The Crystal Structure of Potassium Pentacyanonitrosylvanadate(I), $K_3V(CN)_5NO \cdot 2H_2O$

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The crystal structure of potassium pentacyanonitrosylvanadate, $K_3V(CN)_5NO \cdot 2H_2O$, previously formulated as $K_5V(CN)_5NO \cdot H_2O$, has been determined by single crystal X-ray methods. The unit cell is orthorhombic, space group No. 56, *Pccn*, and has the dimensions $a=15.498\pm0.003$ Å, $b=7.145\pm0.001$ Å, and $c=11.666\pm0.002$ Å.

The structure was solved by means of three-dimensional Patterson and electron density calculations and refined by least squares methods to a final R-value of 0.078, based on 481 independent reflections.

Potassium pentacyanonitrosylvanadate(I) contains discrete distorted octahedral $V(CN)_5NO^{3-}$ ions in which the V−N bond distance is 1.66 Å as compared with a mean V−C distance of 2.17 Å. The orientation of the complex ions is disordered with respect to one of the diad axes of *Pccn* which means that the nitrosyl group and one of the cyanide groups occupy their crystallographic sites statistically.

The infrared spectrum of pure $K_3V(CN)_5NO \cdot 2H_2O$ has been recorded.

In recent years much attention has been focused on the transition metal pentacyanonitrosyl ions. Their electronic structures have been discussed in detail,[1-6] and the crystal structures of several compounds containing such ions have been investigated. Manoharan and Hamilton [7] have determined the structure of sodium nitroprusside, $Na_2Fe(CN)_5NO \cdot 2H_2O$, while Vannerberg *et al.* have determined the crystal structures of $K_3Cr(CN)_5NO$,[8] $K_3Mn(CN)_5NO \cdot 2H_2O$,[9] and $K_4Mo(CN)_5NO$.[10] The $M(CN)_5NO^{n-}$ complex ions studied hitherto are all characterised by a tetragonally distorted octahedral configuration and a very short M−NO bond. In order to extend this series of investigations it was decided to determine the crystal structure of potassium pentacyanonitrosylvanadate, reported [11] to contain the complex ion $V(CN)_5NO^{5-}$ which would be isoelectronic with $Mn(CN)_5NO^{3-}$ and $Fe(CN)_5NO^{2-}$. Preliminary data on the crystal structure of potassium pentacyanonitrosylvanadate have been published in a previous paper,[12] and a complete report on the structural investigation is submitted here. In the previous paper,[12] evidence was provided to show that potassium pentacyanonitrosylvanadate

ought, in fact, to be formulated as $K_3(CN)_5NO \cdot 2H_2O$ rather than as $K_5V(CN)_5NO \cdot H_2O$, *i.e.* as a complex of vanadium(I) rather than of vanadium($-I$). The final stages of the investigation have confirmed this belief.

PREPARATION AND ANALYSIS OF $K_3V(CN)_5NO \cdot 2H_2O$

Potassium pentacyanonitrosylvanadate(I) was prepared according to the method of Griffith, Lewis and Wilkinson,[11] whereby ammonium vanadate was dissolved in a cooled solution of potassium hydroxide and treated with excess of a solution of potassium cyanide. Hydroxylammonium chloride was then added and the solution was heated, with occasional stirring, on a steam-bath until the evolution of ammonia ceased. The orange oil which separated when the subsequently cooled and filtered solution was poured on to alcohol was washed several times with alcohol, dissolved in water, reseparated with alcohol and then allowed to stand under alcohol. After several days, bright orange plate-like crystals of suitable size for single crystal X-ray methods separated from the oil. These were picked out under the microscope, freed from an adhering yellow, partly crystalline layer, containing potassium cyanide and presumably also potassium hexacyanovanadate(III), with a needle and dried between filter papers.

The *potassium/vanadium* molar ratio was determined by means of atomic absorption spectroscopy using a Perkin Elmer 303 spectrometer. The aqueous solution analysed, which was prepared from a pure, *ca.* 0.5 mg sample of crystals picked out singly under the microscope, yielded 14.6 ppm V and 33.4 ppm K which corresponds to a K/V molar ratio of 2.98.

The *cyanide* content was determined by means of potentiometric titration. Approximately 10 mg of the crystals were picked out singly under the microscope and placed under alcohol to prevent their decomposition during the accumulation of a sufficiently large crystal sample. After drying between filter papers, the crystals were weighed and dissolved in 15 ml 0.01 M sodium hydroxide, 10 ml of the solution being subsequently transferred to a wash-bottle and diluted to 40 ml. Argon, previously freed from carbon dioxide by passage through "Ascarite", was then allowed to bubble through the solution and 10 ml conc., chloride-free $HClO_4$ (Merck, "Suprapur") were added. The wash-bottle was then heated to $70-90°C$ for 2 h, and the HCN evolved was carried over by the argon carrier and absorbed quantitatively in a solution prepared from 15 ml 0.01643 M $AgNO_3$ and 85 ml H_2O. The excess Ag^+ was then back-titrated potentiometrically with 0.01634 M chloride using a silver rod electrode with a saturated calomel electrode as reference and 0.05 M KNO_3 as salt bridge. The emf was registered on a high precision digital voltmeter and the equivalence point evaluated by means of the Gran function

$$F_1 \equiv (100 + v) \exp F(E - 300)/RT \ln 10$$

the straight line obtained when F_1 was plotted against v ml titrant added being extrapolated to $F_1 = 0$ to give an intercept on the v-axis of $v = v_{eq}$. Analysis of two different crystal samples yielded $CN^-/K_3V(CN)_5NO \cdot 2H_2O$ molar ratios of 5.08 and 5.12, respectively.

A direct potentiometric titration of $K_3V(CN)_5NO \cdot 2H_2O$ with Ag^+ to $Ag(CN)_2^-$ was attempted using the same electrode system, but gave less satisfactory results, owing to the inert nature of the various vanadium cyanide complexes. A clearly discernible inflexion point on the titration curve indicated, moreover, that three of the cyanide groups were more labile than the remaining two.

It was not possible to determine the *water* content owing to the insolubility of $K_3V(CN)_5NO \cdot 2H_2O$ in the Karl Fischer reagent. In view of the accuracy of the structure determination, the values obtained for the potassium/vanadium molar ratio, the cyanide content and the experimental density must, however, be regarded as providing sufficient confirmation that $K_3V(CN)_5NO \cdot 2H_2O$ is the correct chemical formula of the compound investigated.

UNIT CELL AND SPACE GROUP

The crystals of $K_3V(CN)_5NO \cdot 2H_2O$ are plate-like with well-developed faces of the forms {100}, {010}, and {001}, those used in this investigation having the approximate dimensions $0.003 \times 0.016 \times 0.007$ cm³. Crystals were mounted in glass capillaries and rotation photographs and Weissenberg photographs of the layers $h0l - h4l$, $0kl - 6kl$, and $hk0 - hk2$ were registered using multiple film equi-inclination Weissenberg techniques and $CuK\alpha$ radiation. The relative intensities of the reflections thus recorded were estimated visually by comparison with a standard scale.

The crystals were found to be orthorhombic with the approximate cell dimensions:

$$a = 15.6 \text{ Å}, \quad b = 7.2 \text{ Å}, \quad \text{and} \quad c = 11.7 \text{ Å}$$

as determined from Weissenberg and rotation photographs. In order to obtain more accurate cell dimensions, substantially KCN-free crystals, picked out singly under the microscope, were pulverised and powder photographs were taken in a Guinier focusing camera with $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å). Lead nitrate ($a = 7.8564$ Å[13]) was used as an internal standard and $\sin^2\theta_{obs}$ values were obtained from the measured s values using the program PEPP.[14] Refinement of the cell dimensions, based on 23 indexed reflections, with the

Table 1. X-Ray powder diffraction data for $K_3V(CN)_5NO \cdot 2H_2O$. Guinier camera. $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

$h\,k\,l$	$10^6\sin^2\theta_{obs}$	$10^6\sin^2\theta_{calc}$	I_{calc}	I_{obs}
2 0 0	9874	9880	98	vw
1 1 0	14094	14092	293	m
1 1 1	18466	18452	221	m
2 1 2	38962	38940	966	s
1 2 1 } 1 1 3 }	53344	53319 53328	41 } 1 }	vw
2 2 0	56450	56369	86	w
4 1 2	68642	68581	268	m
0 0 4	69772	69752	100	w
3 2 1 } 3 1 3 }	73067	73079 73088	417 } 764 }	vs
0 1 4	81353	81374	83	w
4 2 0 } 3 2 2 }	86078	86010 86158	302 } 1 }	m
1 2 3	88172	88195	25	vvw
2 1 4	91273	91255	129	w
4 0 4	109319	109272	155	w
5 2 1 } 5 1 3 }	112649	112600 112608	90 } 66 }	w
0 3 2	122014	122040	257	w
2 2 4	126137	126122	90	w
6 2 0	135313	135410	68	vw
4 3 2	161644	161560	130	w

program POWDER,[15] written for the IBM 360/50 computer, yielded the following values:

$a = 15.498 \pm 0.003$ Å, $b = 7.145 \pm 0.001$ Å, $c = 11.666 \pm 0.002$ Å, and $V = 1292$ Å^3.

Observed and calculated $\sin^2\theta$ values are listed in Table 1.

The calculated density based on four formula units of $K_3V(CN)_5NO \cdot 2H_2O$ in the unit cell is 1.87 g cm^{-3} (2.18 g cm^{-3} for four formula units of $K_5V(CN)_5NO \cdot H_2O$). The experimental density, as determined by the method of flotation using mixtures of bromoform and carbon tetrachloride, is 1.83 g cm^{-3}.

The observed conditions of reflection:

$$0kl: \; l = 2n$$
$$h0l: \; l = 2n$$
$$hk0: \; h + k = 2n$$

are in accordance only with space group No. 56, $Pccn$.[13]

STRUCTURE DETERMINATION

At the commencement of the investigation only the $h0l - h4l$ data (463 reflections) were available, and the intensities of the reflections from the different layers were scaled together approximately assuming a linear relationship between intensity and time of exposure. Since the linear absorption coefficient for $K_3V(CN)_5NO \cdot 2H_2O$ is 152 cm^{-1}, there were appreciable absorption errors in the data, but a correction for absorption was performed first after an approximate structure had been deduced. After correction for Lorentz and polarisation effects, a three-dimensional Patterson synthesis of the $h0l - h4l$

Table 2. Analysis of the dominant vectors in the Patterson synthesis of the $h0l - h4l$ data for $K_3V(CN)_5NO \cdot 2H_2O$. Double weight vectors are denoted by an asterisk. Height of origin peak $= 3400$.

Peak No.	u	v	w	Peak height	Interpretation
1	0.500	0.000	0.000	1050	K(1)−V
2	0.000	0.000	0.500	1700	K(1)−K(1); V−V
3	0.500	0.000	0.500	2500	K(2)−K(2); K(1)−V
4	0.000	0.173	0.285	480	K(2)−K(2)
5	0.249	0.150	0.212	500	K(2)−V *; K(2)−K(1) *
6	0.251	0.150	0.288	500	K(2)−V *; K(2)−K(1) *
7	0.500	0.168	0.212	490	K(2)−K(2)
8	0.000	0.291	0.500	860	K(2)−K(2)
9	0.500	0.299	0.000	740	K(2)−K(2)
10	0.249	0.350	0.000	1100	K(2)−V *; K(2)−K(1) *
11	0.250	0.350	0.500	1100	K(2)−V *; K(2)−K(1) *
12	0.000	0.500	0.215	1380	K(1)−V; K(2)−K(2)
13	0.500	0.500	0.208	580	K(1)−K(1); V−V
14	0.500	0.500	0.308	1440	K(2)−K(2); K(1)−K(1); V−V

data was calculated, from which it proved to be possible to locate the potassium and vanadium atoms. The coordinates of the dominant peaks in the Patterson synthesis are listed in Table 2 together with the observed peak heights.

At this stage in the investigation the chemical analysis had not yet been performed, and it was assumed that potassium pentacyanonitrosylvanadate had the formula $K_5V(CN)_5NO \cdot H_2O$. The twenty potassium atoms were therefore expected to be distributed between two eightfold and one fourfold position in *Pccn*, while the vanadium atom was expected to occupy a fourfold position. The peaks 1, 2, 3, 12, 13, and 14 were attributed to vectors between fourfold positions and by considering all possible combinations of potassium and vanadium positions in accordance with these vectors, the locations *Pccn:* 4*d* with $z = 0.35$ for K(1) and *Pccn*: 4*c* with $z = 0.15$ for V were selected as being the most feasible. The peaks 3, 4, 7, 8, 9, 12, and 14 were the only ones which could be identified as $K-K$ vectors between potassium atoms in an eightfold position. It proved, however, to be impossible to place sixteen potassium atoms in two eightfold positions consistent with these vectors, without violating the closest distance of approach. The vectors must therefore represent a single eightfold potassium position, and this provided the first indication that the chemical formula could not be $K_5V(CN)_5NO \cdot H_2O$.

Structure factor calculations based on each of the several eightfold potassium positions consistent with the above vectors, combined with the preliminary K(1) and V positions, and an overall temperature coefficient, $B = 3.5$ Å², indicated that the most satisfactory set of positions for the heavy atoms was

	x	y	z
K(1)	0.25	0.75	0.35
K(2)	0.00	0.10	0.35
V	0.25	0.25	0.15

An analysis of the dominant peaks in the Patterson synthesis is given in Table 2. The discrepancies between observed peak heights and their expected values can be attributed partly to the approximate scaling of the layers, but are mainly due to overlap from heavy atom-light atom and light atom-light atom vectors.

An electron density calculation based on the above preliminary potassium and vanadium positions showed no indication as to the presence of further potassium atoms, but revealed the oxygen atom O(1) of a water molecule in *Pccn*: 8*e* with $x = -0.001$, $y = 0.230$, $z = 0.070$. This suggested that potassium pentacyanonitrosylvanadate had the formula $K_3V(CN)_5NO \cdot 2H_2O$ analogous to $K_3Mn(CN)_5NO \cdot 2H_2O$. Successive electron density calculations revealed the positions of the remaining light atoms in an approximately octahedral configuration about vanadium, all ligands being treated, at this stage, as cyanide. A structure factor calculation based on these preliminary atomic coordinates and an overall temperature coefficient, $B = 3.5$ Å², yielded an R-value of 0.151.

After three cycles of isotropic block diagonal least squares refinement using a program written by Abrahamsson [18] and Aleby [19] for the SAAB D21 computer, the R-value converged to $R = 0.117$ and the preliminary positions listed in Table 1 of the previous paper [12] were obtained.

A correction was then applied for absorption using the program DATAP2 [20] and an IBM 360/50 computer. A structure factor calculation based on the same preliminary positions and isotropic temperature coefficients then yielded an R-value of 0.098.

It was obvious that since vanadium occupies the position $4c$ and no ligands are aligned along the diad axis, the structure must be disordered, and, as expected, there were two shorter $V - C$ distances of 1.79 Å, ($V - C(2)$) and four longer $V - C$ distances, two of 2.20 Å ($V - C(1)$) and two of 2.16 Å ($V - C(3)$). If $Pccn$ is the correct space group, the nitrosyl group and a cyanide group must therefore occupy the $C(2)$, $N(2)$ positions statistically. On the other hand, if the reflections $h0l$: $l = 2n + 1$ in $Pccn$ are unobserved rather than absent, the structure can equally well be described in terms of space group No. 33, $Pna2_1$ [13] (transformation matrix $001|100|010$; new origin at $+\frac{1}{4}00$ in $Pna2_1$) which does not require statistical occupation for the nitrosyl and $C(2)$, $N(2)$ cyanide groups.

Refinement was therefore continued in $Pna2_1$ using the least squares full matrix program LALS,[20] $C(2)$, $N(2)$ being denoted as $C(3)$, $N(3)$ and $C(4)$, $N(4)$ in $Pna2_1$. The atomic scattering factors of Cromer and Waber [21] were used, and each F_o value was weighted according to Cruickshank's weighting scheme [22] ($w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$) with $a = 10.8$, $c = 0.05$, and $d = 0$. Separate scale factors were refined for each layer. After three cycles, the isotropic temperature coefficients of $C(4)$, $N(4)$ were considerably lower than those of $C(3)$, $N(3)$ and $C(4)$, $N(4)$ were therefore assigned the labels $N(4)$, $O(3)$, respectively. After a further three cycles, however, the $V - C(3)$ bond distance had shortened to 1.72 Å, while the $V - N(4)$ distance had lengthened to 1.84 Å, the R-value remaining constant at 0.098. The atoms were then relabelled, $C(3)$, $N(3)$ becoming $N(4)$, $O(3)$ and *vice versa*, whereupon the $V - N(4)$ and $V - C(3)$ bond distances both converged to 1.77 Å while the $N(4) - O(3)$ and $C(3) - N(3)$ bond distances, which had been normal in the previous labelling, were reversed, *i.e.* 1.14 Å and 1.26 Å, respectively.

This seemed to indicate that the arrangement of the complex ions was, in fact, disordered, and F_{calc} values for the unobserved or absent $hk0$: $h = 2n + 1$ ($Pccn$, $h0l$: $l = 2n + 1$) reflections were generated. The presence of several fairly strong reflections which ought to have been clearly visible supported the theory of a disordered structure based on $Pccn$.

Further support is provided by the somewhat peculiar situation that, in $Pna2_1$, it is not possible to realise both normal $V - N(4)$ and $V - C(3)$ distances *and* normal $N(4) - O(3)$ and $C(3) - N(3)$ distances. In $Pccn$, however, the statistically distributed $O(3)$ and $N(3)$ (labelled $O(2)$ and $N(2)$ in $Pccn$) may be exchanged without it being necessary to exchange $N(4)$ and $C(3)$ (labelled $N(4)$ and $C(2)$ in $Pccn$), thus yielding bond distances more in accordance with those normally observed for the nitrosyl and cyanide ligands. In addition, much improved standard deviations of the atomic parameters were obtained in $Pccn$.

The possibility that the complex ion contained two nitrosyl groups *i.e.* had the formula $V(CN)_4(NO)_2^{3-}$, could be discounted on the basis of the results of the cyanide analysis.

At this stage in the investigation, the $hk0-hk2$ and $0kl-6kl$ data were available, the latter being, however, of such poor quality that they were not used in the refinement. The $hk0-hk2$ data, which consisted of 105 reflections, were scaled together using the $h0l-h4l$ data, corrected for Lorentz and polarisation effects and for absorption. A structure factor calculation based on the atomic parameters obtained in the last cycle of refinement in *Pccn* yielded an *R*-value of 0.120. Owing to the paucity of the $hk0-hk2$ data it was not considered worth-while to refine the structure using these data only. The *c*-axis data was therefore combined with the *b*-axis data, a mean value of F_{obs} being calculated for the common reflections, thus yielding a total of 481 independent reflections. Anisotropic thermal parameters were then introduced for all atoms except the statistically distributed C(2), N(2), N(4), and O(2) atoms which were refined isotropically. An overall scale factor was refined, the total number of parameters refined thus being 81. After three cycles of refinement the *R*-value converged to 0.078 and all parametral shifts, except those of the statistically distributed atoms, were less than 10 % of the corresponding standard deviations, the shifts of the statistically distributed atoms being less than 30 % of the standard deviations.

The final atomic parameters are given in Table 3. The observed and calculated structure factors are listed in Table 4, the F_{obs}-values of the non-observed reflections being denoted by a dash. No attempt has been made to account for the contributions of the hydrogen atoms to the structure factors. The most interesting interatomic distances and angles are given with their standard deviations in Tables 5 and 6.

The proposed structure was tested by means of a three dimensional $F_o - F_c$ Fourier synthesis in which the highest peak was found to be less than one eighth of the height of a carbon atom peak.

Table 3. Atomic coordinates, expressed as fractions of the cell edges, (standard deviations within parentheses) and thermal parameters, for $K_3V(CN)_5NO \cdot 2H_2O$. The anisotropic temperature coefficient is $\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}$. The atoms O(2), C(2), N(2) and N(4) have occupation numbers 0.5 and isotropic temperature coefficients of the form $\exp\{-B(\sin^2\theta/\lambda^2)\}$.

Atom		x	y	z	$B(\text{Å}^2)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	4d	0.2500	0.7500	0.3804(4)		0.0047	0.0165	0.0127	0.0009	0	0
K(2)	8e	−0.0012(2)	0.1047(4)	0.3454(2)		0.0039	0.0161	0.0078	0.0017	−0.0004	−0.0005
V	4c	0.2500	0.2500	0.1555(2)		0.0028	0.0173	0.0064	−0.0002	0	0
O(1)	8e	−0.0002(4)	0.2317(13)	0.0696(7)		0.0036	0.0270	0.0095	−0.0005	0.0013	0.0015
C(1)	8e	0.3331(7)	0.1237(17)	0.2859(9)		0.0029	0.0200	0.0087	−0.0004	0.0007	0.0012
C(3)	8e	0.1654(8)	0.0155(22)	0.1784(9)		0.0035	0.0235	0.0073	−0.0045	−0.0008	−0.0006
N(1)	8e	0.3814(6)	0.0480(13)	0.3453(9)		0.0039	0.0146	0.0112	0.0027	0.0004	0.0014
N(3)	8e	0.1232(8)	0.8880(15)	0.1924(10)		0.0049	0.0173	0.0119	−0.0010	−0.0025	−0.0002
O(2)	8e	0.1485(15)	0.0316(37)	0.4888(19)	3.41						
C(2)	8e	0.3153(20)	0.3747(62)	0.5465(24)	1.76						
N(2)	8e	0.3386(18)	0.4597(46)	0.4701(24)	3.34						
N(4)	8e	0.1963(21)	0.1340(67)	0.5547(30)	3.11						

Table 4. Observed and calculated structure factors for $K_3V(CN)_5NO \cdot 2H_2O$. The columns are h, F_o, and F_c, respectively. F_o values corresponding to unobserved reflections are denoted by a dash.

```
H 0 0                 7   -    -2         4   16  -13        8    -    -5        H 2 4                 2    -    -7
2   45  -49           8   30  -31         5    -   12         9    -   13        0   74   74            3   14  -13
4  180  154           9   -    15         6  100  -99        10    -    6        1   22  -21            4   15  -15
6  166  122          10   16  -18         7   20  -21        11   18   1?        2  101  -95            5   14  -15
8  216  203          11   19  -19         8   14  -18        12    -    7        3   37   36            6    -   -10
10   -    1          12   22  -22         9    -    6        13    -    6        4   57   60            7   23  -22
12  114  115         13   11   12        10   60  -64        14    -   -4        5   57  -56            8    -   -2
14   -   -9                               11    -    2                           6   57  -55            9    -  -12
16  59   62          H 0 12              12    -   -5        H 1 10              7   56   55           10    -    9
18  11   10          0   13   16         13    -    1        0    -    5         8   33   39           11    -   -8
                     1    -   14         14   25  -26        1   30   32         9   24  -24           12    -   -5
H 0 2                2    -   14         15    -   -6        2    -    1        10   56  -56           13   11  -11
0   72  -67          3   14  -17         16    -  -10        3   22  -24        11    -    7           14    -    2
1   36  -31          4   16   18         17    -    4        4    -    0        12   35   33
2    -   -3          5   13   14         18   19  -17        5   18   19        13    -   -9           H 2 10
3   35   32          6    -    4                             6    -    7        14   24  -21           0   14   13
4    7    6          7    -   -6         H 1 5               7   20  -20        15   19   18           1    -   -5
5   13  -13          8   18   22         1    -    5         8    -   -2        16   12   10           2   25  -23
6   20   20          9    -    7         2    -   -7         9    -   -1        17   15  -14           3   16   16
7   16  -15         10    -    2         3   31  -30        10    -   -1        18   18  -16           4   12   12
8   50  -48                              4   25  -25        11    -   -9                               5   27  -24
9    -   -5          H 1 0               5    -  -12        12    -    5        H 2 5                 6   16  -15
10    -    7         3   36   37         6   24   24        13    -   10        1   66   64            7   20   20
11    -    8         5   15   13         7    -   -3                            2    9   10            8   11    8
12  16  -16          7   22  -21         8    -    1        H 2 0               3   55   52            9   12   -8
13  15  -14          9    -    3         9    -   -5        0   31  -34         4   10   10           10   17  -17
14    -   12        11   22   24        10   19  -20        2   68   85         5  103   86           11    -    1
15    -    7        13   18  -20        11    -    0        4  206 -198         6   16  -16           12   10    9
16    -  -10        15   14   13        12    -    3        6  127  122         7   29   33           13    -   -4
17  14  -14        17    -   -5        13    -   -9        8   59  -69         8    -   -5
18    -   -9        19    -    7        14    -   -2       10   38   39         9   26   26           H 2 11
                                        15    -   -7       12   40  -43        10   15   14           1   25   23
H 0 4               H 1 1              16    -   -2       14   28   31        11   44   43           2    -    0
0  178 -145         1   52  -52        17    -    5       16   33  -31        12    -    0           3   22   23
1   56   50         2    -   -1                            18   21   25        13   20   20           4    -    6
2   18  -14         3   19  -24        H 1 6                                    14    -   -7           5   20   19
3   27  -25         4    -    7        0   24   24         H 2 1               15   19   18           6    -   -7
4  195 -163         5   96  -81        1   46  -45         1   37  -40        16    -    4           7   18   19
5   26   27         6    -    8        2   77  -74         2   31   31        17   13   13           8    -    2
6   46   43         7   33  -32        3   45   44         3  156 -150                               9   13   14
7   48  -44         8    -   -8        4    -    1         4   34  -36        H 2 6                10    -    5
8  129 -121         9    -   -4        5   43  -41         5  100  -89        0   53   42           11   13   13
9   60   56        10    -    5        6   57  -57         6   10   11        1    9   10           12    -   -4
10    -   -7        11   22  -23        7   38   40         7   35  -42        2   59   55
11  30  -34        12    -   10        8   19   21         8    -    1        3   12  -12           H 2 12
12  55  -50        13   20  -22        9   31  -32         9   39  -41        4   29  -30           0    -    0
13  18   18        14    -   -2       10   46  -49        10    -   -7        5    -    4           1   13  -13
14    -    7        15   13  -13       11   27   28        11   34  -35        6   71   70           2    -    4
15    -   -4        16    -    1       12    -   12        12    -    3        7    -    2           3    -   11
16  42  -40        17    -   -1       13   18  -19        13   37  -38        8    -    2           4    -   -7
17    -    6        18    -    4       14   22  -23        14    -   -7        9    -    4           5    -  -10
18    -    3        19    -   -5       15   14   14        15   21  -21       10   28   28           6    -    7
                                       16    -    0        16    -    2       11    -   -7           7   10   11
H 0 6               H 1 2              17    -   -9        17    -   -7       12    -   -1           8    -   -3
0  180  136         0   86  -78                            18    -    1       13    -    1           9    -   -7
1   24  -24         1   10   12        H 1 7               19   11  -11       14   21   21          10    -    3
2    -   -1         2  155  167        1   52  -48                            15    -    3
3    -    4         3   37  -33        2   19  -20         H 2 2              16    -   -5           H 3 0
4   27   29         4  138 -117        3   32  -30         0   16  -15        17    -    0           1   37  -41
5    -   -8         5   33   31        4   13   12         1   14   15                               3    -   -7
6   18   17         6  107  116        5   38  -38         2   58  -60        H 2 7                5   46   48
7   19   21         7   16  -18        6    -   12         3    8    7        1   17  -16           7   34  -34
8   80   74         8   30  -37        7   38  -43         4   19  -14        2    -   -6           9   20   19
9    -    8         9   27   21        8   15  -17         5    -    5        3   39  -37          11    -    3
10    -  -12        10  69   70        9    -  -13         6   27  -31        4    -   -6          13    -    3
11    -  -18        11  20  -25       10    -    5         7   29  -33        5   23  -22          15    -   -4
12  36   36        12  32  -36       11   16  -17         8    -   -6        6    -    0          17   14   13
13    -    7        13  15   17       12    -   -9         9   13   14        7   23  -22
14    -    0        14  42   43       13   26  -26        10  35  -38        8    -   11          H 3 1
15    -   14        15   -   -4       14    -   -9        11   -   -1        9    -   -8          2    8   -7
16  24   20        16  18  -19       15    -   -7        12   -    2       10   12  -11          3    -    8
17    -   -7        17   -    0       16    -    3        13   -    1       11    -  -11          4   35   36
                    18  24   27                           14  11   -8       12    -  -10          5   18   19
H 0 8               H 1 3              H 1 8              15  11  -13       13   23  -21          6   23  -23
0   19  -19         1   10   -7        0    -   -3        16   -   -4       14    -    9          7    8  -10
1   40  -41         2   14   12        1   20   20        17   -    8       15    -   -3          8   18  -19
2   17  -17         3  204  203        2   76   69        18  11  -11       16    -   -3          9   13   13
3   53   53         4    -    3        3   24  -23                                               10   28   26
4   12   14         5   76   76        4    -    4        H 2 3              H 2 8                11   17   15
5   36  -38         6    -    1        5   16   14        1   49  -41        0    -   -5          12    -    2
6   30  -33         7    -    9        6   44   45        2   34   34        1   49   45          13    -   -9
7    -    9         8   23  -16        7    -   -1        3   20  -19        2   30   31          14   13  -13
8   14   13         9   57   56        8    -   10        4   34  -33        3   27  -26          15    -    6
9    -  -15        10  14   10        9    -    1        5    -   -8        4    -   -3          16    -    6
10  21  -21        11  36   36       10   32   35        6   11   13        5   19   20          17    -    6
11  22   25        12   -   11       11    -   -7        7   36  -39        6   20   21
12    -    3        13  26   26       12    -   -3        8   15   17        7   32  -33          H 3 2
13  25  -25        14   -  -11       13    -    8        9    -  -10        8    -    1          0  211  226
14    -   -2        15  24   25       14   29   27       10   13  -14        9   25   26          1   40  -43
15  13   14        16   -    2       15    -   -5       11    -   -6       10   14   15          2   11   11
                    17   -    8                          12    -    2       11   19  -19          3   16   17
H 0 10             18   -    4        H 1 9              13   16  -18       12    -   -4          4  137  134
0   57  -56                            1   17   17       14    -    8                              5    9  -10
1   35   36        H 1 4               2    -    6       15    -    1       H 2 9                6    -   -3
2    -  -11         0  133 -100        3   27   26       16    -   -1       1   28  -26          7   16   15
3   15  -15         1   15  -15        4    -    4       17    -   -6                             8  138  140
4   59  -54         2   99  -95        5   30   31       18    -    0                             9   18  -17
5    -   -2         3    8    7        6    -   -3                                               10    -   -2
6    -  -10                            7    -    7                                               11    -    4
```

Table 4. Continued.

```
12  68  65     14   -    8       H 3 12      15   -    0         H 4 8         H 5 1
13   -  -5     15  14  -13    0  20  -19     16   -    0      0  17   17     1  34   33
14   -  -4     16  22  -17    1  16   15     17   -    1      1  13  -12     2   -   -3
15   -   7                    2   -   -9                      2  27  -25     3  34   35
16  44  42       H 3 7        3  12  -14       H 4 4          3  27   24     4   -   13
17  13 -11     1  23   23     4  21  -22    0  31  -29        4   -   -2     5  37   41
              2  13  -13      5   -   10    1  58   52        5  31  -31     6   -  -11
   H 3 3      3  19   20      6   -   -4    2  86   89        6  13  -14     7   -   18
1  49 -49     4  20   20      7   -   -4    3  49  -46        7  26   29     8   -  -13
2   -  -8     5   -    9      8  16  -18    4  18  -15        8   -    2     9   -   21
3  11 -12     6   -   -8                    5  12   13        9  17  -17    10   -   14
4   9   8     7  16   18        H 4 0       6  61   66       10   9   -8    11   -   24
5  21 -21     8   -  -11     0  16   19     7  10   11       11  15   13    12   -   -4
6   -  -5     9  13   16     2  86 -110     8  10   -8       12   -   -3
7. 42 -42    10  13   13     4  31   34     9   -    5       13  11   -9       H 5 2
8   -   5    11   -   10     6  98  -97    10  40   42       14   -   -7    0  58  -56
9   - -11    12   -   -1     8  32   33    11  29  -28                      1   -   14
10  -  -2    13   -    6    10  67  -80    12  10   -9         H 4 9        2  32   36
11  -  -3    14   -   -5    12  25   21    13  26   24       1  11  -11     3   -  -13
12  -  -3    15   -    3    14  32  -33    14  40   35       2   -    8     4  65  -71
13 21 -20                   16   -    0    15  11  -10       3   -   -7     5  15   18
14  -   6      H 3 8        18   -  -20    16  10   -8       4   -   -2     6  28   29
15  -  -4    0  64   55                    17   -    4       5  11  -11     7   -  -18
16  -  -3    1   -  -12       H 4 1                          6   -   -3     8  41  -45
17  -  -5    2  12   13     1  11  -11       H 4 5           7   -  -10     9   -    1
             3   -    4     2   -    3     1  19   17        8   -    3    10   -   30
   H 3 4     4  52   45     3  24  -29     2   7    9        9   -   -4    11   -    5
0  90 -90    5   -   -7     4   -  -10     3  50   42       10   -    2    12  36  -38
1  11 -11    6   -    2     5  35  -38     4   -   -4       11   -   -5    13   -    3
2  12  13    7  20   19     6   -   -3     5  34   33       12   -    1    14   -   11
3   8   9    8  52   48     7  13  -14     6   -   -4       13   -   -6
4  24 -25    9  13  -14     8   -   10     7  13   16                        H 6 0
5   -   6   10   -    2     9   -    0     8   -    3         H 4 10       0  82  -77
6   -   4   11   -    6    10   -   -7     9  12   13       0   -    8     2   -    3
7  18 -20   12  26   24    11  15  -15    10   -    1       1  13   13     4  75  -69
8  38 -40   13   -    0    12   -   -8    11  17   17       2  27   24     6   -   17
9   -  -6   14   -    4    13  17  -17    12   -   -3       3  12  -12     8  67  -63
10  -  -7                  14   -    3    13  16   15       4   -    8    10   -    2
11  -  12     H 3 9        15   -   -5    14   -    0       5   9    8    12  31  -32
12 18 -15   1  18  -19     16   -    1    15   7    8       6  29   29    14   -    5
13  - -10   2   -   -3     17   -   -1    16   -    0       7   -   -6
14  -   9   3  11   12     18   -   -4                      8   -   -4      H 6 1
15  -  -3   4   -    1                      H 4 6          9   8    8    1   -   14
16 27 -23   5  15  -15       H 4 2       0   -   -3       10  22   22    2   -   -5
17  -  -4   6   -    1     0  32   35     1   -    3       11   8   -9    3  35   35
            7  -.  -10     1   7    6     2  82  -76       12   -    2    4   -    1
   H 3 5    8   -    0     2  46   50     3   -    6                      5   -   10
1   -  -4   9   -    1     3  15   16     4  28  -26         H 4 11      6   -   -3
2  28 -26  10   -   -1     4   -   -4     5   -   -7       1   -    4    7   -   12
3  25  22  11   -   -9     5   -  -10     6  43  -42       2   -    2    8   -    8
4  15  13  12   -    0     6  38   42     7   -    2       3  10   10    9   -   23
5  10   9  13   -   -2     7   -   -3     8  18  -20       4   -    1   10   -   -2
6   -   3                  8  23   26     9   -   -7       5   -    8
7   -  -5     H 3 10       9   -   -5    10  46  -43       6   -    0      H 6 2
8   -  -1   0   -   -5    10  14   12    11  11   11       7   -    2    0   -   18
9   -   6   1  12  -13    11  24   22    12   -   -2       8   -    0    1   -    0
10  -  -2   2  19  -17    12  10    9    13   -   -5       9   -    5    2   -   -2
11  -   7   3  21   21    13  13  -13    14  32  -27      10   -    2    3   -   -1
12  -  -6   4  13  -13    14  21   19    15   -   -4                     4   -    8
13  -   1   5  21  -20    15   -    1    16   -   -5        H 4 12      5   -    7
14  -   6   6   -   -4    16   -   -2                     0   -    8    6   -   -3
15  -   1   7   -   13    17   -    3      H 4 7          1   7    8    7   -   -4
16  -  -1   8  11  -12                   1  10  -10       2  15  -16    8   -   13
            9  18  -18      H 4 3        2   -   -4       3   -   -7    9   -    9
   H 3 6   10  11  -11    1   -   -1     3   -   -1       4   -   -6   10   -    0
0  41 -42  11  17   17    2  31   30     4   -   -7       5   -    7
1  34  32  12   -   -1    3   7    7     5  13  -15       6   -   -3      H 7 2
2  22  23                 4   6   -7     6   -    3       7   -  -11    0   -    8
3  47 -42    H 3 11       5   -   -3     7   -   -9       8   -   -6    1   -   -6
4  64 -58  1   -   -3     6   -  -12     8   -    4                     2  56  -52
5  47  42  2   -   -5     7   -   -2     9   -    3        H 5 0       3   -    9
6  25  24  3   -   -1     8  10   12    10   -   -7      1   -  -20    4   -    4
7  26 -24  4   -    2     9   -    4    11   -   -5      3   -  -16    5   -   -4
8  30 -29  5   -   -2    10   -    6    12   -   -6      5   -   13    6  48  -45
9  20  21  6   -    3    11   -   -1    13   9   -9      7   -   26    7   -    0
10  -   3  7   -    1    12   -   -1    14   -    1      9   -  -24    8   -    4
11 14 -16  8   -   -4    13   -   -1    15   -    0     11   -    9    9   -   -7
12 18 -18  9   -   -5    14   -    6                    13   -    2   10  36  -29
13 21  18 10   -    0
          11   -   -1
```

The Lorentz and polarisation correction, the Patterson synthesis, the earlier structure factor calculations, electron density calculations, and the block diagonal least squares refinement were calculated on a SAAB D21 computer at the Gothenburg Universities' Computing Centre using programs written by Abrahamsson *et al.*[16-19] The absorption correction, the full matrix least squares refinement, the $F_o - F_c$ Fourier synthesis, and the calculation of distances and angles were performed on an IBM 360/50 computer at the

Table 5. Interatomic distances in K$_3$V(CN)$_5$NO·2H$_2$O. (Standard deviations are given within parentheses.)

Superscript	Atom at			Superscript	Atom at		
none	$x,$	$y,$	z	$'''$	$1/2+x,$	$-y,$	$1/2-z$
$'$	$1/2-x,$	$1/2-y,$	z	$*$	$-x,$	$1/2+y,$	$1/2-z$
$''$	$1/2-x,$	$y,$	$1/2+z$	$**$	$x,$	$1/2-y,$	$1/2+z$
				$***$	$-x,$	$-y,$	$-z$

Within the complex ion

V—C(1)	2.187(11) Å		C(1) —N(1)	1.154(15) Å
V—C(1)$'$	2.187(11)		C(1)$'$ —N(1)$'$	1.154(15)
V—C(2)$''$	1.853(33)		C(2)$''$—N(2)$''$	1.138(45)
V—C(3)	2.144(14)		C(3) —N(3)	1.133(18)
V—C(3)$'$	2.144(14)		C(3)$'$ —N(3)$'$	1.133(18)
V—N(4)$''$	1.662(38)		N(4)$''$—O(2)$''$	1.294(46)

Within the K(1) coordination sphere

K(1)—N(1)	2.974(10) Å		K(1)—C(1)	3.163(12) Å
K(1)—N(1)$'$	2.974(10)		K(1)—C(1)$'$	3.163(12)
K(1)—N(2)	2.699(31)		K(1)—C(2)	3.460(39)
K(1)—N(3)	3.106(12)		K(1)—C(3)	3.296(13)
K(1)—N(3)$'$	3.106(12)		K(1)—C(3)$'$	3.296(13)
K(1)—O(2)	2.850(25)		K(1)—N(4)	3.516(43)

Within the K(2) coordination sphere

K(2)—N(1)$'''$	3.073(10) Å		K(2)—N(3)	3.050(12) Å
K(2)—N(1)$'$	3.100(10)		K(2)—O(1) $*$	2.844(9)
K(2)—N(2)$'$	2.946(28)		K(2)—O(1) $**$	2.866(9)
K(2)—N(3) $*$	2.804(12)		K(2)—O(2) $***$	3.147(24)

Other distances

O(1)—N(1)$'''$	2.889(13) Å
O(1)—N(2)$''$	3.206(30)
O(2)—O(1) $**$	3.011(26)

Table 6. Angles within the V(CN)$_5$NO^{3-} ion. Atomic coordinates are given within square brackets and standard deviations of the angles within parentheses.

C(1) [0.333, 0.124, 0.286]—V[0.250, 0.250, 0.156]—C(1)	[0.167, 0.376, 0.286]	91.9(0.6)°
C(1) [0.333, 0.124, 0.286]—V[0.250, 0.250, 0.156]—C(3)	[0.165, 0.015, 0.178]	87.2(0.5)
C(1) [0.333, 0.124, 0.286]—V[0.250, 0.250, 0.156]—C(3)	[0.335, 0.485, 0.178]	82.9(0.5)
C(1) [0.333, 0.124, 0.286]—V[0.250, 0.250, 0.156]—N(4)	[0.304, 0.134, 0.055]	89.5(1.3)
C(1) [0.333, 0.124, 0.286]—V[0.250, 0.250, 0.156]—C(2)	[0.185, 0.375, 0.047]	175.4(1.3)
C(1) [0.167, 0.376, 0.286]—V[0.250, 0.250, 0.156]—C(2)	[0.185, 0.375, 0.047]	87.6(1.0)
C(1) [0.167, 0.376, 0.286]—V[0.250, 0.250, 0.156]—C(3)	[0.165, 0.015, 0.178]	82.9(0.5)
C(1) [0.167, 0.376, 0.286]—V[0.250, 0.250, 0.156]—C(3)	[0.335, 0.485, 0.178]	87.2(0.5)
C(1) [0.167, 0.376, 0.286]—V[0.250, 0.250, 0.156]—N(4)	[0.304, 0.134, 0.055]	172.9(1.4)
C(3) [0.165, 0.015, 0.178]—V[0.250, 0.250, 0.156]—C(2)	[0.185, 0.375, 0.047]	97.3(1.2)
C(3) [0.165, 0.015, 0.178]—V[0.250, 0.250, 0.156]—N(4)	[0.304, 0.134, 0.055]	90.3(1.5)
C(3) [0.335, 0.485, 0.178]—V[0.250, 0.250, 0.156]—C(2)	[0.185, 0.375, 0.047]	92.5(1.3)
C(3) [0.335, 0.485, 0.178]—V[0.250, 0.250, 0.156]—N(4)	[0.304, 0.134, 0.055]	99.9(1.5)
C(3) [0.335, 0.485, 0.178]—V[0.250, 0.250, 0.156]—C(3)	[0.165, 0.015, 0.178]	165.7(0.6)
C(2) [0.185, 0.375, 0.047]—V[0.250, 0.250, 0.156]—N(4)	[0.304, 0.134, 0.055]	91.6(1.7)
V[0.250, 0.250, 0.156]—C(1) [0.333, 0.124, 0.286]—N(1)	[0.381, 0.048, 0.345]	172.8(1.0)
V[0.250, 0.250, 0.656]—C(2) [0.315, 0.375, 0.547]—N(2)	[0.339, 0.460, 0.470]	165.4(2.9)
V[0.250, 0.250, 0.156]—C(3) [0.165, 0.015, 0.178]—N(3)	[0.123, −0.112, 0.192]	177.5(1.2)
V[0.250, 0.250, 0.656]—N(4) [0.196, 0.134, 0.555]—O(2)	[0.149, 0.032, 0.489]	171.4(3.1)

Gothenburg Universities' Computing Centre using the programs DATAP2, LALS, DRF, and DISTAN,[20] respectively.

Infrared spectrum. As reported in the previous paper,[12] the infrared spectrum of $K_3V(CN)_5NO \cdot 2H_2O$, incompletely purified from potassium cyanide, showed peaks at 2110 cm^{-1} and 1530 cm^{-1} which could be attributed to the cyanide and nitrosyl stretching frequencies, respectively, of the complex ion. The infrared spectrum of a pure sample of $K_3V(CN)_5NO \cdot 2H_2O$, prepared from crystals picked out singly under the microscope, recorded on a Beckman IR 9 spectrophotometer, using the KBr technique, is reproduced in Fig. 1. Peaks
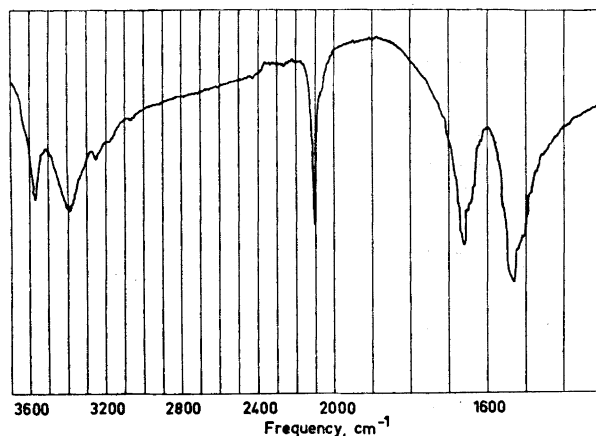
Fig. 1. The infrared spectrum of $K_3V(CN)_5NO \cdot 2H_2O$. (The monochromator was changed at 2000 cm^{-1}.)

corresponding to the cyanide and nitrosyl frequencies of the complex ion are seen to occur at 2105 cm^{-1} and 1530 cm^{-1}, respectively, the former frequency being somewhat higher and the latter somewhat lower than the corresponding values reported by Griffith, Lewis and Wilkinson[11] (2095 cm^{-1} and 1575 cm^{-1}, respectively). A qualitative comparison of the spectrum shown in Fig. 1 with that of sodium nitroprusside, registered under identical conditions, using the same amount of sample, showed the ratio of the nitrosyl and cyanide absorbances to be of the same order of magnitude in both compounds. Nor could any splitting of the nitrosyl peak be detected. There is thus no reason to believe that the vanadium complex ion contains more than one nitrosyl group, and the spectrum may be considered to provide independent confirmation of the results obtained in the cyanide analysis.

DISCUSSION OF THE STRUCTURE

It has been established that the crystals of potassium pentacyanonitrosyl-vanadate investigated have, without doubt, the formula $K_3V(CN)_5NO \cdot 2H_2O$, and, since they are presumably identical with the orange crystals prepared

by Griffith, Lewis and Wilkinson, it would seem that potassium pentacyano-nitrosylvanadate ought to be reformulated as a complex of vanadium(I) rather than of vanadium(−I), these oxidation states being based on coordination of nitric oxide as NO^+. The assignment of an oxidation state to the central metal atom in compounds in which there is appreciable metal-ligand double bonding can never, however, be more than purely formal.[6,23]
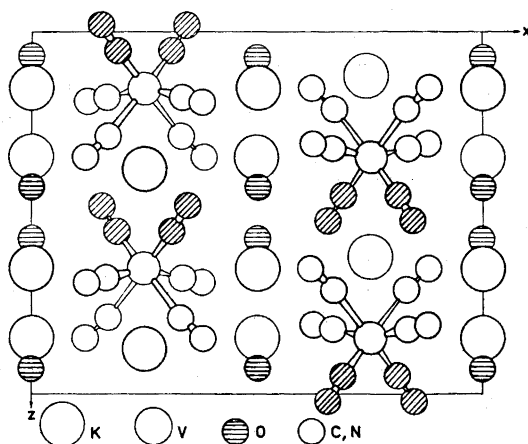
Fig. 2. Projection of the unit cell of $K_3V(CN)_5NO \cdot 2H_2O$ along [010]. The diagonally shaded rings represent the mean values of the statistically distributed cyanide and nitrosyl groups.

As may be seen from Fig. 2, the crystal structure of $K_3V(CN)_5NO \cdot 2H_2O$ is composed of potassium ions, disordered complex $V(CN)_5NO^{3-}$ ions and water molecules packed in a similar way to that found in $K_3Mn(CN)_5NO \cdot 2H_2O$.[9]

Owing to the disordered nature of the complex ions it is perhaps unwise to be too categorical concerning their geometry. The configuration of ligands about the central vanadium atom (cf. Fig. 3) appears, however, to be tetragonally distorted octahedral, the V−N−O bond being axially directed. The
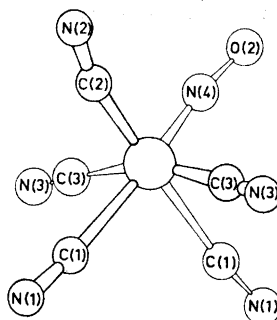
Fig. 3. The $V(CN)_5NO^{3-}$ complex ion.

$V-C$ bond distances range from 1.85 to 2.19 Å, the value 1.85 Å corresponding to the distance between vanadium and the statistically distributed cyanide group. The mean $V-C$ bond distance is thus 2.17 Å if $V-C(2)$ is excluded and 2.10 Å including $V-C(2)$. Both these values are somewhat longer than the sum of the covalent radii, 1.995 Å.[24] The $V-N$ distance is extremely short, 1.66 Å, and corresponds to an axial compression of 0.51 Å which is very much greater than the values found for $Fe(CN)_5NO^{2-}$, $Mn(CN)_5NO^{3-}$, and $Mo(CN)_5NO^{4-}$, i.e. 0.29 Å, 0.32 Å, and 0.18 Å, respectively. This would indicate a strong axial $V{\rightarrow}\pi^*NO$ transfer, which is also supported by the relatively long $N-O$ bond of 1.29 Å (cf. 1.21 Å in $Mn(CN)_5NO^{3-}$ and 1.23 Å in $Mo(CN)_5NO^{4-}$). The $V-C(3)-N(3)$ and $V-N(4)-O(2)$ linkages are linear, within the limits of experimental error, while $V-C(1)-N(1)$ is almost linear. The $V-C(2)-N(2)$ bond angle differs, however, appreciably from 180°, but, owing to the statistical location of $C(2)$, $N(2)$, too much weight should not perhaps be attached to this observation.

The geometry of the $V(CN)_5NO^{3-}$ ion can thus be considered to conform with the model for $M(CN)_5NO^{n-}$ suggested by Manoharan and Gray.[6] In $Fe(CN)_5NO^{2-}$ and $Mn(CN)_5NO^{3-}$ the metal atom is displaced from the centre of the octahedron in the direction of the nitrosyl group. This has been attributed[9] to the slight antibonding nature of the d_{xy} orbital resulting from $M-\pi CN$ interactions.[2,3,5,6] Both $Fe(CN)_5NO^{2-}$ and $Mn(CN)_5NO^{3-}$ have the ground state configuration[6] ....$(6e)^4(2b_2)^2$, whereas $V(CN)_5NO^{3-}$ would be expected to have the configuration ....$(6e)^4$. This means that in $V(CN)_5NO^{3-}$ the d_{xy} orbital is empty so that a displacement of the vanadium atom from the equatorial plane to the same extent as in $Mn(CN)_5NO^{3-}$ and $Fe(CN)_5NO^{2-}$ would not be expected. Unfortunately, however, it has not, owing to the statistical orientation of the $V(CN)_5NO^{3-}$ ions in $K_3V(CN)_5NO\cdot2H_2O$, been possible to decide whether the vanadium atom lies in the equatorial ligand plane or whether it is displaced very slightly towards the nitrosyl group.

The nitrosyl and cyanide bond lengths and infrared stretching frequencies for three transition metal pentacyanonitrosyl dihydrates are compared in Table 7. It is apparent that, whereas the cyanide bond lengths and infrared stretching frequencies are approximately the same in all the compounds, the

Table 7. Nitrosyl and cyanide bond lengths and infrared stretching frequencies for some transition metal pentacyanonitrosyl dihydrates. The C−N bond length is the mean of five values. [a] Ref. 25. [b] Ref. 7. [c] Ref. 26. [d] Ref. 9. [e] This work.

Compound	ν_{NO} cm^{-1}	(N−O) Å	ν_{CN} cm^{-1}	(C−N) Å	% π^*NO in 6e level.[6]
$Na_2Fe(CN)_5NO\cdot2H_2O$	1939 [a]	1.13 [b]	2173.4 [a] 2161.6 2156.7 2143.4	1.15 [b]	25
$K_3Mn(CN)_5NO\cdot2H_2O$	1725 [c]	1.21 [d]	2100 [c] 2060 2138	1.16 [d]	42
$K_3V(CN)_5NO\cdot2H_2O$	1530 [e]	1.29 [e]	2105 [e]	1.14 [e]	74

decrease in the nitrosyl stretching frequency observed in going from iron to vanadium is accompanied by a corresponding increase in the $N-O$ bond length. Manoharan and Gray have correlated [6] the decrease in ν_{NO} with an increased π^*NO contribution to the $6e$ orbital, this orbital thus being supposed to be predominantly $d_{xz}d_{yz}$ in the nitroprusside ion but predominantly π^*NO in the vanadium complex. Although all calculations involving the latter were based on the $V(CN)_5NO^{5-}$ ion, the long $N-O$ bond and the extremely short $V-N$ bond found in $K_3V(CN)_3NO \cdot 2H_2O$ might provide support for such a theory.

The K(1) potassium ions are surrounded by a distorted octahedral configuration of five nitrogen atoms and one oxygen atom at distances of 2.70 – 3.11 Å (cf. Table 5). As in $K_3Mn(CN)_5NO \cdot 2H_2O$ there are, however, five carbon atoms and one nitrogen atom at very slightly longer distances, so that K(1) can be regarded as having twelve nearest neighbours. Whereas in $K_3Mn(CN)_5NO \cdot 2H_2O$ the remaining potassium atoms were nine-coordinated, in $K_3V(CN)_5NO \cdot 2H_2O$ they are surrounded by five nitrogen and three oxygen atoms, at distances of 2.80 – 3.10 Å (cf. Table 5), in the form of a somewhat distorted square antiprism.

The short $O(1)-N(1)$, $O(1)-O(2)$, and $O(1)-N(2)$ distances of 2.89, 3.01, and 3.21 Å, respectively, are of hydrogen bond order, and it is probable that the complex ions are linked by means of hydrogen bonds to the water molecules as in $K_3Mn(CN)_5NO \cdot 2H_2O$.[9] Owing to the disordered orientation of the complex ions, no attempt has, however, been made to locate the hydrogen atoms.

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