

# The Crystal Structure of Potassium Hexacyanovanadate(II), $K_4[V(CN)_6]$

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The crystal structure of potassium hexacyanovanadate (II),  $K_4[V(CN)_6]$ , has been determined from X-ray single crystal diffractometer data.  $K_4[V(CN)_6]$  crystallizes with a disordered structure characterised by the OD groupoid symbol:

$Pma(b)$

$\{c_2 n_2, \frac{1}{2} (n_4, 1)\}$

The unit cell of the ordered monoclinic form (MDO<sub>2</sub>) has the dimensions:  $a = 8.5770(6)$  Å,  $b = 21.5271(26)$  Å,  $c = 7.5270(8)$  Å, and  $\beta = 106.55(1)^\circ$  and belongs to space group  $P2_1/a$ , with  $Z = 4$ . Following a determination of the superposition structure, the MDO<sub>2</sub> structure was determined and refined to  $R = 0.053$  ( $R_w = 0.055$ ), using full-matrix least squares refinement based on 757 independent reflections, the positional and thermal parameters being constrained so as to comply with the partial symmetry operations of the OD groupoid symbol. The complex ion has octahedral symmetry with mean V—C and C—N bond lengths of 2.161(4) and 1.153(7) Å, respectively.

Variations in  $\sigma$  and  $\pi$  contributions to metal-ligand bonds in transition metal hexacyanides and cyanocomplexes have been the subject of much attention in recent years. It ought to be possible to clarify such variations by correlating the bond lengths and geometries of the complex ions, obtained from crystal structure determinations, and information concerning the charges on the central metal atoms and ligands, obtained from X-ray photoelectron spectra, with existing semi-empirical molecular orbital calculations.<sup>1-5</sup>

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In connection with such an investigation, in progress at the Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, the crystal structures of the hexacyanovanadates were of interest. These complexes were originally thought to have the formulae  $K_2[V(CN)_6]$ ,  $K_3[V(CN)_6]$ , and  $K_4[V(CN)_6]$ .  $K_3[V(CN)_6]$  has, however, been shown<sup>6</sup> to be  $K_3[VO(CN)_6]$ , whose crystal structure has recently been determined.<sup>7</sup> It was suspected<sup>2,8,8-11</sup> that  $K_3[V(CN)_6]$  was in fact  $K_4[V(CN)_7] \cdot 2H_2O$ , final confirmation being provided by a crystal structure determination by Towns and Levenson.<sup>12,13</sup> The crystal structure of the last member of the series,  $K_4[V(CN)_6]$ , has now been determined. Although yellow crystals of potassium hexacyanovanadate(II) have been reported<sup>8-11</sup> to have the formula  $K_4[V(CN)_6] \cdot 3H_2O$ , the compound studied in this investigation had the formula  $K_4[V(CN)_6]$ , which is in accordance with the findings of Bennett and Nicholls.<sup>6</sup>

## PREPARATION AND ANALYSIS

Potassium hexacyanovanadate(II) was prepared according to a modification of the method described by Bennett and Nicholls.<sup>6</sup>  $VCl_3$  (5.5 g) was dissolved in 0.01 M HCl (15 ml) and the solution was passed through a zinc reductor (20 mesh). The resulting violet solution was allowed to drop, under an atmosphere of hydrogen, into a saturated solution of potassium cyanide, at a rate of approximately 1 drop/s. The cyanide solution was stirred and cooled to 0 °C, a yellow powder being deposited. This was filtered off, washed with methanol, and dissolved in 3 M potassium cyanide, the solution then being set aside to crystallize in an argon-filled desiccator. After a few days, yellow, needle-shaped crystals of suitable size for single

crystal X-ray work were deposited. Although aqueous solutions of potassium hexacyanovanadate(II) decompose rapidly on exposure to air, the solid substance can be stored for several weeks in dry air. X-Ray photoelectron spectroscopic studies suggest that the decomposition product is  $K_3[VO(CN)_6]$ .

The potassium and vanadium contents were determined by means of atomic absorption spectroscopy, using a Perkin Elmer 403 spectrometer. The cyanide content was determined by potentiometric titration with  $Ag^+$ . [Found: K 43.8; V 13.9; CN 43.1. Calc. for  $K_4[V(CN)_6]$ : K 43.0; V 14.0; CN 43.0].

The infra-red spectrum, registered with a Beckman IR 9 spectrophotometer, agreed well with that given by Bennett and Nicholls.<sup>6</sup> That the compound studied had the formula  $K_4[V(CN)_6]$  and not  $K_4[V(CN)_6] \cdot 3H_2O$  is evident from the results of the crystal structure determination, the infra-red spectrum, and the chemical analysis.

### OD STRUCTURE

Rotation photographs of crystals mounted along the  $a$  axis showed layer lines composed of

discrete reflections for  $A \approx 4.29 \text{ \AA}$  and diffuse streaks corresponding to  $a = 2A \approx 8.58 \text{ \AA}$ . It was thus apparent that  $K_4[V(CN)_6]$  crystallized with a disordered crystal structure of OD type,<sup>14</sup> i.e. a structure which consists of ordered, equivalent layers whose mode of stacking is disordered. Weissenberg photographs of diffuse layer lines showed that there were intensity maxima on the streaks with monoclinic symmetry which would necessitate a doubling of the  $c$  axis corresponding to the discrete reflections, i.e.  $c_{app} = 2c \approx 28.86 \text{ \AA}$ .

If the  $c$  direction is defined as that of non-periodicity, the conditions limiting possible reflection for  $K_4[V(CN)_6]$  may be summarized:

- (i) discrete reflections,  $hkl$ , for  $h = 2H$ ; diffuse streaks,  $hk\zeta$ , for  $h = 2H + 1$ , where  $\zeta$  can take any value
- (ii)  $Hkl$ :  $H + l = 2n$
- (iii)  $hk0$ :  $k = 2n$
- (iv)  $h0\zeta$ :  $h = 2n$

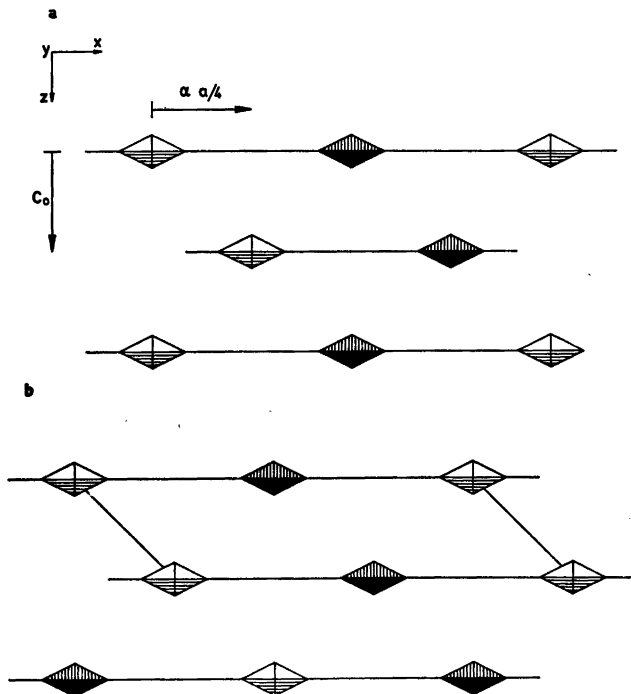


Fig. 1. Schematic representation of the stacking of layers in (a) the ordered orthorhombic structure (MDO<sub>1</sub>) and (b) the ordered monoclinic structure (MDO<sub>2</sub>).  $c_0$  is the unit vector perpendicular to the layers in the non-periodic direction, while  $\alpha$  is a factor which can take the value +1 or -1. Notation: empty triangles:  $y$ ; filled triangles:  $-y$ ; vertically shaded triangles:  $\frac{1}{2} - y$ ; and horizontally shaded triangles:  $\frac{1}{2} + y$ .

where  $hkl$  refer to an orthogonal unit cell with the approximate dimensions:  $a=8.58$  Å,  $b=21.53$  Å, and  $c=14.43$  Å.

According to reflection conditions (i) and (ii), the superposition structure,<sup>14</sup> corresponding to the family reflections,  $Hkl$ , has an  $a$  axis of one-half  $8.58$  Å and is  $B$  face-centred with  $Bmmb$  or  $B2_1mb$  as possible space groups [cf. also reflection condition (iii)].

According to reflection conditions (iii) and (iv), the minimum layer symmetry is  $P2_1a(b)$ . Owing to the high symmetry of the building units,<sup>15-17</sup> the layer symmetry has, however, been assumed to be  $Pma(b)$ . The  $B$  face-centring of the superposition structure requires that each layer be related to the next by a translation  $\alpha \vec{a}/4 + \vec{c}_0$ , where  $\alpha$  can take the value  $\pm 1$  and  $\vec{c}_0$  is the unit vector perpendicular to the layers in the non-periodic direction. This means that the symmetry elements converting a given layer,  $L_0$ , into the next,  $L_1$ , are  ${}_{0,1}[c_2 n_{2,\frac{1}{2}} (n_{\frac{1}{2},1})]$  or  ${}_{0,1}[c_2 n_{2,\frac{1}{2}} (n_{\frac{1}{2},1})]$ . These symmetry elements are illustrated in Fig. 1.

$K_4[V(CN)_6]$  thus crystallizes as a family of structures characterized by the OD groupoid symbol:<sup>14</sup>

$Pma(b)$

$\{c_2 n_{2,\frac{1}{2}} (n_{\frac{1}{2},1})\}$

this symbol giving the total symmetry of any pair of consecutive layers.

There are two ordered extreme structures, or "structures of maximum degree of order" (MDO).<sup>14</sup> One is orthorhombic, obtained by a zig-zag stacking of layers ( $\alpha$ =alternately  $+1$  and  $-1$ , cf. Fig. 1a), while the other is monoclinic, obtained by an oblique stacking of layers ( $\alpha$ =  $+1$  or  $-1$ , only, cf. Fig. 1b). The orthorhombic structure (MDO<sub>1</sub>) has a unit cell with the approximate dimensions:  $a=8.58$  Å,  $b=21.53$  Å, and  $c=14.43$  Å and belongs to space group  $Pcab$ , while the unit cell of the monoclinic structure (MDO<sub>2</sub>) has the approximate dimensions:  $a=8.58$  Å,  $b=21.53$  Å,  $c=7.53$  Å, and  $\beta=106^\circ$ , the space group being  $P2_1/a$ .

Since the crystals studied showed streaks with intensity maxima of monoclinic symmetry, only, they must contain much larger regions of MDO<sub>2</sub>-type structure than of MDO<sub>1</sub>-type structure. The apparent doubling of the  $c$

axis ( $c_{app} \approx 28.86$  Å) can be explained by the presence of regions corresponding to both the MDO<sub>2</sub> "twins", i.e. that with the stacking sequence given by  $\alpha = +1$  and that with  $\alpha = -1$ .

The fictitious superposition structure,  $\hat{q}(x, y, z)$ , which is related to the real structure,  $q(x, y, z)$  by

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

has the approximate unit cell dimensions:  $A=4.29$  Å,  $b=21.53$  Å,  $c=14.43$  Å and belongs to space group  $Bmmb$ . The disorder in  $K_4[V(CN)_6]$  is thus very similar to that found in  $K_4[Mo(CN)_6NO]$ , the superposition and MDO<sub>1</sub> structures of which have been solved.<sup>18</sup>

#### ACCURATE UNIT CELL DIMENSIONS

Powder photographs of  $K_4[V(CN)_6]$  were taken in a Guinier focusing camera with  $CuK\alpha_1$  radiation, using lead nitrate as an internal standard ( $a=7.8564$  Å).<sup>19</sup> Thirty-one family reflections were indexed and used to refine the unit cell dimensions of the superposition structure with the program Powder.<sup>20</sup> The following values were obtained (standard deviations,  $\times 10^4$ , in parentheses):  $A=4.2885(3)$  Å,  $b=21.5271(26)$  Å, and  $c=14.4308(16)$  Å. Observed and calculated  $\sin^2 \theta$  values are listed in Table 1. The calculated density corresponding to a cell content of four formula units is  $1.81$  g cm<sup>-3</sup>. The experimental density, as determined by the method of flotation, using bromoform and carbon tetrachloride, is  $1.83$  g cm<sup>-3</sup>.

The unit cell dimensions of the MDO<sub>2</sub> structure were derived from those of the superposition structure, the following values being obtained (standard deviations,  $\times 10^4$  for  $a, b, c$  and  $\times 10^2$  for  $\beta$ , in parentheses):  $a=8.5770(6)$  Å,  $b=21.5271(26)$  Å,  $c=7.5270(8)$  Å and  $\beta=106.55(1)^\circ$ . There are four formula units of  $K_4[V(CN)_6]$  per unit cell of the MDO<sub>2</sub> structure.

#### DETERMINATION OF THE SUPERPOSITION AND MDO<sub>2</sub> STRUCTURES

A crystal of  $K_4[V(CN)_6]$  with the approximate dimensions  $0.055 \times 0.005 \times 0.015$  cm was mounted along the  $a$  axis, in a glass capillary, and the intensities of the family reflections ( $hkl$ ,  $h=2H$ ) and of the streaks ( $hk\zeta$ ,  $h=2H+1$ )

Table 1. X-Ray powder diffraction data for  $K_4[V(CN)_6]$ . Guinier camera,  $CuK\alpha_1$  radiation ( $\lambda = 1.54050 \text{ \AA}$ ).

$H k l$	$10^6 \sin^2 \theta_{obs}$	$10^6 \sin^2 \theta_{calc}$	$I_{calc}$ (relative scale)	$I_{obs}$
0 2 0	512	512	16	w
0 4 0	2046	2048	3	vw
0 3 2	2291	2292	14	w
0 4 2	3187	3188	21	m
1 0 1	3516	3511	3	vw
1 1 1	3641	3639	12	w
1 2 1	4024	4023	16	w
0 5 2	4342	4340	100	vs
0 0 4	4560	4558	16	w
1 3 1	4665	4663	20	m
0 6 2	5748	5748	59	s
1 1 3	5920	5918	49	m
1 2 3	6305	6302	151	vvs
1 5 1	6709	6711	2	vvw
1 3 3	6941	6942	92	vs
0 7 2	7411	7413	21	m
1 5 3	8996	8990	4	vw
1 7 1	9782	9784	16	w
1 8 1	11706	11704	51	s
1 7 3	12073	12063	3	vw
0 4 6	12301	12304	14	w
1 4 5	12403	12397	36	m
2 0 0	12908	12904	35	m
0 5 6	13456	13457	22	w
1 8 3	13984	13984	14	w
2 2 2	14557	14555	1	vvw
1 7 5	16627	16621	8	vw
2 5 2	17243	17244	21	m
2 0 4	17458	17462	6	vw
2 3 4	18614	18614	2	vw
2 7 2	20315	20316	3	vw

at the reciprocal lattice points corresponding to the MDO, "twins" were measured with an Arndt-Phillips linear diffractometer.  $MoK\alpha$  radiation was selected by a graphite monochromator and data were collected for layers  $0kl-10kl$ , for  $h=2H$ , and  $1kl-5kl$ , for  $h=2H+1$ .

Symmetry-related family reflections were averaged and correction was made for Lorentz and polarisation effects, using the program G4,<sup>21</sup> assuming the graphite monochromator to behave as an ideal mosaic crystal. The intensities of the maxima on the streaks were processed with a function of the background  $v \cdot \sin \theta$ , obtained from data collected for a "layer" midway between  $0kl$  and  $1kl$ . This was achieved by modifying G4,<sup>21</sup> the averaging of symmetry related reflections being carried out in the same way as for the family reflections. A total of 757 independent reflections for which  $F_o^2 > 3.0\sigma(F_o^2)$

according to counting statistics, *i.e.* 641 family reflections and 116 non-family reflections from the larger "twin", were used in the subsequent calculations. No correction was made for absorption (linear absorption coefficient for  $K_4[V(CN)_6]$  in  $MoK\alpha$  radiation =  $19.9 \text{ cm}^{-1}$ ).

The superposition structure of  $K_4[V(CN)_6]$ , ( $A = 4.2885(3) \text{ \AA}$ ,  $b = 21.5271(26) \text{ \AA}$ ,  $c = 14.4308(16) \text{ \AA}$ ,  $Z = 4$ , space group  $Bmmb^*$ ) which proved to be isomorphous with that of  $K_4[Mo(CN)_6NO]$ ,<sup>18</sup> was determined from a Patterson function and a subsequent electron density calculation (FORDAP)<sup>21</sup> based on the family reflections,  $Hkl$ . Positional and isotropic thermal parameters were refined with the full-

\* Equipoints of general position of  $Bmmb$  (conventional setting,<sup>19</sup> No. 63,  $Cmcm$ ):  $(0,0,0, \frac{1}{2}, 0, \frac{1}{2}) \pm (x, y, z; x, \bar{y}, \bar{z}; x, \frac{1}{2} - y, z; x, \frac{1}{2} + y, \bar{z})$ . Equipoints of general position of  $P2_1/a$  (conventional, setting,<sup>19</sup> No. 14,  $P2_1/c$ ):  $\pm (x, y, z, \frac{1}{2} + x, \frac{1}{2} - y, z)$ .

Table 2. Atomic coordinates, expressed as fractions of the cell edges and isotropic thermal parameters ( $\text{\AA}^2$ ) for the superposition structure of  $K_4[V(CN)_6]$ . Standard deviations ( $\times 10^4$ ) and ( $\times 10^3$ ), respectively, are given in parentheses.

Atom	Site	Occupation No.	$x$	$y$	$z$	$B$
K(1)	4c	1.0	0.5000	0.2500	0.1528(3)	2.76(7)
K(2)	8f	1.0	0.0000	0.0479(1)	0.1367(2)	2.13(4)
K(3)V	8f	1.0	0.0000	0.1390(1)	0.4067(2)	2.58(5)
N(1)	8f	1.0	0.0000	0.1699(6)	0.0564(9)	4.35(26)
N(2)	8f	1.0	0.5000	0.0746(6)	0.2650(9)	4.00(25)
N(3)	8f	0.5	0.0000	0.2532(30)	0.2877(11)	2.86(41)
N(4)	8f	0.5	0.0000	0.0140(11)	0.4885(18)	2.21(54)
C(1)	16h	0.5	0.3557(34)	0.1583(6)	0.5057(9)	1.68(21)
C(2)	16h	0.5	0.3552(36)	0.0930(6)	0.3145(10)	1.82(23)
C(3)	8f	0.5	0.0000	0.2116(10)	0.3330(16)	2.14(38)
C(4)	8f	0.5	0.0000	0.0337(12)	0.4781(18)	1.61(42)

matrix least squares program LINUS<sup>21</sup> to an  $R$  value of 0.090. The atomic scattering factors due to Cromer and Mann<sup>22</sup> were used for all atoms, mean values of the scattering factors for potassium and vanadium being used for the four potassium and four vanadium atoms occupying the same eight-fold site, *i.e.* K(3)V. Unit weights were assigned to all reflections. The resulting parameters are given in Table 2.

The positions of the atoms in the  $MDO_2$  structure ( $a = 8.5770(6)$   $\text{\AA}$ ,  $b = 21.5271(26)$   $\text{\AA}$ ,  $c = 7.5270(8)$   $\text{\AA}$ ,  $\beta = 106.55(1)^\circ$ ,  $Z = 4$ , space group  $P2_1/a^*$ ) were calculated from the atomic parameters of the superposition structure, best agreement being obtained for an origin corresponding to  $\frac{1}{2} 0 \frac{1}{2}$  in the superposition structure. Preliminary refinement of positional and anisotropic thermal parameters for the potassium and vanadium atoms and isotropic thermal parameters for the remaining atoms, together with a separate scale-factor for the non-family reflections yielded  $R$  values of between 0.08 and 0.09. The refinement was extremely unstable and did not converge satisfactorily, very poor agreement being obtained for the streak reflections. The factor scaling the latter reflections obtained, moreover, unrealistic values.

#### REFINEMENT OF THE $MDO_2$ STRUCTURE

As will be described elsewhere,<sup>23</sup> it would seem to be a logical consequence of OD theory to constrain positional and thermal parameters during the refinement of an  $MDO$  structure so as to comply with the partial symmetry ele-

ments of the OD groupoid symbol. The  $MDO_2$  structure of  $K_4[V(CN)_6]$ , which contains a single layer only, was therefore constrained to have  $Pma(b)$  symmetry by the introduction of the following equivalent positions:  $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, z; \frac{1}{2} + \frac{1}{2}z - x, y, z; \frac{1}{2} + \frac{1}{2}z - x, \frac{1}{2} - y, z)$ . The  $z$  coordinates of the atoms situated on the mirror plane (*viz.* K(1), K(3), V, C(3), N(3), C(4), and N(4)) were refined, while the  $x$  coordinates were reset according to  $x = \frac{1}{2} + \frac{1}{2}z$ . Similarly, the  $\beta_{12}$  and  $\beta_{13}$  parameters of these atoms were reset according to  $\beta_{12} = \frac{1}{2}\beta_{23}$  and  $\beta_{13} = \frac{1}{2}\beta_{33}$ , respectively. The refinement became stable and converged to an  $R$  value of 0.053 ( $R_w = 0.055$ ), the standard deviations of the parameters and the agreement for the non-family reflections being considerably improved compared with the previous refinement. The ratio between the scale factors for the non-family and family reflections attained a credible value, *i.e.* 1.84, with respect to film observations.

The constraints were then released. After three cycles of refinement, the  $R$  value dropped to 0.049 ( $R_w = 0.051$ ), but several of the ligand atoms obtained negative temperature factors. The hypothesis that the constrained refinement (89 parameters) provided a more satisfactory model than the unconstrained refinement (155 parameters) was tested by means of an  $R$  factor ratio test,<sup>24</sup> using the approximation due to Pawley.<sup>25</sup> The  $R$  factor ratio ( $R_{w, \text{constr.}} / R_{w, \text{unconstr.}} = 1.0734$ ) indicated that, although the hypothesis could be rejected at the 0.05 probability level ( $\mathcal{P}_{0.05, 0.05} = 1.0702$ ) it could

Table 3. Atomic coordinates, expressed as fractions of the cell edges, and mean square vibration amplitudes,  $U_{ij}$  ( $\text{\AA}^2$ ) for the  $\text{MDO}_4$  structure of  $\text{K}_4[\text{V}(\text{CN})_6]$ . The estimated standard deviations of the parameters ( $\times 10^4$ ) are given in parentheses.

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
K(1)	0.3265	0.2526(4)	0.8059(4)	0.0281(11)	0.0429(16)	0.0333(12)	0.0022	0.0095	0.0078(36)
K(2)	0.0689(8)	0.4522(1)	0.7736(2)	0.0237(17)	0.0322(8)	0.0248(7)	-0.0022(20)	0.0021(33)	-0.0006(6)
K(3)	0.2003	0.3596(2)	0.3013(11)	0.0338(17)	0.0170(20)	0.0267(22)	-0.0028	0.0076	-0.0098(19)
V	0.2054	0.1246(1)	0.3217(7)	0.0186(11)	0.0103(15)	0.0179(16)	0.0005	0.0051	0.0018(15)
N(1)	0.5021(18)	0.3299(4)	0.6108(12)	0.0369(116)	0.0394(40)	0.0354(37)	-0.0030(37)	0.0127(40)	0.0012(33)
N(2)	0.9013(35)	0.4252(4)	0.0292(12)	0.0508(145)	0.0423(40)	0.0409(38)	0.0084(54)	0.0183(65)	0.0117(34)
N(3)	0.1445	0.2569(9)	0.0780(16)	0.0365(52)	0.0207(78)	0.0349(47)	0.0020	0.0099	0.0070(74)
N(4)	0.2561	-0.0140(5)	0.5243(28)	0.0382(70)	0.0125(88)	0.0255(86)	0.0050	0.0073	0.0177(74)
C(1)	0.5728(11)	0.3430(3)	0.5100(12)	0.0285(43)	0.0110(34)	0.0222(38)	0.0013(32)	0.0075(38)	-0.0034(31)
C(2)	0.8349(11)	0.4064(4)	0.1295(12)	0.0224(43)	0.0213(40)	0.0262(41)	0.0034(33)	0.0049(35)	0.0032(32)
C(3)	0.1674	0.2108(6)	0.1698(18)	0.0258(72)	0.0291(67)	0.0246(58)	0.0006	0.0070	0.0020(55)
C(4)	0.2384	0.0353(7)	0.4536(32)	0.0152(64)	0.0275(88)	0.0212(88)	-0.0037	0.0060	-0.0132(84)



Table 5. Bond distances (Å) and angles (°) within the  $[\text{V}(\text{CN})_6]^{4-}$  complex ion. Standard deviations of the distances ( $\times 10^3$ ) and the angles are given in parentheses.

Notation: no superscript, atom in  $x, y, z$ ; ', atom in  $x - \frac{1}{2}, \frac{1}{2} - y, z$ ; '', atom in  $\frac{1}{2} + \frac{1}{2}z - x, \frac{1}{2} - y, z$ .

Distances			
V-C(1)''	2.169(10)	C(1)'-N(1)'	1.134(14)
V-C(2)''	2.165(10)	C(2)'-N(2)'	1.141(22)
V-C(3)	2.153(13)	C(3)-N(3)	1.194(20)
V-C(4)	2.146(17)	C(4)-N(4)	1.177(19)
Angles			
V-C(1)''-N(1)''	175.8(0.7)	C(2)'-V-C(2)''	89.4(0.5)
V-C(2)''-N(2)''	177.3(0.9)	C(3)-V-C(1)''	92.4(0.4)
V-C(3)-N(3)	176.8(1.1)	C(3)-V-C(2)''	86.6(0.4)
V-C(4)-N(4)	179.3(1.2)	C(3)-V-C(4)	175.8(0.7)
C(1)'-V-C(1)''	90.5(0.5)	C(4)-V-C(1)''	90.5(0.6)
C(1)'-V-C(2)''	90.0(0.3)	C(4)-V-C(2)''	90.4(0.6)
C(1)'-V-C(2)'	178.9(0.4)		

No attempt was made to scale and average the intensity data used in the above calculations with the data corresponding to the smaller  $\text{MDO}_2$  "twin". Refinement based on the latter data yielded, however, substantially the same parameters as listed in Table 3, but with somewhat larger standard deviations.

#### DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A stereoscopic projection of a unit cell of the  $\text{MDO}_2$  structure of  $\text{K}_4[\text{V}(\text{CN})_6]$  along  $[010]$ , drawn with the program ORTEP,<sup>21</sup> is shown in Fig. 2. The unit cell is composed of a single

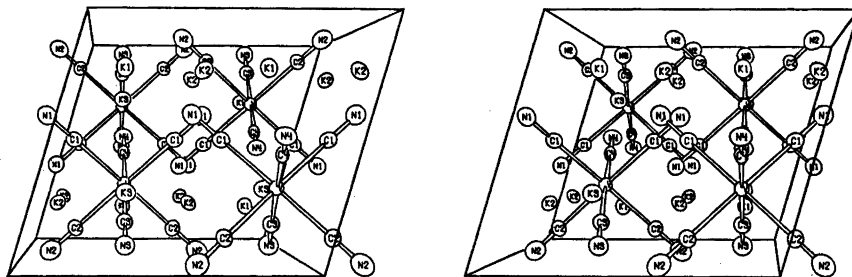


Fig. 2. Stereoscopic projection of a unit cell of the  $\text{MDO}_2$  structure of  $\text{K}_4[\text{V}(\text{CN})_6]$  along  $[010]$ . The  $a$  axis is horizontal.

Table 6. A comparison of V-C and C-N bond distances in some cyanocomplexes of vanadium.

Compound	Formal Oxid. No.	Ground State Config.	Mean V-C (Å)	Mean C-N (Å)	Ref.
$\text{K}_3[\text{V}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$	I	$d^4$	2.166(6)	1.142(8)	28
$\text{K}_4[\text{V}(\text{CN})_6]$	II	$d^2$	2.161(4)	1.153(7)	present work
$\text{K}_4[\text{V}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$	III	$d^2$	2.147(3)	1.145(4)	12, 13
$\text{K}_3[\text{VO}(\text{CN})_5]$	IV	$d^1$	2.137(14)	1.154(21)	7



Table 7. Me—C and C—N bond lengths and infra-red stretching frequencies for some transition metal hexacyanides.

Compound	Ground State Config.	Mean Me—C (Å)	$\nu_s$ (cm <sup>-1</sup> ) (Me—C stretch)	Mean C—N (Å)	$\nu_s$ (cm <sup>-1</sup> ) (C—N stretch)	Ref.
$K_3[Cr(CN)_6]$	} $d^3$	2.077(5)	339	1.136(7)	2128	11, 17, 32
$K_4[V(CN)_6]$		2.161(4)	328	1.153(7)	2080 (2065,2050)	6, 11, present work
$K_2[Mn(CN)_6]$	$d^4$	2.002(8)	361	1.142(12)	2112	11, 15, 32
$K_3[Fe(CN)_6]$	} $d^5$	1.950(9)	389	1.143(14)	2118	11, 16, 32
$Na_4[Mn(CN)_6] \cdot 10H_2O$		1.95(3)	386 <sup>a</sup>	1.16(3)	2060 <sup>a</sup>	11, 29
$K_3[Co(CN)_6]$	} $d^6$	1.896(6)	416	1.154(9)	2129	11, 16, 32
$Na_4[Fe(CN)_6] \cdot 10H_2O$		1.91(1)		1.17(1)	29	29
$K_4[Fe(CN)_6] \cdot 3D_2O$		1.925(1)	416 <sup>b</sup>	1.167(1)	2044 <sup>b</sup>	11, 30

<sup>a</sup> for  $K_4[Mn(CN)_6] \cdot 3H_2O$  <sup>b</sup> for  $K_4[Fe(CN)_6] \cdot 3H_2O$ .

layer of the OD structure (*cf.* Fig. 1b). The superposition structure may be visualized by translating one-half of the unit cell in the  $a$  direction through  $\vec{a}/2$  and superimposing it on the original arrangement.

As may be seen from Table 5, the  $[V(CN)_6]^{4-}$  complex ion has almost regular octahedral symmetry, there being, however, significant deviation of a few angles from 90 or 180°. The V—C bond lengths do not differ from one another and the mean value, 2.161(4) Å, is in good agreement with V—C bond lengths found in other cyanocomplexes of vanadium (see Table 6). Nor is there any significant difference between the C—N bond lengths found in  $K_4[V(CN)_6]$ . The mean value, 1.153(7) Å, is also consistent with C—N distances determined for other cyanocomplexes (*cf.*, *e.g.*, Table 6). Although the V—C(2)—N(2), V—C(3)—N(3), and V—C(4)—N(4) linkages are linear, the V—C(1)—N(1) angle [175.8(0.7)°] would appear to differ from 180°. The unconstrained refinement also yielded a  $[V(CN)_6]^{4-}$  ion with the same trend towards distortion, *i.e.* corresponding angles showed similar deviations from 90 or 180°.

A comparison of V—C and C—N bond lengths found in some cyanocomplexes of vanadium is given in Table 6. Although the comparison is obviously not strictly relevant, since vanadium is seven-coordinated in one of the complexes, and, although there is no significant difference between the V—C bond lengths found in the four compounds, there would, however, appear

to be a slight trend towards shorter V—C distances the higher the formal oxidation state of vanadium, or the lower the number of  $d$  electrons in its ground-state configuration. Molecular orbital calculations<sup>26,5</sup> on  $[V(CN)_7]^{4-}$  and  $[V(CN)_5NO]^{3-}$  and X-ray photoelectron spectroscopic studies<sup>27</sup> on  $[V(CN)_5NO]^{3-}$  indicate that the  $\pi$  contributions to the V—C bonds are slight in these complexes. This is in accordance with the observed trend in V—C bond lengths, which must simply just reflect the decrease in  $\sigma$  bond strength with decreasing formal oxidation state.

Crystal structure determinations of hexacyanoferrates<sup>18,28,30</sup> and hexacyanomanganates<sup>15,29</sup> and X-ray photoelectron spectra of the former<sup>21</sup> indicate, however, that  $\pi$  contributions to the Fe—C and Mn—C bonds increase with decreasing oxidation state. Bond lengths and infra-red stretching frequencies for some transition metal hexacyanides are given in Table 7. Molecular orbital calculations<sup>1</sup> for the  $d^6$  configuration indicate that the decrease in carbon to metal  $\sigma$  bonding in going from Co(III) in  $[Co(CN)_6]^{3-}$  to Fe(II) in  $[Fe(CN)_6]^{4-}$  is largely compensated for by an increase in metal to carbon  $\pi$  bonding. This is supported by the similarity in Co(III)—C and Fe(II)—C bond lengths and infra-red stretching frequencies, and by the slight increase in C—N bond length and corresponding decrease in  $\nu_s(C-N)$  from Co to Fe. It is apparent that there are similar trends for the  $d^5$  (*cf.* also Ref. 2) and  $d^3$  configurations. The somewhat larger discrepancy

between the Cr(III)–C and V(II)–C distances and stretching frequencies and the somewhat smaller drop in  $\nu_s(\text{C}-\text{N})$  from Cr to V would, however, appear to indicate that  $\pi$  contributions to the Me(II)–C bonds (Me=metal) are of less importance in  $[\text{V}(\text{CN})_6]^{4-}$  than in the corresponding Mn(II) and Fe(II) complexes. This is in contrast to  $[\text{Me}(\text{CN})_5\text{NO}]^{n-}$  where the  $\pi$  contribution to Me–N(NO) increases from iron to vanadium.<sup>27</sup> The observed decrease in the Me–C bond length in  $[\text{Me}(\text{CN})_6]^{4-}$  from vanadium to iron can thus be attributed to increases in both  $\sigma$  and  $\pi$  contributions.

The potassium-nitrogen contacts range from 2.908–3.274 Å for K(1) ( $\sigma \sim 0.010$ ), from 2.766–3.119 Å for K(2) ( $\sigma \sim 0.016$ ) and from 2.736–3.126 Å for K(3) ( $\sigma \sim 0.016$ ). K(2) and K(3) are octahedrally coordinated, whereas K(1) is surrounded by a trigonal prism of nitrogen atoms. All three coordination polyhedra are severely distorted. Each potassium ion has six carbon contacts at distances only slightly longer than the K–N distances and can thus, alternatively, be regarded as being twelve-coordinated, *i.e.* octahedrally or trigonal prismatic coordinated by six cyanide ligands.

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