of the solid complex apart from some slight shifts in band position and leave little doubt that the configuration of the nitrate ligands—two bidentate and one unidentate—remains unchanged.

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