bonylferrocene-1,1'-bis(dimethylarsine)nickel(II),[7] 5° in diferrocenyl ketone[21] and dichlorodiferrocenyl,[22] 4° in diethyldiferrocenyl,[23] and the fully eclipsed configuration in 1,1',3,3'-bis(trimethylene)ferrocene[24] and the ferrocenium ion.[6] Figure 4 illustrates the packing of the molecule in the unit cell.

In conclusion it should be reemphasized that the initial intensity data collected by standard moving-film techniques and refined to an R value of 0.166 led to the consideration of inherent disorder and large extinction effects as properties of 1,2-bis(ferrocenyl)ethane and such possible properties have been reported for other related ferrocene compounds.[13,15,19,25] The intensity data obtained during this study through the use of the automated diffractometer clearly exclude these phenomena as properties of this compound. Instead, those errors inherent to visually obtained intensity data resulted in the initial inability to assign accurately and refine the structure 1,2-bis(ferrocenyl)ethane. Furthermore, this study and the other recent[6,7] X-ray studies involving ferrocene derivatives are indicative that low standard errors may be obtainable for ferrocene compounds when modern automated intensity data collection techniques are employed.

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Registry No. 1,2-Bis(ferrocenyl)ethane, 12156-05-7.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-101.

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Crystal and Molecular Structure of Potassium Heptacyanovanadate(III) Dihydrate

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The structure of potassium heptacyanovanadate(III) dihydrate, $K_4[V(CN)_7]\cdot 2H_2O$, consists of discrete pentagonal-bipyramidal $V(CN)_7{}^{4-}$ anions. The molecular structure was determined by a single-crystal X-ray crystallographic study using Mo Kα radiation. The space group was chosen as $I1$ with lattice constants $a = 9.229$ (1), $b = 9.097$ (1), $c = 9.341$ (1) Å; $\alpha = 90.02$ (1), $\beta = 92.49$ (1), $\gamma = 90.00$ (1)°. The observed and calculated densities are 1.77 ± 0.02 and 1.80 g cm^{-3}, respectively, for $Z = 2$. A total of 824 independent nonzero reflections were collected by the stationary-crystal, stationary-counter method with a General Electric XRD-7 manual diffractometer equipped with balanced zirconium-yttrium filters ($\sin \theta_{\max} = 0.38$). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the final atom (conventional) R value being 2.5%. The central vanadium(III) atom is coordinated to seven cyanide anions in a linear fashion to produce a structure of approximate D_{5h} symmetry. The averaged V–C distance is 2.15 (1) Å, there being no significant difference between equatorial and axial V–C distances. The two axial cyanides give rise to C_{ax}–V–C_{ax} = 171.0°. The average C_{eq}–V–C_{eq} = 72.0 (6)°. The standard deviation of the distances of the vanadium and the five equatorial carbons from a least-squares plane is 0.03 Å with the greatest distance from the plane being 0.05 Å for one of the carbon atoms. A discussion of the bonding and the factors pertaining to this geometry is presented.

Introduction

There are relatively few examples of seven-coordinate complexes containing only simple monodentate ligands. Among structures proposed as being ideal for this coordination number are the pentagonal bipyramid (of symmetry D_{5h}), the monocapped trigonal prism (C_{2v}), the monocapped octahedron (C_{3v}), and the tetragonal base-trigonal base structure. Factors which may influence the geometry any given compound assumes have been discussed by Muetterties.[2] Definitive structures of seven-coordinate compounds as determined by X-ray crystallography include very few in which there are seven identical ligands. To date, the only discrete (*i.e.*, mononuclear) ML_7 (L = monodentate ligand) compounds which are known are those for which L equals fluoride. Among these are $UF_7{}^{3-}$ (D_{5h})[3a] and $NbF_7{}^{2-}$ (C_{2v}).[3b] Other seven-coordinate structures contain either more than one type of ligand (*e.g.*, $UO_2F_5{}^{3-}$ (D_{5h})[4]) or multidentate ligands (*e.g.*, $Zr(acac)_3Cl$[5] and the $[Fe^{III}(OH_2)EDTA]^-$ anion[6]). In these latter examples, because of ligand complexities, it is difficult to assess the relative merits of the several seven-coordinate geometries. In addition, MF_7 complexes reported to date have had d^0 electronic configurations, and thus no assessment of ligand-electron repulsive effects for seven-coordination has been possible.

The nature of the cyano complex of vanadium(III) has been

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the subject of several recent publications. Analytical data supporting the formulations $K_4V(CN)_7{\cdot}2H_2O$,[7,8] $K_4V(CN)_7{\cdot}H_2O$,[9] $K_4V(CN)_7$,[10] and $K_3V(CN)_6$[11] have been reported to result from various preparative procedures. $V(CN)_6{}^{3-}$ has commonly been accepted as the ion in solution.[12]

Alexander and Gray reported a material which they described as $K_3[V(CN)_6]{\cdot}3H_2O{\cdot}0.15KCN$; they subsequently interpreted the electronic spectrum in terms of an octahedral structure.[13] The infrared spectrum of solid $K_4V(CN)_7$ has been shown to be consistent with pentagonal-bipyramidal geometry.[10] It should be noted, however, that solid-state infrared spectral studies on transition metal cyanide complexes are known to give misleading results.[7] There is the additional consideration that a structure should not be inferred solely on the basis of analytical data. For example, assuming the formula $K_4V(CN)_7{\cdot}H_2O$, one cannot decide among the structural possibilities of $K_3[V(CN)_6]{\cdot}KCN{\cdot}H_2O$, $K_4[V(CN)_7]{\cdot}H_2O$, and $K_4[V(CN)_7OH_2]$ which are six-, seven-, and eight-coordinate, respectively. We report here the results of a single-crystal X-ray crystallographic study of $K_4[V(CN)_7]{\cdot}2H_2O$. Preliminary results of this investigation have been communicated elsewhere,[14] and here we present additional details of the structure and a discussion of the factors which may be operating to produce the seven-coordinate geometry found for the $V(CN)_7{}^{4-}$ anion.

Experimental Procedure

Crystals suitable for an X-ray investigation were prepared by a modification of the method of Locke and Edwards.[11,15] A deep scarlet, multifaceted crystal measuring 0.20 × 0.22 × 0.24 mm was selected and mounted in a 0.5-mm thin-walled capillary under a nitrogen atmosphere in a glove bag.

Precession photographs taken with Ni-filtered Cu Kα radiation revealed no systematic absences and indicated a monoclinic system. Upon further investigation using the diffractometer, however, small but significant differences in intensities across the apparent mirror plane were observed, and the crystal system was therefore determined to be triclinic. The body-centered space group $I\bar{1}$ was chosen for convenience. Lattice constants were determined by a least-squares fit of 77 reflections whose 2θ values were measured very carefully at fine conditions (1° takeoff angle and 0.05° receiving slit) with Cu Kα radiation. The 2θ values were sufficiently large that the Kα_1 (λ 1.5405 Å) and Kα_2 (λ 1.5443 Å) lines were resolved. The lattice constants for the body-centered cell are $a = 9.229$ (1), $b = 9.097$ (1), and $c = 9.341$ (1) Å; and $\alpha = 90.02$ (1), $\beta = 92.49$ (1), and $\gamma = 90.00$ (1)°. The calculated density of 1.80 g cm^{-3} (assuming the body-centered lattice and two $K_4V(CN)_7{\cdot}2H_2O$ formula weights per unit cell) compares favorably with the observed density of 1.77 ± 0.02 g cm^{-3} measured by flotation in a bromoform–carbon tetrachloride mixture.

The data were collected with a General Electric XRD-7 quarter-circle manual diffractometer by the stationary-crystal, stationary-counter technique using balanced zirconium–yttrium filters and Mo Kα radiation (λ 0.71069 Å). Ten-second counts using a scintillation counter were measured with each filter. Three standard reference reflections were measured at approximately 2.5-hr intervals. There was no variation over the entire data collection period greater than that expected from normal counting statistics.

Data were collected to a maximum 2θ of 45°. A previous data set using Cu Kα radiation on the same crystal had produced few measurable reflections beyond an equivalent sphere. The data were corrected for Lorentz and polarization effects by

$$(LP)^{-1} = (\sin 2\theta)/(1 + \cos^2 2\theta)$$

The linear absorption coefficient for this complex with Mo Kα radiation is 17 cm^{-1}. Measurement of axial reflections at $\chi = 90°$ and in 10° increments in ϕ showed no variations greater than those expected from normal counting statistics, agreeing with the predicted ratio calculated from the crystal size. Therefore, no absorption correction was made. A background correction for scattering by the capillary was made as a function of 2θ and was added directly to the background count from the yttrium filter. The criterion for an observed reflection was taken as

$$(I_{Zr} - 2\sigma(I_{Zr})) - (I_Y + 2\sigma(I_Y)) \geqslant 100 \text{ counts}$$

where I_{Zr} and I_Y are the measured intensities for the zirconium and yttrium filters, respectively; I_Y also includes the glass-scattering correction. With this requirement, 824 reflections (approximately 82%) were considered observable and assigned $w > 0$. $\sigma(F)$ was calculated from the expression

$$\sigma(F) = \frac{1}{2}\sqrt{(LP)^{-1}\frac{I_{Zr} + I_Y}{I_{Zr} - I_Y}}$$

Structure Determination and Refinement

The structure was solved using a previous data set taken with copper radiation because a molybdenum-target X-ray tube was not available to us at that time. The solution of the structure was accomplished by standard Patterson, Fourier, and least-squares techniques. By assuming the vanadium to be at the origin (in $I\bar{1}$), the locations of the potassium atoms were found from the three-dimensional Patterson calculation. A series of Fourier and difference Fourier syntheses interspersed with least-squares using the identified atoms led eventually to the locations of all nonhydrogen atoms.

The quantity minimized in the least-squares calculations was $\Sigma w||F_o| - |F_c||^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and the weighting factor was taken as the reciprocal of the variances $\sigma(F_o)^2$. The atomic scattering factors were those of Cromer and Waber.[16] The anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) used for K and V throughout the refinement were those of Cromer.[17]

Five cycles of block-diagonal least-squares refinement (using the copper data) of the atomic positions and individual isotropic thermal parameters for the V and four K atoms resulted in R and R_w values of 0.26 and 0.36, respectively, where

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

$$R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o{}^2}\right]^{1/2}$$

The inclusion of all other nonhydrogen atoms (seven N, seven C, and two O) lowered the R and R_w to 0.08 and 0.07, respectively, for the isotropic refinement.

By this time, the molybdenum X-ray tube had arrived and the data collection described earlier was completed. All subsequent refinement was done using the Mo data. Nine cycles of block-diagonal refinement of the atomic positions and individual isotropic thermal parameters decreased the R and R_w to 0.05 and 0.06, respectively. Anisotropic refinement of the thermal parameters of all atoms led to final R and R_w values of 0.028 and 0.022, respectively, after nine cycles. The large thermal parameters for the oxygen atoms in the waters of solvation suggested possible disordering of these atoms, but no other peaks could be located in a difference Fourier calculated from structure factors in which the oxygen contribution was omitted. It was assumed that the large vibrations of the oxygen atoms were the result of either weak binding of these waters of solvation or a disorder of the hydrogen atoms around the oxygen atoms, probably the latter. In the final cycle of least squares, no parameter shift except those for the oxygen atoms was greater than one-tenth its estimated standard deviation. Five cycles of least-squares refinement using unit weights yielded R and R_w values of 0.025 and 0.028. No significant differences between either positional or thermal parameters were observed

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on comparison of the results of unit weight and $(1/\sigma^2)$-weighted refinement. The standard deviation of unit weight is 0.776. The positional and anistropic thermal parameters taken from the last cycle of least-squares $(1/\sigma^2)$ are presented in Tables I and II, respectively, along with the associated standard deviations estimated from the inverse matrix. The principal atomic distances and angles for the anion are presented in Table III. The final values of $10F_o$ and $10F_c$ are presented in Table IV for the 824 reflections used in the refinement.[18,19]

Description of the Structure

As can be seen from the ORTEP drawing of the complex anion in Figure 1, the cyanides are arranged in a pentagonal-bipyramidal fashion about the vanadium atom. Slight distortions from perfect D_{5h} symmetry were observed, these being most evident in the bond angles involving the axial ligands. Two major points of interest in the structural investigation (once the geometric arrangement of the ligands was determined) were the relative lengths of the axial and equatorial metal-ligand bonds and the length of the vanadium(III)-carbon linkage. The individual V-C distances are listed in Table III. The V-C_{eq} bond distances average 2.149 ± 0.006 Å,[20] and the V-C_{ax} bond distances average 2.144 ± 0.012 Å, thereby indicating no significant difference between the two types of bonds. The distance for the V-C bond is quite long for a first-row transition metal cyanide complex. It is longer than the Cr^{IV}-C bonds found in the seven-coordinate $[Cr(O_2)_2(CN)_3]^{3-}$ anion (2.09 Å),[21] but a V^{III}-C bond is expected to be longer than a Cr^{IV}-C bond. The C-N bonds average 1.145 ± 0.005 Å, a value consistent with other structural results;[22] the estimated standard deviations for these bond lengths vary from 0.010 to 0.012 Å.

One interesting facet of the structure is the angle C_{ax}-V-C_{ax} (171.0°) which differs significantly from 180°. This bending effect is apparently caused by the interaction of the ligands with the cations surrounding the complex. The closest K-N_{ax} distances are 2.84 Å for K2-N7 and 2.83 Å for K3-N6 (see Figure 2). These will have the effect of bending the axial ligands in the observed directions (toward C3 and C4). The next closest K-N_{ax} distances are 3.16 Å for K2-N6 and 3.17 Å for K3-N7. The C6-V-C7 angle is very nearly bisected by the least-squares plane containing the vanadium and five equatorial carbons; this plane has a standard deviation of 0.031 Å. Those equatorial nitrogens with the closest cation contact distances are farthest from the least-squares plane, *viz.*, K2-N3 at 2.79 Å (0.08 Å from the plane), K3-N4 at 2.78 Å (0.10 Å from the plane) and K3-N5 at 2.87 Å (0.06 Å from the plane) and K3-N5 at 2.87 Å (0.06 Å from the plane). Other least-squares plane data are included in Table V.

Table I. Atomic Fractional Coordinates[a]

Atom	x	y	z
V	0.0	0.0	0.0
K1	0.2544 (2)	0.4042 (3)	0.0900 (2)
K2	−0.1309 (2)	−0.4189 (2)	0.2790 (2)
K3	0.1263 (2)	−0.4190 (2)	−0.2788 (2)
K4	−0.2595 (2)	0.4043 (3)	−0.0898 (2)
C1	0.0000 (13)	−0.2345 (8)	−0.0003 (9)
N1	−0.0004 (16)	−0.3614 (10)	0.0004 (11)
C2	−0.0575 (8)	−0.0713 (7)	0.2100 (8)
N2	−0.0857 (8)	−0.1088 (7)	0.3216 (7)
C3	−0.0414 (9)	0.1931 (7)	0.1249 (8)
N3	−0.0639 (10)	0.2973 (8)	0.1886 (8)
C4	0.0399 (9)	0.1933 (8)	−0.1250 (9)
N4	0.0636 (10)	0.2980 (8)	−0.1880 (8)
C5	0.0555 (8)	−0.0707 (8)	−0.2103 (8)
N5	0.0842 (8)	−0.1096 (7)	−0.3212 (7)
C6	0.2212 (9)	0.0186 (8)	0.0727 (8)
N6	0.3377 (8)	0.0454 (10)	0.1123 (9)
C7	−0.2233 (8)	0.0185 (8)	−0.0753 (8)
N7	−0.3406 (8)	0.0439 (10)	−0.1129 (9)
O1	−0.3493 (18)	−0.3220 (12)	0.0010 (13)
O2	0.3500 (18)	−0.3225 (12)	−0.0022 (13)

[a] Estimated standard deviations ×10⁴ in parentheses.

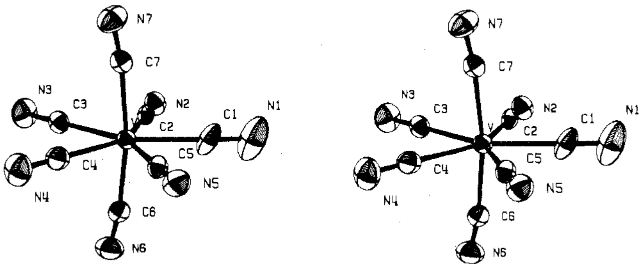

Figure 1. Stereodrawing of the $V(CN)_7{}^{4-}$ anion.

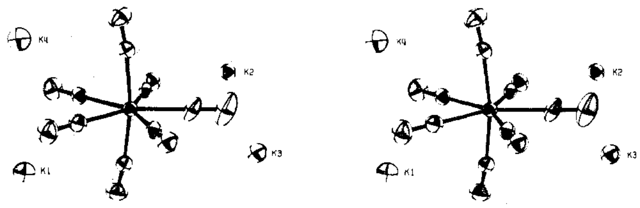

Figure 2. Stereodrawing of $V(CN)_7{}^{4-}$ showing the arrangement of the K^+ ions. The orientation of the anion is the same as in Figure 1.

The C_{eq}-V-C_{eq} angle for adjacent ligands in the equatorial plane average 72.0 ± 0.6°. The V-C_{eq}-N_{eq} angles are close to 180° as expected, averaging 178.8 ± 0.5°, which is not a significant bending effect. The V-C_{ax}-N_{ax} angles, on the other hand, average 172.5 ± 0.3°, a value significantly different from linearity and also indicative of the ligand-cation interaction. The equatorial ligands most distant from the least-squares plane also exhibit the smallest V-C_{eq}-N_{eq} angles. This may also be attributed to the ligand-cation interaction described earlier.

The potassium atoms pack in an approximate tetrahedral arrangement around the complex anion (see Figure 2). Of the four nearest potassium atoms, two are 4.15 Å from the vanadium atom and the other two are 4.44 Å from the vanadium atom. The two waters of hydration bind loosely (as indicated from their temperature factors) in the vacancies around the complex and the cations. The closest distances involving oxygen atoms are 2.77 Å (O1-K4) and 2.79 Å (O2-K1). There is also an apparent disordering of the hydrogen atoms surrounding the oxygens, as evidenced by our inability to locate the hydrogens. The other intermolecular distances observed are normal.

Discussion

The most interesting aspect of the structure of the $V(CN)_7{}^{4-}$ ion is its coordination number. That is, why should the cyano complex of V(III) be seven- and not six- or eight-coordinate? Indeed, six-coordination had long been assumed,[13] although seven-coordination had also been suspected.[7,10] However, the other known d^2 cyanide complex ions, *i.e.*,

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(18) See paragraph at end of paper regarding supplementary material.

(19) In addition to local programs for the IBM-360(65) computer, the following programs or modifications were used: Sparks and Trueblood's BDLS, a block-diagonal least-squares program; Fritchie's FOUR, a Fourier synthesis program; Davis' INCON, a data reduction program; Johnson's ORTEP, the thermal ellipsoid plotting program; Trueblood's LSLAT for calculating least-squared lattice constants; and Harris' PLANE, a program for calculating least-squares planes.

(20) Estimated standard deviations for any parameter are shown in parentheses, while average deviations are given as "±."

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Table II. Anisotropic Thermal Parameters[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	0.0065 (1)	0.0058 (1)	0.0060 (1)	0.0000 (2)	0.0004 (2)	0.0000 (2)
K1	0.0128 (3)	0.0166 (3)	0.0097 (3)	−0.0001 (5)	0.0010 (5)	−0.0012 (5)
K2	0.0092 (2)	0.0074 (2)	0.0096 (2)	−0.0001 (4)	0.0014 (4)	−0.0004 (4)
K3	0.0089 (2)	0.0076 (2)	0.0093 (2)	0.0004 (4)	0.0014 (4)	0.0007 (3)
K4	0.0129 (3)	0.0165 (3)	0.0095 (3)	0.0006 (5)	0.0007 (4)	0.0021 (5)
C1	0.0299 (22)	0.0052 (11)	0.0075 (12)	0.0004 (25)	0.0064 (26)	0.0004 (19)
N1	0.0551 (32)	0.0110 (12)	0.0129 (13)	−0.0004 (33)	0.0117 (34)	0.0009 (21)
C2	0.0073 (10)	0.0049 (9)	0.0063 (9)	0.0016 (16)	−0.0012 (15)	0.0000 (15)
N2	0.0144 (12)	0.0064 (9)	0.0098 (10)	−0.0001 (16)	0.0014 (17)	−0.0002 (14)
C3	0.0096 (11)	0.0043 (10)	0.0085 (11)	−0.0005 (17)	−0.0001 (18)	0.0008 (15)
N3	0.0197 (14)	0.0079 (10)	0.0139 (12)	0.0011 (18)	0.0019 (23)	−0.0037 (19)
C4	0.0081 (11)	0.0060 (10)	0.0096 (11)	0.0008 (17)	0.0004 (18)	−0.0002 (16)
N4	0.0184 (13)	0.0087 (10)	0.0131 (12)	−0.0011 (18)	0.0036 (22)	0.0023 (18)
C5	0.0076 (10)	0.0054 (9)	0.0065 (9)	−0.0004 (16)	−0.0004 (16)	−0.0001 (15)
N5	0.0126 (11)	0.0084 (9)	0.0091 (9)	0.0013 (16)	0.0012 (16)	0.0008 (15)
C6	0.0090 (11)	0.0084 (11)	0.0069 (10)	0.0004 (18)	0.0014 (17)	0.0002 (16)
N6	0.0088 (11)	0.0177 (12)	0.0116 (10)	−0.0019 (18)	−0.0005 (17)	0.0025 (17)
C7	0.0087 (11)	0.0079 (11)	0.0064 (10)	−0.0007 (17)	0.0014 (17)	0.0002 (16)
N7	0.0089 (12)	0.0184 (12)	0.0106 (10)	0.0024 (19)	−0.0016 (17)	−0.0015 (17)
O1	0.0697 (40)	0.0211 (18)	0.0309 (22)	−0.0172 (43)	0.0155 (48)	−0.0038 (30)
O2	0.0730 (42)	0.0207 (18)	0.0298 (22)	0.0181 (44)	0.0137 (49)	0.0044 (30)

[a] Estimated standard deviations ×10^4 in parentheses. The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Principal Bond Distances and Angles for the $[V(CN)_7]^{4-}$ Anion

Distances,[a] Å			
V-C1	2.134 (8)	C1-N1	1.155 (12)
V-C2	2.155 (7)	C2-N2	1.139 (10)
V-C3	2.152 (7)	C3-N3	1.143 (10)
V-C4	2.152 (7)	C4-N4	1.146 (10)
V-C5	2.150 (7)	C5-N5	1.137 (10)
V-C6	2.131 (8)	C6-N6	1.148 (11)
V-C7	2.156 (8)	C7-N7	1.147 (11)
Angles,[b] Deg			
C1-V-C2	72.5 (3)	C4-V-C6	85.6 (3)
C1-V-C5	72.5 (3)	C4-V-C7	86.7 (3)
C1-V-C6	94.6 (4)	C5-V-C6	93.0 (3)
C1-V-C7	94.5 (4)	C5-V-C7	89.3 (3)
C2-V-C3	72.3 (3)	C6-V-C7	171.0 (3)
C2-V-C6	90.2 (3)	V-C1-N1	179.5 (9)
C2-V-C7	92.9 (3)	V-C2-N2	179.0 (7)
C3-V-C4	70.5 (3)	V-C3-N3	178.5 (7)
C3-V-C6	87.3 (3)	V-C4-N4	177.9 (7)
C3-V-C7	85.6 (3)	V-C5-N5	179.3 (6)
C4-V-C5	72.3 (3)	V-C6-N6	172.2 (7)
		V-C7-N7	172.8 (7)

[a] Estimated standard deviations ×10^3 in parentheses. [b] Estimated standard deviations ×10 in parentheses.

Table V. Distances of Atoms from Least-Squares Planes for $V(CN)_7^{4-}$ [a]

Atom	Plane 1	Plane 2	Plane 3
V	0.005	0.004	(0.005)
C1	0.003	0.004	0.005
N1	(0.000)	0.003	0.003
C2	0.023	0.023	0.023
N2	(0.053)	0.053	0.053
C3	−0.046	−0.049	−0.048
N3	(−0.083)	−0.088	−0.087
C4	0.046	0.043	0.044
N4	(0.098)	0.094	0.095
C5	−0.032	−0.032	−0.032
N5	(−0.056)	−0.056	−0.056
p	0.951	0.951	0.951
q	0.001	0.000	0.000
r	0.308	0.308	0.308
d	0.005	0.004	0.005
δ	0.031	0.051	0.053

[a] Distances not in parentheses indicate atoms used to define the least-squares plane. The equation is defined as $px + qy + rz - d = 0$; δ defines the calculated standard deviation of distances from the plane. All distances in Å.

$Mo(CN)_8^{4-}$,[23] $W(CN)_8^{4-}$,[24] and $Re(CN)_8^{3-}$,[25] are known to be eight-coordinate. Since the average V–C distance of 2.15 Å is intermediate between the Mo–C distances of 2.12 and 2.16 Å found for the eight-coordinate $Mo(CN)_8^{3-}$ [26] and $Mo(CN)_8^{4-}$ [23] ions respectively, the size of the V(III) ion cannot be the determining factor. The most likely explanation (or better, rationalization) is the "nine-orbital" or "eighteen-electron" rule as discussed by Parish[27] for first-row transition metal complexes with strong-field ligands. The two electrons of the paramagnetic $V(CN)_7^{4-}$ ion ($\mu_{eff} = 2.8$ BM[7]) will occupy two separate orbitals, allowing seven ligands to donate electron pairs, thereby achieving the number of orbitals of the rare gas krypton. There are also a number of seven-coordinate Cr(IV) paramagnetic complexes[28] which can be explained in the same manner. Since spin pairing is easier for the second- and third-row transition elements, the other d^2 cyanide complexes are diamagnetic and attain a noble gas configuration by addition of eight ligand electron pairs.

The geometries that may be assumed by seven-coordinate molecules have been discussed by others[2,29-31] with the conclusion that the energetics of the various polyhedra are very similar upon consideration of ligand-ligand repulsions. Among possible explanations for the pentagonal-bipyramidal geometry found for $V(CN)_7^{4-}$, crystal field stabilization seems the most reasonable. For complexes having only a few d electrons, stabilizing just one or two d orbitals relative to the others will produce a net lowering of energy, thereby favoring one geometry over all others; this has been noted by Orgel for the $Mo(CN)_8^{4-}$ ion.[32] It thus appears that placing two electrons in the doubly degenerate d_{xz} and d_{yz}

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orbitals in pentagonal-bipyramidal coordination achieves the state of lowest energy for the V(III) complex with the strong-field cyanide ligand. What would have been the other t_{2g} orbital in octahedral symmetry, d_{xy}, becomes *much* higher in energy and will be degenerate with the $d_{x^2-y^2}$ orbital, these orbitals being effectively antibonding. Of the other possible seven-coordinate geometries, only the capped octahedron (symmetry C_{3v}) will have the two lowest d orbitals degenerate; because of insufficient experimental precedent, a definitive statement concerning the relative crystal field stabilization energies of the D_{5h} and C_{3v} geometries is unwarranted. The other geometries, having lower symmetry, will not have degenerate orbitals and one electron will have to be placed above the others, thus lowering the maximum possible crystal field stabilization energy. From the compilation of d-orbital energy levels in terms of Dq presented by Basolo and Pearson,[33] the pentagonal bipyramid is more stable than the so-called "octahedral wedge" for the d^2 configuration by 1.88Dq (the "octahedral wedge" is closely related to the capped octahedron). Pentagonal-bipyramidal geometry may be particularly well suited to seven-coordinate compounds of the first-row transition metals, since in addition to the $V(CN)_7^{4-}$ ion, it is known for complexes of Ti,[34] Cr,[28] Mn,[35] and Fe,[36] although in more complicated ligand systems. There are as yet an insufficient number of seven-coordinate complexes known with equivalent monodentate ligands to assess the relative merits of ligand–ligand interactions and crystal field stabilization energy.

An additional factor operating to stabilize the $V(CN)_7^{4-}$ may be a "ring current" as was postulated for the square-planar $Ni(CN)_4^{2-}$ ion.[37] A combination of the π orbitals on the five equatorial cyanides can form a very stable (and stabilizing) π-bonding orbital, the so-called "ring" π orbital. Additionally, the individual cyanide ligands will not only act as π acceptors and stabilize the d_{xz} and d_{yz} orbitals, but a molecular orbital made up of π^* orbitals on the equatorial ligands should increase that stabilization. Since the five cyanide ligands are only 72° apart, overlap, and therefore stabilization, should be greater than in square-planar and octahedral complexes in which four ligands are 90° apart.

The equivalency of the bond lengths for $V\text{–}C_{ax}$ and $V\text{–}C_{eq}$ may be explained in terms of ligand–electron interactions. Since the electrons in the d_{xz} and d_{yz} orbitals point away from the ligands, the electron–ligand repulsions will be quite small and approximately equal for the axial and equatorial cyanides.

A compound of similar formula, $K_4Mo(CN)_7 \cdot 2H_2O$, has been examined by Rossman, *et al.*,[38] who deduced that the $Mo(CN)_7^{4-}$ ion was indeed pentagonal bipyramidal in solution but that in the solid state the anion was a capped trigonal prism. The powder patterns of $K_4V(CN)_7 \cdot 2H_2O$ and $K_4Mo(CN)_7 \cdot 2H_2O$ are clearly not isomorphous.[39] The question of the solution behavior of the $V(CN)_7^{4-}$ ion is a complicated one. While it is known to disproportionate partially,[9] $V(CN)_7^{4-}$, however, does appear to retain the pentagonal-bipyramidal geometry.[40]

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Supplementary Material Available. Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-105..

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