

The Crystal Structure of Potassium Oxopentacyanovanadate(IV), $K_3[VO(CN)_5]$

SUSAN JAGNER and NILS-GÖSTA VANNERBERG

*Department of Inorganic Chemistry, University of Göteborg and Chalmers University of
Technology, P.O. Box, S-402 20 Göteborg 5, Sweden*

The crystal structure of potassium oxopentacyanovanadate(IV), $K_3[VO(CN)_5]$, has been determined by single crystal X-ray methods. $K_3[VO(CN)_5]$ crystallizes with a so-called OD structure and the crystal structure of $K_3[VO(CN)_5]$ can be characterised in terms of the family of structures represented by the OD groupoid symbol:

$$\begin{array}{c} P \quad m \quad 2_1 \quad (n) \\ \{c_2 \quad 2_1 \quad (n_{\frac{1}{2},1})\} \end{array}$$

Following an approximate determination of the superposition structure, the structure of the ordered orthorhombic form (MDO₁) has been determined from Weissenberg data and refined with least squares methods to an *R* value of 0.083, based on a total of 527 reflections. The superposition structure belongs to space group No. 36, *Cmc*2₁ with *A* = 4.2646 ± 0.0003 Å, *b* = 13.4700 ± 0.0012 Å, *c* = 9.7818 ± 0.0015 Å and *Z* = 2, whereas the MDO₁ structure belongs to space group No. 33, *Pna*2₁ with *a* = 13.4700 ± 0.0012 Å, *b* = 8.5292 ± 0.0006 Å, *c* = 9.7818 ± 0.0015 Å and *Z* = 4.

Potassium oxopentacyanovanadate(IV) contains discrete $[VO(CN)_5]^{3-}$ ions in which the V=O bond distance is 1.64 Å, the mean V-C(eq) bond distance is 2.14 Å and the V-C(ax) bond distance is 2.31 Å. The $[VO(CN)_5]^{3-}$ ion would thus appear to exhibit the distortion characteristic of many vanadyl(IV) complex ions, namely a long vanadium-ligand bond *trans* to the V=O²⁺ entity.

Although vanadium forms a wide range of complex cyanides,¹ few of these are well-characterised. In connection with an investigation on transition metal hexacyanides and cyanide complexes in progress at this department, the crystal structures of $K_2[V(CN)_6]$, $K_3[V(CN)_6]$ and $K_4[V(CN)_6]$ were of considerable interest. The crystal structure of $K_3[V(CN)_5NO] \cdot 2H_2O$,² previously thought to be $K_5[V(CN)_5NO] \cdot H_2O$,³ had already been determined in connection with a series of investigations on transition metal pentacyanonitrosyl ions.⁴⁻⁶

In their investigation on complex cyanides of vanadium, Bennett and Nicholls⁷ were unable to confirm the reported preparation⁸ of $K_2[V(CN)_6]$,

and instead obtained $K_3[VO(CN)_5]$. Similarly, they found the vanadium(III) cyanide to be more consistent with the formula $K_4[V(CN)_7] \cdot H_2O$ than $K_3[V(CN)_6]$.⁹ This was in accordance with the findings of Chadwick and Sharpe¹ who had formulated the scarlet compound as $K_4[V(CN)_7] \cdot 2H_2O$. The complex cyanide of vanadium(III) has now unequivocally been shown to be $K_4[V(CN)_7] \cdot 2H_2O$ in a recent crystal structure determination by Towns and Levenson.¹⁰ The crystal structure of $K_4[V(CN)_6]$, which is, like that of $K_3[VO(CN)_5]$, an OD structure, is now under investigation by the authors.

Although Bennett and Nicholls⁷ were the first to characterise the potassium salt of $[VO(CN)_5]^{3-}$, other oxopentacyanovanadates, namely those of caesium, tetramethylammonium, and tetraethylammonium, had been prepared previously.¹¹ For the purposes of comparison with $K_3[V(CN)_5NO] \cdot 2H_2O$, to which $K_3[VO(CN)_5]$ was expected to show structural similarities, and in order to obtain more information concerning V—C coordination distances in cyanovanadates, it was decided to investigate the crystal structure of $K_3[VO(CN)_5]$. The oxopentacyanovanadate(IV) ion has additional interest in that it contains the VO^{2+} entity which has been the subject of much attention in recent years.^{12,13}

PREPARATION AND ANALYSIS

Single crystals of potassium oxopentacyanovanadate(IV) were prepared from $VOSO_4 \cdot 5H_2O$, according to a slightly modified version of the original method due to Bennett and Nicholls.⁷ $VOSO_4 \cdot 5H_2O(s)$ was added to saturated aqueous potassium cyanide at room temperature, the resulting green solution was filtered from undissolved solid and methanol was slowly added. After re-filtration, the solution was allowed to crystallize in an argon-filled desiccator, green needle-shaped crystals of suitable size for single crystal X-ray work being deposited after a few weeks.

The potassium and vanadium contents were determined by means of atomic absorption spectroscopy using a Perkin Elmer 403 spectrometer. [Found: K 36.3; V 16.2. Calc. for $K_3[VO(CN)_5]$: K 37.4; V 16.2]. No attempt was made to determine the oxygen and cyanide contents. The infra-red spectrum, registered with a Beckman IR9 spectrophotometer, showed complete agreement with that given by Bennett and Nicholls.⁷ This, together with the experimental density and the results of the potassium and vanadium analyses and of the crystal structure determination, can leave little doubt that the compound investigated was indeed $K_3[VO(CN)_5]$.

OD STRUCTURE

Crystals of $K_3[VO(CN)_5]$ were mounted along the needle-axis in glass capillaries, and rotation photographs were recorded about this axis, which will in the following be assumed to coincide with the crystallographic c axis. The rotation photographs showed continuous streaks perpendicular to the layer lines, indicating a lack of periodicity in the c direction. It was thus apparent that potassium oxopentacyanovanadate(IV) crystallizes with a so-called OD structure,¹⁴ that is, a structure which can be described in terms of ordered layers stacked in a disordered manner in the c direction. Weissenberg photographs recorded for layer lines corresponding to a c axis of approximately 13.5 Å showed, apart from discrete reflections, truncated horizontal streaks (constant Y). The discrete or "family" reflections had orthorhombic symmetry

as did those parts of the streaks corresponding to a unit cell with the approximate dimensions: $a = 8.5 \text{ \AA}$, $b = 9.7 \text{ \AA}$, and $c = 13.5 \text{ \AA}$.

The following conditions of reflection were noted:

- (i) discrete reflections, hkl , for $h = 2H$
diffuse streaks, $hk\zeta$, for $h = 2H + 1$, where ζ can assume any value
- (ii) Hkl : $H + l = 2n$
- (iii) $hk0$: $h + k = 2n$
- (iv) $0kl$: $l = 2n$

According to (i) and (ii), the superposition structure,¹⁴ corresponding to the family reflections, Hkl , has an a axis of one-half 8.5 \AA and is B face-centred with $Bmmb$ and $Bm2_1b$ as possible space groups [*cf.* (ii) and (iii)]. Reflection condition (iii) indicates the presence of an n glide perpendicular to the c direction. This is independent of the mode of stacking of the layers and must therefore be a layer symmetry operation. Reflection condition (iv) is a special case of (ii) but also indicates the presence of a c glide perpendicular to the a axis in the larger orthorhombic cell, *i.e.* that with the approximate dimensions $a = 8.5 \text{ \AA}$, $b = 9.7 \text{ \AA}$, and $c = 13.5 \text{ \AA}$.

The information which could be obtained from the reflection conditions was thus that the space group of the superposition structure was $Bmmb$ or $Bm2_1b$, that one of the ordered extreme structures, *i.e.* so-called "structure of maximum degree of order," MDO,¹⁴ was orthorhombic, belonging to space group $Pc2_1n$, and that the unit cell of the former structure was related to that of the latter by a halving of the a axis. From this information it was then possible to determine the OD groupoid.¹⁴

The derivation of the OD groupoid may be illustrated by means of symbols as, for example, in Fig. 1a. This figure shows the packing of the layers L_0 , L_1 , and L_2 in the orthorhombic structure of maximum degree of order, MDO₁. According to reflection condition (iii), the minimum symmetry of a single layer is $P11(n)$. The B face-centring of the superposition structure implies, as will be seen later, that L_1 is related to L_0 by a translation of $\vec{a}/4$. In the ordered orthorhombic structure, MDO₁, there is a c glide plane perpendicular to the a axis [*cf.* reflection condition (iv)]. This means that the third layer, L_2 , must come directly under the first in the c direction and, moreover, that the minimum layer symmetry $P11(n)$ is insufficient, the true layer symmetry being $Pm2_1(n)$. The symmetry operations which convert L_0 into L_1 are then seen to be $0,1[c_2 2_1 n_{\frac{1}{2},1}]$, while L_1 is converted into L_2 by the operations $1,2[c_2 2_1 n_{\frac{1}{2},1}]$.

Potassium oxopentacyanovanadate(IV) can thus be said to crystallize as a family of structures whose symmetry is characterised by the OD groupoid symbol¹⁴

$$P \quad m \quad 2_1 \quad (n) \\ \{c_2 \quad 2_1 \quad (n_{\frac{1}{2},1}^-)\}$$

This symbol gives the total symmetry of any pair of consecutive layers, L_p and L_{p+1} .

Whereas the c_2 glide is a total symmetry operation in the ordered orthorhombic structure, it can be just a partial operation, as illustrated in

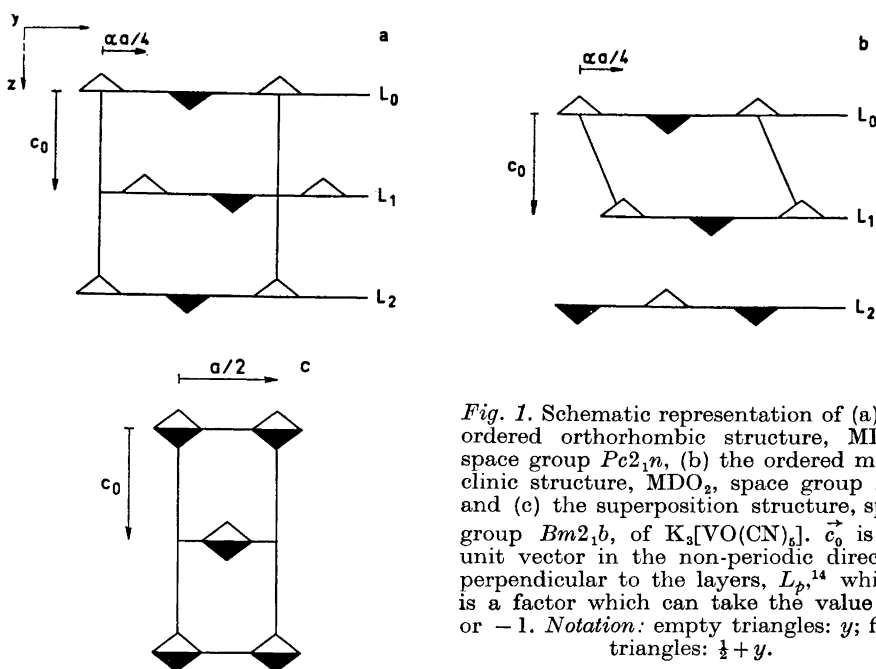


Fig. 1. Schematic representation of (a) the ordered orthorhombic structure, MDO_1 , space group $Pc2_1n$, (b) the ordered monoclinic structure, MDO_2 , space group $P2_1$, and (c) the superposition structure, space group $Bm2_1b$, of $K_3[VO(CN)_6]$. \vec{c}_0 is the unit vector in the non-periodic direction perpendicular to the layers, L_i ,¹⁴ while α is a factor which can take the value +1 or -1. Notation: empty triangles: y ; filled triangles: $\frac{1}{2} + y$.

Fig. 1b. This gives rise to a monoclinic structure which is the other ordered extreme structure (MDO_2).

In other words, successive layers may be regarded as being related to one another by the translation $\alpha \vec{a}/4$, where α can take the value +1 or -1. If α is alternately $= \pm 1$, an ordered orthorhombic structure (MDO_1) with the approximate unit cell dimensions $a = 8.5 \text{ \AA}$, $b = 9.7 \text{ \AA}$, and $c = 2c_0 = 13.5 \text{ \AA}$ is obtained. As is apparent from Fig. 1a, the space group of this structure is $Pc2_1n$ (conventional setting:¹⁵ No. 33, $Pna2_1$). An oblique stacking of the layers, *i.e.* $\alpha = +1$ (or $\alpha = -1$) only, as illustrated in Fig. 1b, results in a monoclinic structure (MDO_2), belonging to space group $P2_1$, whose unit cell is given by $\vec{a}_{\text{mon}} = \vec{a}$, $\vec{b}_{\text{mon}} = \vec{b}$, $c_{\text{mon}} = \frac{1}{4}\vec{a} + \vec{c}_0$ and $\beta \approx 107^\circ$. In principle, each crystal can exhibit a different sequence of α values so that the structure of a given crystal is most appropriately described in terms of contributions from the two ordered extreme structures.

The superposition structure is obtained by taking any given arrangement, translating through $\vec{a}/2$ and superimposing on the original arrangement (*cf.* Fig. 1c), *i.e.*

$$\hat{\rho}(x, y, z) = \frac{1}{2}[\rho(x, y, z) + \rho(x + \frac{1}{2}, y, z)]$$

where $\rho(x, y, z)$ represents the superposition structure and $\rho(x, y, z)$ the real structure. This structure is a fictitious structure which is the same for all members of the OD family. As is apparent from Fig. 1c, the space group of

this structure can unequivocally be derived to be $Bm2_1b$ (conventional setting:¹⁵ No. 36, $Cmc2_1$).

There is another OD groupoid which is consistent with the reflection conditions, namely

$$\begin{array}{c} P \quad m \quad m \quad (n) \\ \{c_2 \quad n_{2,\frac{1}{2}} \quad (n_{\frac{1}{2},1})\} \end{array}$$

The possibility that $K_3[VO(CN)_5]$ crystallized as a family of structures characterised by this OD groupoid could, however, be ruled out since the groupoid implies the centrosymmetric $Pcmn$ (conventional setting:¹⁵ No. 62, $Pnma$) as space group for the orthorhombic structure of maximum degree of order. As will be apparent from the atomic coordinates obtained in $Pna2_1$, this would necessitate statistical occupation for vanadium, which would be most unlikely to occur in an ordered extreme structure.

ACCURATE UNIT CELL PARAMETERS

Crystals of $K_3[VO(CN)_5]$ were picked out of their mother-liquor under a microscope, dried between filter papers and pulverised. Powder photographs

Table 1. X-Ray powder diffraction data for $K_3[VO(CN)_5]$. Guinier camera, $CuK\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$).

| $H k l$ | $10^5 \sin^2 \theta_{\text{obs}}$ | $10^5 \sin^2 \theta_{\text{calc}}$ | I_{calc} (relative scale) | I_{obs} |
|---------|-----------------------------------|------------------------------------|---------------------------------------|------------------|
| 0 2 0 | 1311 | 1308 | 63 | m |
| 0 0 2 | 2479 | 2480 | 68 | m |
| 1 1 0 | 3588 | 3589 | 208 | s |
| 0 2 2 | 3785 | 3788 | 714 | vs |
| 1 1 1 | 4211 | 4209 | 74 | m |
| 0 4 0 | 5231 | 5232 | 68 | m |
| 1 3 0 | 6202 | 6205 | 638 | vs |
| 1 3 1 | 6826 | 6825 | 666 | vs |
| 0 4 2 | 7714 | 7712 | 21 | vw |
| 1 3 2 | 8674 | 8685 | 153 | m-s |
| 1 1 3 | 9170 | 9170 | 335 | s |
| 0 0 4 | 9914 | 9921 | 60 | w |
| 0 6 1 | 12394 | 12391 | 47 | w |
| 2 0 0 | 13044 | 13049 | 160 | m-s |
| 1 5 2 | 13906 | 13917 | 169 | m-s |
| 0 6 2 | 14256 | 14252 | 115 | m |
| 0 4 4 | 15152 | 15153 | 46 | w |
| 2 2 2 | 16837 | 16837 | 109 | m |
| 2 4 0 | 18284 | 18281 | 47 | w |
| 2 4 1 | 18900 | 18901 | 8 | vvw |
| 1 7 1 | 19901 | 19904 | 36 | w |
| 0 8 0 | 20922 | 20927 | 10 | vvw |
| 2 6 1 | 25438 | 25440 | 22 | vw |
| 2 6 2 | 27302 | 27300 | 73 | m |
| 2 4 4 | 28206 | 28202 | 32 | vw |
| 3 3 1 | 32918 | 32923 | 21 | vw |

were taken in a Guinier focusing camera with $\text{CuK}\alpha_1$ radiation, using KCl as an internal standard ($a_{\text{KCl}} = 6.2919_4$ at 20°C ¹⁶). Twenty-six family reflections, Hkl , were indexed and used to refine the unit cell dimensions of the superposition structure with the program POWDER.¹⁷ The following values were obtained:

$$\begin{aligned} A &= 4.2646 \pm 0.0003 \text{ \AA} \\ b &= 13.4700 \pm 0.0012 \text{ \AA} \\ c &= 9.7818 \pm 0.0015 \text{ \AA} \\ V &= 562 \text{ \AA}^3 \end{aligned}$$

the axes being labelled in accordance with the conventional setting¹⁵ of $Bm2_1b$, *i.e.* $Cmc2_1$. Observed and calculated $\sin^2 \theta$ values are listed in Table 1.

The calculated density based on two formula units of $\text{K}_3[\text{VO}(\text{CN})_5]$ in the unit cell of the superposition structure is 1.86 g cm^{-3} . The experimental density as determined by the method of flotation using bromoform and carbon tetrachloride is 1.88 g cm^{-3} .

The unit cell dimensions of the ordered orthorhombic structure, MDO_1 , are thus $a = 13.4700 \pm 0.0012 \text{ \AA}$, $b = 8.5292 \pm 0.0006 \text{ \AA}$, $c = 9.7818 \pm 0.0015 \text{ \AA}$, and $V = 1124 \text{ \AA}^3$, the axes being labelled in accordance with space group No. 33, $Pna2_1$. Each unit cell contains four formula units of $\text{K}_3[\text{VO}(\text{CN})_5]$.

DETERMINATION OF THE SUPERPOSITION STRUCTURE

A crystal was mounted along the b axis (direction of non-periodicity when axes labelled in accordance with space groups No. 63,¹⁵ $Cmcm$ and No. 36,¹⁵ $Cmc2_1$, *i.e.* $A = 4.2646 \text{ \AA}$, $b = 13.4700 \text{ \AA}$, $c = 9.7818 \text{ \AA}$) and Weissenberg photographs of the layers $h0l - h7l$ were registered with $\text{CuK}\alpha$ radiation, using multiple film equi-inclination techniques. The intensities of the 121 discrete, or "family", reflections, Hkl , were estimated visually by comparison with a logarithmic intensity scale and the reflections from the different layers were scaled together approximately according to the times of exposure. Since the linear absorption coefficient for $\text{K}_3[\text{VO}(\text{CN})_5]$ in $\text{CuK}\alpha$ radiation is 177 cm^{-1} , there were appreciable absorption errors in the data.

After correction of the $H0l - H7l$ data for Lorentz and polarisation effects with the program DATAP2,¹⁷ a three-dimensional Patterson calculation (program DRF¹⁷) revealed the position of the vanadium atom and of one of the potassium atoms (K1). The approximate positions of the remaining atoms were obtained from successive electron density calculations (DRF¹⁷). Owing to the poor quality of the films, it was not at this stage possible to ascertain the symmetry of the diffuse streaks and thus unequivocally determine the OD groupoid. The superposition structure was therefore, for the time being, assumed to belong to the centrosymmetric space group No. 63,¹⁵ $Cmcm$, this space group occurring far more often than $Cmc2_1$ as space group for superposition structures.¹⁴ As mentioned above, once the OD groupoid had been determined, it was, however, possible to show that $Cmc2_1$ was the correct space group for the superposition structure.

After a few cycles of refinement of the positional and isotropic thermal parameters for all atoms, using the block diagonal least squares program BLOCK,¹⁷ an R value of 0.154 was obtained. Owing to the paucity of data and the overlap of atoms, this refinement was conducted in a series of small steps, only a few parameters being varied at a time, individual layer scale factors being refined alternately with an overall scale factor. The atomic scattering factors of Cromer and Waber¹⁸ were used for all atoms and each F_o value was weighted according to Cruickshank's weighting scheme,¹⁹ $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$, with $a = 10.0$, $c = 0.05$ and $d = 0$. The positional and thermal parameters thus obtained are listed in Table 2.

Table 2. Approximate positional and thermal parameters in the superposition structure of $K_3[VO(CN)_6]$ according to space group No. 63, $Cmcm$.

| Atom | Occupation No. | x | y | z | B (\AA^2) |
|------|----------------|------|-------|-------|------------------------|
| V | 4a | 0.50 | 0.000 | 0.000 | 5.0 |
| K(1) | 8f | 0.50 | 0.000 | 0.264 | 4.1 |
| K(2) | 8f | 0.25 | 0.500 | 0.470 | 4.6 |
| N(1) | 8f | 1.00 | 0.500 | 0.157 | 8.3 |
| N(2) | 8f | 0.25 | 0.500 | 0.420 | 8.7 |
| C(1) | 16h | 0.50 | 0.339 | 0.091 | 8.9 |
| C(2) | 8f | 0.25 | 0.500 | 0.445 | 4.6 |
| O(1) | 8f | 0.25 | 0.500 | 0.446 | 7.9 |

As will be apparent after the description of the ordered orthorhombic structure, there is considerable overlap of atoms in the superposition structure. It was not therefore considered worthwhile to refine the structure further or to attempt to locate the positions of the individual atoms more accurately by trial and error. The nitrogen position, N(1), for example, arises from the superposition of four different nitrogen equipoints [N(1) – N(4)] in the ordered orthorhombic structure. Similarly, the position C(1) is a crude approximation of the superposition of C(1) – C(4) in the ordered orthorhombic structure, the positions of these atoms when superimposed by no means eclipsing one another completely. For the same reason, the separation of C(2), N(2), and O(1) in the superposition structure is essentially arbitrary. Nor was it considered worthwhile, once the ordered orthorhombic structure had been determined, to re-determine the superposition structure in the correct space group, $Cmc2_1$. The superposition structure is, after all, essentially fictitious and has value only as a means to determining the true structure, approximate to one, or both, of the ordered extremes, since bond distances and angles derived from such a superposition structure must inevitably be mean values.

DETERMINATION AND REFINEMENT OF THE MDO_1 STRUCTURE

A new crystal was mounted along the a axis (direction of non-periodicity when axes labelled in accordance with space group No. 33,¹⁵ $Pna2_1$, *i.e.* $a =$

13.4700 Å, $b = 8.5292$ Å, and $c = 9.7818$ Å) and Weissenberg photographs of the layers $0kl - 12kl$ were recorded with $\text{MoK}\alpha$ radiation, using multiple film equi-inclination techniques. The intensities of the 292 family reflections, hkl , and of the streaks at the orthorhombic lattice points (*i.e.* corresponding to a unit cell of the dimensions $a = 13.4700$ Å, $b = 8.5292$ Å, and $c = 9.7818$ Å) were estimated visually by comparison with a logarithmic intensity scale. Owing to the way in which the data were collected, *i.e.* for an a axis of 13.4700 Å, it was not possible to estimate the intensities of the streaks at the monoclinic lattice points and thus also determine the MDO_2 structure.

For each of the layers $0kl - 12kl$, the reflections were divided into two groups, one comprising the family reflections, hkl , with $k = 2K$ and one the non-family reflections, hkl , with $k = 2K + 1$. Each group was assigned a separate scale factor, provision thus being made for twenty-six "layers", rather than thirteen. Approximate layer scale factors were calculated from exposure times and the data were corrected for Lorentz and polarisation effects with the program DATAP2.¹⁷ No correction was applied for absorption (linear absorption coefficient for $\text{K}_3[\text{VO}(\text{CN})_5]$ in $\text{MoK}\alpha$ radiation = 20.2 cm^{-1}).

A Patterson synthesis of the non-family data ($0kl - 12kl$, with $k = 2K + 1$, 235 reflections in all) was calculated with the program DRF.¹⁷ From such a calculation¹⁴ it is possible to obtain vectors between atoms within a single layer. The most dominant peaks, together with their relative heights and interpretation are listed in Table 3. It was thus possible to obtain the positions of the K(1) and K(2) potassium atoms relative to vanadium, these being a single position, K(1), in the superposition structure. Unfortunately no constructive information concerning the relative positions of K(3) and V could be obtained from the Patterson synthesis.

Table 3. Analysis of the most dominant vectors in the Patterson synthesis of the $0kl - 12kl$, $k = 2K + 1$ data for $\text{K}_3[\text{VO}(\text{CN})_5]$. Height of origin peak = 999.

| Peak No. | u | v | w | Peak height | Interpretation |
|----------|--------|--------|--------|-------------|----------------|
| 1 | 0.0000 | 0.5000 | 0.0891 | 374 | V - K(3) |
| 2 | 0.2998 | 0.0002 | 0.2170 | 160 | V - K(1) |
| 3 | 0.2637 | 0.5001 | 0.2875 | 151 | V - K(2) |
| 4 | 0.0000 | 0.0000 | 0.4160 | 318 | V - K(3) |
| 5 | 0.0000 | 0.5000 | 0.5000 | 459 | V - V |

In the superposition structure the vanadium atom was found to occupy the position $Cmcm: 4a$. Initially, therefore, V was placed in $Pna2_1: 4a$ with $x = \frac{1}{2}$, $y = \frac{1}{2}$, $z = 0$, which corresponds to the origin in the superposition structure. Successive electron density calculations (DRF¹⁷) using the signs obtained with the potassium and vanadium atoms in the following approximate positions:

| | | <i>x</i> | <i>y</i> | <i>z</i> |
|------|------------|----------|----------|----------|
| V | 4 <i>a</i> | 0.250 | 0.125 | 0.000 |
| K(1) | 4 <i>a</i> | 0.050 | 0.375 | 0.217 |
| K(2) | 4 <i>a</i> | 0.486 | 0.375 | 0.788 |
| K(3) | 4 <i>a</i> | 0.220 | 0.125 | 0.411 |

revealed the positions of the ligand atoms. The other possible positions of K(3) relative to V according to the superposition structure could be discarded since the above set yielded the lowest *R* value (*R* = 0.28). Once the ligand atoms had been determined it became, however, apparent that K(3) and V had been wrongly labelled. This was supported by the results of a few cycles of block diagonal least squares refinement, a much lower isotropic temperature coefficient being obtained for K(3) (1.2 Å²) than for V (4.4 Å²), both K(1) and K(2) having *B* ≈ 3.5 Å².

When the positions of all the atoms had been determined the structure was refined using the block diagonal least squares program, BLOCK.¹⁷ The atomic scattering factors of Cromer and Waber¹⁸ were used for all atoms and Cruickshank's weighting scheme¹⁹ was employed with *a* = 25.0, *c* = 0.02 and *d* = 0. At first all twenty-six scale factors were allowed to vary independently and, after a few cycles of refinement, the mean ratio between the scale factors for the non-family reflections and the family reflections for each layer was seen to be approximately 1.9. An attempt was then made to determine an approximate value for the percentage contribution from the MDO₁ structure in order to be able to hold this parameter constant in the subsequent refinement. The structure was therefore refined with the non-family data only. This refinement had to be carried out in small steps, a few parameters being varied at a time, owing to the paucity of the data (235 reflections). The layer scale factors thus obtained were then used to scale the data into two 'layers', one comprising all the family reflections and the other all the non-family reflections. Refinement based on this data set then yielded a scale factor between the *F*_o values of the non-family and the family reflections and thus an estimate of the percentage of MDO₁ structure in the actual crystal studied. This procedure was repeated, a scale factor of 1.89 being finally adopted. This would appear to correspond to a MDO₁ contribution of just over 50 %. (Attempts were made to find a crystal which had a structure better approximating that of either the MDO₁ or the MDO₂ structure. Those crystals investigated all yielded, however, approximately the same intensity distribution as the crystal described in this paper, *i.e.* they all contained roughly equal contributions from the two MDO structures.)

The data were then re-stored in the thirteen layers 0*kl*–12*kl*, the *F*_o values of all the non-family reflections being multiplied by 1.89. Individual layer scale factors, atomic parameters and isotropic temperature coefficients were refined with the program BLOCK.¹⁷ For the final cycles of refinement the full matrix least squares program LALS¹⁷ was used with an overall scale factor and anisotropic temperature coefficients for K(1), K(2), K(3) and V. The refinement was terminated when the parametral shifts for the majority of the atoms were less than 10 % of the standard deviations, those for *z*_{N(3)} and *z*_{C(3)} being approximately 20 % of the corresponding e.s.d.'s. A final *R*

Table 4. Atomic coordinates, expressed as fractions of the cell edges, and thermal parameters for $K_3[VO(CN)_4]$. The estimated standard deviations of the parameters ($\times 10^4$; $\times 10^3$ for B) are given within parentheses. Anisotropic temperature coefficients are of the form $\exp\{-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}\}$ and isotropic temperature coefficients of the form $\exp\{-B(\sin^2\theta/\lambda^2)\}$.

| Atom | x | y | z | B (\AA^2) | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|------|------------|------------|------------|------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| V | 0.2251(3) | 0.1279(6) | 0.4226(6) | | 0.0038(2) | 0.0076(4) | 0.0072(3) | 0.0000(7) | 0.0021(5) | 0.0017(22) |
| K(1) | 0.0197(4) | 0.3672(24) | 0.2171(9) | | 0.0044(4) | 0.0087(12) | 0.0119(6) | 0.0012(12) | -0.0050(7) | -0.0073(24) |
| K(2) | 0.4899(5) | 0.3608(21) | 0.7411(8) | | 0.0047(4) | 0.0057(17) | 0.0130(7) | 0.0010(9) | -0.0003(6) | 0.0015(17) |
| K(3) | 0.2534(4) | 0.1256(9) | 0.0000 | | 0.0047(3) | 0.0101(6) | 0.0094(5) | -0.0003(12) | 0.0007(6) | 0.0034(25) |
| N(1) | 0.3986(21) | 0.4013(31) | 0.3868(25) | 4.95(57) | | | | | | |
| N(2) | 0.4139(19) | 0.3542(50) | 0.0624(22) | 3.83(55) | | | | | | |
| N(3) | 0.0864(18) | 0.3933(51) | 0.5565(22) | 3.84(53) | | | | | | |
| N(4) | 0.1004(20) | 0.3535(44) | 0.8989(28) | 5.00(53) | | | | | | |
| N(5) | 0.3332(31) | 0.1306(46) | 0.7303(58) | 4.41(38) | | | | | | |
| C(1) | 0.3360(21) | 0.2988(27) | 0.3951(25) | 3.34(48) | | | | | | |
| C(2) | 0.3678(21) | 0.4478(30) | 0.0042(30) | 2.75(43) | | | | | | |
| C(3) | 0.1332(22) | 0.3027(30) | 0.5207(28) | 3.08(50) | | | | | | |
| C(4) | 0.1610(26) | 0.4523(34) | 0.9091(41) | 3.90(53) | | | | | | |
| C(5) | 0.2979(31) | 0.1315(44) | 0.6359(42) | 3.83(40) | | | | | | |
| O(1) | 0.1739(13) | 0.1325(29) | 0.2703(15) | 3.54(29) | | | | | | |

Table 5. Continued.

| | | | | | | | | | | | | | | | | | | | |
|---|----|----|--------|----|----|----|--------|----|----|----|--------|----|----|----|--------|---|----|----|--------|
| 3 | - | 5 | 1.56* | 3 | - | 4 | -3.02* | 7 | 17 | 18 | 1.64 | 6 | 15 | 15 | -2.53 | 2 | 13 | 13 | 2.34 |
| 4 | - | 10 | -2.24* | | 12 | 0 | L | 8 | 13 | 14 | 2.67 | 7 | - | 9 | 1.88* | 3 | 14 | 14 | -1.16 |
| 5 | 15 | 13 | 1.39 | 4 | 31 | 29 | 0.21 | 9 | 12 | 11 | -0.46 | 8 | - | 10 | 2.03* | 4 | - | 6 | 0.93* |
| 6 | - | 8 | 2.94* | 5 | - | 5 | 2.54* | 10 | - | 3 | 0.30* | 9 | - | 5 | 2.73* | 5 | - | 3 | -2.85* |
| 7 | - | 3 | 2.31* | 6 | 13 | 12 | 2.53 | | | | | 10 | - | 7 | 2.33* | 6 | - | 12 | 0.77* |
| 8 | - | 9 | 2.50* | 7 | 17 | 17 | -1.50 | 0 | 12 | 8 | L | | | | | 7 | - | 9 | -1.17* |
| | 11 | 7 | L | 8 | 13 | 13 | -0.45 | 1 | 14 | 15 | 2.11 | 1 | 12 | 3 | L | 8 | - | 7 | -1.11* |
| 0 | - | 3 | 3.14* | 9 | 14 | 15 | 2.62 | 2 | - | 5 | 1.53* | 2 | 18 | 19 | -1.17 | | 12 | 7 | L |
| 1 | - | 10 | -1.42* | 10 | - | 4 | -2.36* | 3 | 23 | 22 | -0.19 | 3 | - | 7 | 0.77* | 0 | - | 3 | 3.14* |
| 2 | 17 | 17 | 2.33 | 11 | - | 8 | 2.90* | 4 | 20 | 20 | 0.28 | 4 | 18 | 15 | -2.59 | 1 | - | 7 | -2.13* |
| 3 | - | 2 | -2.46* | | 12 | 4 | L | 5 | - | 1 | -1.15* | 5 | - | 9 | -0.66* | 2 | 13 | 11 | 2.10 |
| 4 | 19 | 16 | 0.77 | 0 | 28 | 28 | 3.14 | 6 | - | 4 | 0.44* | 6 | 15 | 16 | -2.67 | 3 | - | 6 | -1.99* |
| 5 | - | 7 | -1.91* | 1 | 25 | 29 | -1.06 | 7 | 11 | 11 | -1.52 | 7 | - | 5 | 2.02* | 4 | - | 7 | 0.51* |
| 6 | - | 7 | 0.41* | 2 | 6 | 8 | -1.36 | 8 | 9 | 9 | -0.44 | 8 | - | 9 | 2.03* | 5 | - | 4 | -2.60* |
| | 11 | 9 | L | 3 | 43 | 41 | 2.98 | 8 | 12 | 1 | L | 9 | - | 5 | 2.12* | 6 | - | 8 | 0.55* |
| 0 | - | 3 | -3.14* | 4 | 35 | 34 | -2.86 | 3 | 14 | 16 | 1.88 | | | | | 7 | - | 5 | -1.64* |
| 1 | - | 8 | -1.22* | 5 | - | 2 | 0.89* | 4 | 11 | 11 | -2.46 | 0 | - | 8 | 3.14* | | | | |
| 2 | - | 4 | 2.12* | 6 | - | 4 | -1.78* | 5 | - | 5 | 0.20* | 1 | 14 | 16 | -1.96 | | | | |

Table 6. Bond distances (Å) and angles (°) within the $[\text{VO}(\text{CN})_5]^{3-}$ complex ion. Standard deviations of the distances ($\times 10^3$) and the angles are given within parentheses.

Distances

| | | | |
|--------|-----------|-----------|-----------|
| V—C(1) | 2.102(26) | C(1)—N(1) | 1.220(37) |
| V—C(2) | 2.136(28) | C(2)—N(2) | 1.160(44) |
| V—C(3) | 2.161(28) | C(3)—N(3) | 1.057(45) |
| V—C(4) | 2.148(32) | C(4)—N(4) | 1.178(46) |
| V—C(5) | 2.306(41) | C(5)—N(5) | 1.039(68) |
| V—O(1) | 1.642(16) | | |

Angles

| | | | |
|-------------|------------|-------------|------------|
| C(1)—V—C(2) | 164.1(1.1) | C(3)—V—C(5) | 80.4(1.2) |
| C(1)—V—C(3) | 89.3(1.0) | C(3)—V—O(1) | 98.4(1.1) |
| C(1)—V—C(4) | 88.1(1.1) | C(4)—V—C(5) | 76.2(1.4) |
| C(1)—V—C(5) | 78.7(1.2) | C(4)—V—O(1) | 105.1(1.3) |
| C(1)—V—O(1) | 99.6(1.0) | C(5)—V—O(1) | 177.9(1.3) |
| C(2)—V—C(3) | 89.7(1.0) | V—C(1)—N(1) | 176.0(2.2) |
| C(2)—V—C(4) | 86.6(1.2) | V—C(2)—N(2) | 172.5(2.5) |
| C(2)—V—C(5) | 85.5(1.3) | V—C(3)—N(3) | 173.0(2.6) |
| C(2)—V—O(1) | 96.3(1.1) | V—C(4)—N(4) | 178.0(3.1) |
| C(3)—V—C(4) | 156.5(1.3) | V—C(5)—N(5) | 177.6(4.1) |

value of 0.083 was obtained for the complete data set ($R = 0.080$ for the family reflections and 0.086 for the non-family reflections). The corresponding atomic parameters are given in Table 4 and observed and calculated structure factors in Table 5. The high F_c values corresponding to some of the unobserved non-family reflections are acceptable, bearing in mind the size of the scale factor by which the F_o values of all the non-family reflections have been multiplied. Bond distances and angles within the $[\text{VO}(\text{CN})_5]^{3-}$ ion, calculated with the program DISTAN,¹⁷ are given in Table 6.

The proposed structure was tested by means of a three-dimensional $F_o - F_c$ Fourier synthesis (DRF¹⁷) which showed a maximum electron density of $1.4 \text{ e}/\text{Å}^3$.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The ordered orthorhombic structure of $\text{K}_3[\text{VO}(\text{CN})_5]$ is composed of potassium ions and distorted octahedral $[\text{VO}(\text{CN})_5]^{3-}$ ions packed as illustrated in Fig. 2. If the axes are labelled in accordance with $Pna2_1$, the direction of non-

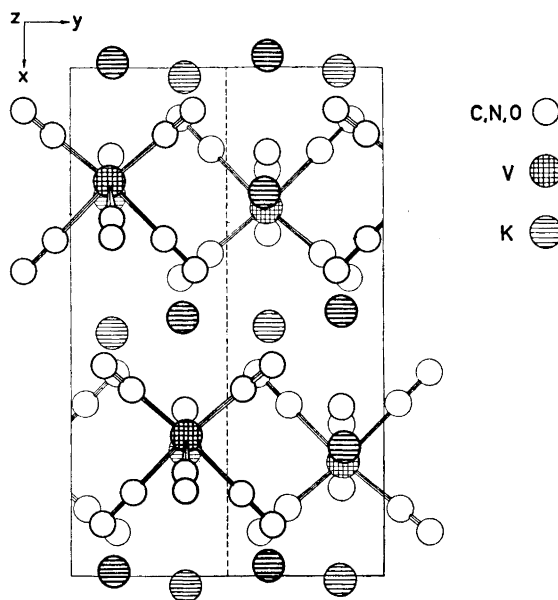


Fig. 2. Projection of the unit cell of the MDO₁ structure of K₅[VO(CN)₆] along [001].

periodicity in the actual crystals coincides with the x direction and the ordered layers are thus perpendicular to this direction. The first such layer, L_0 , (*cf.* Fig. 1a) in the unit cell of the ordered orthorhombic structure, may be visualized as comprising the two $[\text{VO}(\text{CN})_5]^{3-}$ ions and the two K(3) potassium ions in the upper half of the unit cell shown in Fig. 2, together with the K(1) and K(2) potassium ions, four in all, directly above and below these complex ions in the x direction. The second layer, which is identical with the first, is related to the latter by a translation of $\vec{b}/4$, while the third layer is related to the second by a translation of $-\vec{b}/4$ and lies directly under the first layer in the x direction (*cf.* Fig. 1a). Two of the four K(1) and K(2) potassium ions belonging to the third layer are visible at the lower edge of the unit cell illustrated in Fig. 2.

The superposition structure can be visualized by taking the left-hand half of the unit cell depicted in Fig. 2, translating through $\vec{b}/2$ and superimposing it on the right-hand half of the unit cell. The above-mentioned overlap of atoms in the superposition structure then becomes apparent.

As may be seen from Table 6, the $[\text{VO}(\text{CN})_5]^{3-}$ ion has approximately C_{4v} symmetry and shows the distortion characteristic of many vanadyl(IV) complex ions,^{12,13} namely a long vanadium-ligand bond *trans* to the $\text{V}=\text{O}^{2+}$ entity. The $\text{V}-\text{C}(\text{eq})$ bonds range from 2.10 to 2.16 Å with a mean distance of 2.14 Å while the $\text{V}-\text{C}(\text{ax})$ bond is 2.31 Å. The $\text{C}-\text{N}$ distances within the equatorial cyanide groups range from 1.06 to 1.22 Å with a mean distance of 1.15 Å

and the axial C–N distance is 1.04 Å. All the V–C–N linkages are linear within the limits of the standard deviations (3σ).

The spread in the V–C(ax) and C–N bond lengths is rather large, as are the standard deviations of all the bond distances and angles. This ought not to be interpreted in terms of severe distortions from the ideal C_{4v} symmetry, but instead as indicative of a slightly lower accuracy and precision in the determination than is usual, as a consequence of the disorder. That this is necessarily the case is apparent on consideration of Fig. 2 and of the superposition structure derived from this figure. The family reflections, hkl , which yield the superposition structure, are obviously very insensitive to the positions of the individual ligand atoms. The intensities of the non-family reflections, on the other hand, are difficult to determine accurately owing to asymmetric intensity fluctuations along the streaks and to the fact that most of these reflections are very weak, since the contribution from the ordered orthorhombic structure to the structure of the crystal is not more than approximately 50%. The mean V–C(eq) bond length of 2.14 Å, is, however, in good agreement with the V–C bond lengths found in $K_4[V(CN)_7] \cdot 2H_2O$,¹⁰ *i.e.* mean V–C(eq) = 2.149 Å and mean V–C(ax) = 2.144 Å, and is slightly, though not significantly, shorter than the mean V–C distance (2.17 Å) obtained in $K_3[V(CN)_5NO] \cdot 2H_2O$.

The V=O bond length is 1.64 ± 0.02 Å, which agrees well with corresponding distances in other vanadyl(IV) compounds, *e.g.* $[VOSO_4(H_2O)_4] \cdot H_2O$ (1.591 ± 0.005 Å),²⁰ $VOSO_4$ (1.594 ± 0.017 Å),²¹ and $(NH_4)_2[VO(NCS)_4(H_2O)] \cdot 4H_2O$ (1.62 ± 0.06 Å).²² The slight, though not significant, increase in the V=O bond length in the compounds $[VOSO_4(H_2O)_4] \cdot H_2O$, $(NH_4)_2[VO(NCS)_4(H_2O)] \cdot 4H_2O$, and $K_3[VO(CN)_5]$ is in accordance with a decrease in $\nu(V=O)$, as is seen from Table 7. Several attempts have been made^{12,12,23,24} to correlate the

Table 7. V=O bond lengths and infra-red stretching frequencies for some vanadyl(IV) compounds.

| Compound | Ligand atoms other than vanadyl oxygen | $\nu(V=O)$ cm^{-1} | $d(V=O)$ Å | Ref. |
|---|--|-------------------------|-------------------|-----------------|
| $[VOSO_4(H_2O)_4] \cdot H_2O$ | O(H_2O , SO_4^{2-}) | 1003, 975 | 1.591 ± 0.005 | 20,23 |
| $(NH_4)_2[VO(NCS)_4(H_2O)] \cdot 4H_2O$ | N(NCS^-), O(H_2O) | 982, 963 | 1.62 ± 0.06 | 22 |
| $K_3[VO(CN)_5]$ | C(CN^-) | 929 | 1.64 ± 0.02 | 7, present work |

V=O stretching frequency with the environment of the VO^{2+} entity, but, although there would seem to be an obvious correlation for the three compounds cited in Table 7, the general validity of such a correlation would appear to be doubtful.¹²

In order to ascertain whether or not the vanadium atom lies in the equatorial ligand plane, the least squares plane through the four equatorial carbon atoms, C(1), C(2), C(3), and C(4), coordinated to the vanadium atom in $x=$

0.2251, $y = 0.1279$, $z = 0.4226$, was calculated with the program PLANEFIT.¹⁷ The distances of the defining atoms and the vanadium atom from this plane, whose equation (Cartesian coordinates, Å) is

$$-0.3648 X - 0.0011 Y - 0.9311 Z + 5.3256 = 0$$

are $d_{C(1)} = 0.07$ Å, $d_{C(2)} = 0.08$ Å, $d_{C(3)} = -0.07$ Å, $d_{C(4)} = -0.07$ Å, and $d_V = 0.37$ Å. The vanadium atom would thus appear to be displaced slightly, more towards the vanadyl oxygen atom in $[\text{VO}(\text{CN})_5]^{3-}$ than in $[\text{VOSO}_4(\text{H}_2\text{O})_4]$, where the corresponding displacement was found to be 0.28 Å.²⁰

Several theoretical models have been suggested for vanadyl complexes and, in particular, for the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ ion, that due to Ballhausen and Gray²⁵ being most often quoted. Since the molecular orbital description of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ closely resembles that of $[\text{Me}(\text{CN})_5\text{NO}]^{n-}$, where $\text{Me} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$,²⁶⁻²⁸ it is perhaps profitable to compare the geometries of $[\text{VO}(\text{CN})_5]^{3-}$ and $[\text{V}(\text{CN})_5\text{NO}]^{3-}$ in the light of these models. For $[\text{V}(\text{CN})_5\text{NO}]^{3-}$, molecular orbital calculations^{27,28} indicate a strong axial $\text{V} \rightarrow \pi^*\text{NO}$ transfer, which is supported by the extremely short $\text{V}-\text{N}$ distance (1.66 Å) and long $\text{N}-\text{O}$ distance (1.29 Å) obtained for $\text{K}_3[\text{V}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$.² In $[\text{VO}(\text{CN})_5]^{3-}$, by analogy with $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, there is also a strong axial metal-ligand π bond, but this is essentially an oxygen to vanadium transfer. $[\text{VO}(\text{CN})_5]^{3-}$ would thus be expected to have the ground state configuration $\dots(e_\pi)^4(2b_2)^1$, whereas in $[\text{V}(\text{CN})_5\text{NO}]^{3-}$ the $2b_2$ orbital is empty, the ion presumably having the ground state configuration $\dots(6e)^4$. It is interesting, in the light of these ground state configurations, to note that, whereas VO^{2+} ions are generally regarded as $\text{V}(\text{IV})$ or d^1 species, $[\text{V}(\text{CN})_5\text{NO}]^{3-}$ is normally regarded as a d^4 or $\text{V}(\text{I})$ ion. This clearly illustrates that the assignment of an oxidation state to the central metal atom in complex ions in which there is appreciable metal-ligand double bonding must essentially be purely formal.

Another feature of the $[\text{Me}(\text{CN})_5\text{NO}]^{n-}$ ions is that the central metal atom is displaced approximately 0.2 Å (0.16 Å in $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ ⁵ and 0.2 Å in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ ²⁹) from the equatorial ligand plane towards the nitrosyl group. This has been interpreted⁵ in terms of the weak antibonding rather than nonbonding nature of the $2b_2$ (d_{xy}) orbital as a result of the equatorial $\text{M}-\pi(\text{CN})$ and $\text{M}-\pi^*(\text{CN})$ interactions. Since the $2b_2$ orbital is empty in $[\text{V}(\text{CN})_5\text{NO}]^{3-}$, a smaller displacement was expected in this case, but, owing to the disorder, it was not, however, possible to draw any conclusions concerning this feature from the crystal structure of $\text{K}_3[\text{V}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$.² In $\text{K}_3[\text{VO}(\text{CN})_5]$ the displacement of the vanadium atom from the equatorial ligand plane would appear to be slightly larger than in $[\text{VO}(\text{SO}_4)(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$. This could be interpreted in terms of a slightly more antibonding $2b_2$ (d_{xy}) orbital in $[\text{VO}(\text{CN})_5]^{3-}$ as compared with the approximately nonbonding b_2 orbital in $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$,²⁵ and presumably also in $[\text{VO}(\text{SO}_4)(\text{H}_2\text{O})_4]$.²⁶

The $\text{K}(3)$ potassium ion is octahedrally coordinated by five nitrogen atoms and an oxygen atom at distances of 2.85–3.01 Å. There are five carbon atoms only slightly more remote so that the $\text{K}(3)$ potassium ion can be regarded as having eleven nearest neighbours, *i.e.* as being octahedrally coordinated by five cyanide groups and an oxygen atom. The $\text{K}(1)$ and $\text{K}(2)$ potassium ions are, on the other hand, each surrounded by six cyanide groups in the form

of a somewhat distorted trigonal prism, two of the prism faces being capped by a seventh cyanide group and an oxygen atom, respectively. A similar potassium-ligand coordination polyhedron was found in $K_3[Mn(CN)_5NO] \cdot 2H_2O$,⁵ while in $K_3[V(CN)_5NO] \cdot 2H_2O$ ² the potassium ions were octahedrally and square antiprismatically coordinated.

Acknowledgements. The authors thank Professor Georg Lundgren for the interest he has shown in this work and for facilities placed at their disposal. They are indebted to Mrs. Margareta Biéth for skilful help with the collection of the intensity data and to Ing. Kerstin Åren for carrying out the atomic absorption analyses. Financial support from the *Swedish Natural Science Research Council* (Contract No. 2286-18) is gratefully acknowledged.

REFERENCES

1. Chadwick, B. M. and Sharpe, A. G. *Advan. Inorg. Chem. Radiochem.* **8** (1966) 83.
2. Jäger, S. and Vannerberg, N.-G. *Acta Chem. Scand.* **24** (1970) 1988.
3. Griffith, W., Lewis, J. and Wilkinson, G. *J. Chem. Soc.* **1959** 1632.
4. Vannerberg, N.-G. *Acta Chem. Scand.* **20** (1966) 1571.
5. Tullberg, A. and Vannerberg, N.-G. *Acta Chem. Scand.* **21** (1967) 1462.
6. Svedung, D. H. and Vannerberg, N.-G. *Acta Chem. Scand.* **22** (1968) 1551.
7. Bennett, B. G. and Nicholls, D. *J. Chem. Soc. A* **1971** 1204.
8. Yakimach, A. *Compt. Rend.* **191** (1930) 789.
9. Locke, J. and Edwards, G. H. *Amer. Chem. J.* **20** (1898) 594.
10. Towns, R. L. R. and Levenson, R. A. *J. Am. Chem. Soc.* **94** (1972) 4345.
11. Selbin, J. and Holmes, L. H. *J. Inorg. Nucl. Chem.* **24** (1962) 1111.
12. Selbin, J. *Coord. Chem. Rev.* **1** (1966) 293.
13. Selbin, J. *Chem. Rev.* **65** (1965) 153.
14. Dornberger-Schiff, K. *Lehrbuch über OD-Strukturen*, Akademie-Verlag, Berlin 1966.
15. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1959.
16. Hambling, P. *Acta Cryst.* **6** (1953) 98.
17. Modified and in use at this Department, *DATAP2* was originally written by Coppens, P., Leiserowitz, L. and Rabinowich, D., *LALS* by Gantzel, R., Sparks, K. and Trueblood, K., *DRF* and *DISTAN* by Zalkin, A., *POWDER* by Lindqvist, O. and Wengelin, F., *BLOCK* by Lindgren, O. and *PLANEFIT* by Wengelin, F.
18. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
19. Cruickshank, D. W. J. *The Equations of Structure Refinements*, Glasgow 1964.
20. Ballhausen, C. J., Djurinskij, B. F. and Watson, K. J. *J. Am. Chem. Soc.* **90** (1968) 3305.
21. Kierkegaard, P. and Longo, J. M. *Acta Chem. Scand.* **19** (1965) 1906.
22. Hazell, A. C. *J. Chem. Soc.* **1963** 5745.
23. Selbin, J., Holmes, L. H. and McGlynn, S. P. *J. Inorg. Nucl. Chem.* **25** (1963) 1359.
24. Garvey, R. G. and Ragsdale, R. O. *J. Inorg. Nucl. Chem.* **29** (1967) 745.
25. Ballhausen, C. J. and Gray, H. B. *Inorg. Chem.* **1** (1962) 111.
26. Manoharan, P. T. and Gray, H. B. *J. Am. Chem. Soc.* **87** (1965) 3340.
27. Manoharan, P. T. and Gray, H. B. *Inorg. Chem.* **5** (1966) 823.
28. Fenske, R. F. and DeKock, R. L. *Inorg. Chem.* **11** (1972) 437.
29. Manoharan, P. T. and Hamilton, W. C. *Inorg. Chem.* **2** (1963) 1043.

Received June 8, 1973.