

## The Crystal and Molecular Structure of Potassium Hexacyanonitrosovanadate(I)—0.5 Potassium Hydroxide—0.5 Hydrate

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Crystals of the title compound are tetragonal, space group  $P4$ ,  $a = 9.035$  (8),  $c = 9.153$  (8) Å,  $Z = 2$ . The structure of the anion is disordered about a twofold axis — there being two equivalent possible orientations. In the individual anion  $[V(CN)_6(NO)]^{4-}$ , the metal atom is seven-coordinate and has pentagonal-bipyramidal geometry with the nitrosyl group in an axial position [ $V-N$  1.680 (16) Å]. The  $V-C$  distances range from 2.117 (15) to 2.244 (33) Å. The positions of the water molecules and hydroxide ions are also disordered and could not be distinguished.

Recently there has been considerable interest in the heptacyanides of the transition metals. Structures of  $K_5[Mo(CN)_7] \cdot H_2O$  and  $Na_5[Mo(CN)_7] \cdot 10H_2O$  (Drew, Mitchell & Pygall, 1977), and  $K_4[V(CN)_7] \cdot 2H_2O$  (Levenson & Towns, 1974) have been determined by X-ray diffraction and all are pentagonal bipyramidal, though in the case of  $K_5[Mo(CN)_7] \cdot H_2O$  the geometry is considerably distorted by packing effects. Other heptacyanides, such as  $[Ti(CN)_7]^{4-}$  (Nicholls, Ryan & Seddon, 1974),  $[Mo(CN)_7]^{4-}$  (Rossman, Tsay & Gray, 1974) and  $[Re(CN)_7]^{4-}$  (Kiernan & Griffith, 1976), have also been prepared. The structures of the  $Ti^{III}$  and  $Mo^{III}$  heptacyanides (in the solid state) are thought from their spectra to have different geometries from the pentagonal bipyramid, possibly the capped trigonal prism. As a continuation of our study of these compounds, we wished to know the structure of the  $[V(CN)_6NO]^{4-}$  anion in the solid state. Accordingly we have prepared and report here the crystal and molecular structure of  $K_4[V(CN)_6(NO)] \cdot \frac{1}{2}KOH \cdot \frac{1}{2}H_2O$ .

### Experimental

Muller, Werle, Diemann & Aymonino (1972) prepared  $K_4[V(CN)_6(NO)] \cdot H_2O$  by mixing  $NH_4VO_3$  (5 g), KCN (25 g), KOH (20 g) and  $(NH_3OH)Cl$  (8 g) in 70 cc of water and passing  $H_2S$  for 2 h. The resulting compound was filtered and then recrystallized from water/ethanol, washed with ethanol and ether and dried over  $P_4O_{10}$ . The resulting compound gave satisfactory analyses and the powder pattern was indexed as tetragonal with  $a = 9.03$  (3),  $c = 9.10$  (3) Å. Following this method we were unable to get crystals big enough for X-ray work. However, when we used  $H_2S$  for  $\frac{1}{2}$  h and half quantities, crystals were obtained after allowing the solution to stand for 2 days. They were filtered off and dried between filter papers. The crystal structure

analysis showed that these crystals were of stoichiometry  $K_4[V(CN)_6(NO)] \cdot \frac{1}{2}KOH \cdot \frac{1}{2}H_2O$ , a formula which agreed with the observed density and analyses. The IR spectrum obtained was equivalent to that found by Muller *et al.* (1972).

### Crystal data

$K_4[V(CN)_6(NO)] \cdot \frac{1}{2}KOH \cdot \frac{1}{2}H_2O$ ,  $C_6N_7K_{4.5}H_{1.5}O_2V$ ,  $M_r = 430.5$ , tetragonal,  $a = 9.035$  (8),  $c = 9.153$  (8) Å,  $U = 747.2$  Å<sup>3</sup>,  $Z = 2$ ,  $d_m = 1.93$  (2),  $d_c = 1.91$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 19.6$  cm<sup>-1</sup>. Space group  $P4$  from Laue group  $4/m$  with no systematic absences, and the successful structure determination.

A crystal with dimensions  $0.5 \times 0.8 \times 0.7$  mm was mounted with the (110) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus, which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, a scintillation counter and a pulse-height discriminator. Zirconium-filtered X-radiation was used. 715 independent reflexions were measured with  $2\theta < 50^\circ$  by the stationary-crystal-stationary-counter method. No crystal decay was observed during the measurement of data. 590 reflexions with  $I > 3\sigma(I)$  were used in subsequent calculations. No extinction or absorption corrections were applied.

### Structure determination

The positions of the V atom and one K atom were obtained from the Patterson function, and Fourier syntheses were used to determine the positions of the remaining atoms. With  $Z = 2$ , the only possible ordered structure for the anion would be one in which the anion had  $C_2$  symmetry with the twofold axis running through the  $V-N-O$  atoms. However, from our review

of the structures of seven-coordinate compounds (Drew, 1977) we considered this to be an unlikely structure. More probable was a pentagonal bipyramid with the nitrosyl group in an axial position. Such a structure was indeed found but the twofold axes in the unit cell were maintained by a disordered model for the anion with the nitrosyl group in each of the two axial positions 50% of the time. The evidence for such a structure is conclusive.

When the V atom was placed in the special position  $2(g)$  with coordinates  $0, \frac{1}{2}, z$ , least-squares refinement of the anisotropic thermal parameters gave values of 19.3, 111.3, 25.6 and  $7.6 \text{ \AA}^2$  (all  $\times 10^3$ ) respectively for  $U_{11}$ ,  $U_{22}$ ,  $U_{33}$  and  $U_{12}$ ; this indicates that the V atom should be moved off the twofold axis in the  $y$  direction. Final refinement (Table 1) gave  $y = 0.4738(8)$  and reasonable anisotropic thermal parameters. The thermal parameters of the cyanide group [C(4), N(4)] would not converge when the atomic positions were fixed on the twofold axis, but all parameters were refined off it

with half occupancy. It is clear from our proposed structure (Fig. 1) that the axial atom bonded to V should be in roughly the same position whether it is C or N. This atom was refined with a scattering factor of  $\frac{1}{2}(f_C + f_N)$ .<sup>\*</sup> The positions of the O and N atoms were, however, distinct (as might have been expected) and these were refined with half occupancy. Fig. 1 shows that the positions of C(1), C(2) and C(1'), C(2') would be approximately the same whichever of the two orientations of the anion was found.

It was clear from the refinement that there were 4.5 K cations per anion rather than 4. A difference Fourier map based on  $K_{4.5}[V(CN)_6(NO)]$  showed that the only remaining region with positive electron density was around the (0,0,0) position [1(a)]. Refinement was achieved with the coordinates for O(4) found in Table 1 with a  $y$  coordinate well away from the origin. We tried

\* All scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. Final positional parameters ( $\times 10^4$ ) and thermal parameters ( $\text{\AA} \times 10^3$ ) with estimated standard deviations in parentheses

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
V <sup>(a)</sup>	-0076 (15)	4738 (8)	7028 (4)	18.0 (30)	22.7 (65)	23.4 (18)	-5.8 (47)	7.1 (27)	-6.4 (20)
K(1)	2339 (4)	1008 (4)	6689 (5)	41.6 (17)	37.2 (17)	81.5 (29)	-2.7 (14)	7.9 (20)	-13.8 (20)
K(2)	2663 (4)	3554 (4)	1251 (4)	45.8 (19)	72.8 (26)	30.5 (17)	10.2 (17)	2.1 (17)	10.1 (17)
K(3) <sup>(b)</sup>	5000 <sup>(c)</sup>	5000 <sup>(c)</sup>	5000 <sup>(c)</sup>	33.6 (4)	$U_{11}$	69.6 (49)	0 <sup>(c)</sup>	0 <sup>(c)</sup>	0 <sup>(c)</sup>
	$x$	$y$	$z$	$U$		$x$	$y$	$z$	$U$
C(1)	1313 (14)	4636 (14)	5164 (14)	28 (3)	N(3) <sup>(a)</sup>	-0910 (39)	1724 (38)	7051 (43)	60 (8)
N(1)	2042 (14)	4433 (14)	4107 (13)	48 (3)	O(3) <sup>(a)</sup>	-0848 (20)	1657 (20)	6376 (23)	23 (4)
C(2)	2169 (15)	4379 (16)	7740 (12)	28 (3)	C(4) <sup>(a)</sup>	0140 (41)	5510 (33)	9349 (35)	47 (8)
N(2)	3328 (12)	4029 (13)	8177 (14)	39 (3)	N(4) <sup>(a)</sup>	0301 (36)	5709 (35)	10585 (37)	63 (8)
C(N3)	-0579 (15)	2956 (16)	6863 (16)	45 (3)	O(4) <sup>(a)</sup>	-0077 (37)	1228 (32)	0222 (43)	89 (9)

(a) Atom refined with occupancy of 50%. (b) Atom refined with occupancy of 25%. (c) Fixed.

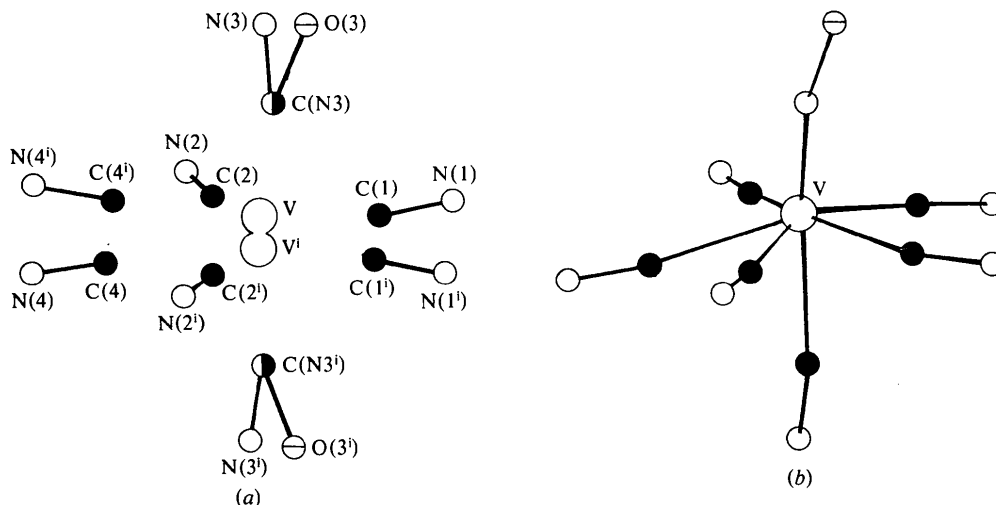


Fig. 1. (a) The refined model of two superimposed anions. (b) The individual anion  $[V(CN)_6(NO)]^{4-}$

several different population parameters for O(4) are the most successful, both in terms of  $R$  value and thermal parameter, was 0.5. This would suggest that the site is shared by an  $OH^-$  anion and a water molecule. The compound can thus be formulated as  $K_4[V(CN)_6(NO)] \cdot \frac{1}{2}KOH \cdot \frac{1}{2}H_2O$ . The presence of the potassium hydroxide is presumably necessary to stabilize this particular unit cell and to permit the formation of crystals. Certainly, when the KOH is removed, as in the original preparation, no useable crystals could be formed.

The structure was refined (V, K anisotropic; O, C, N isotropic) to  $R = 0.077$  (the opposite enantiomorph gave  $R = 0.079$ ) by full-matrix least squares. The weighting scheme, which was chosen to give average values for  $w\Delta^2$  independent of the values of  $F_o$  and  $\sin \theta/\lambda$ , was  $\sqrt{w} = 1$  for  $F_o < 25$  and  $\sqrt{w} = 25/F_o$  for  $F_o > 25$ . Calculations were made on a CDC computer at the University of London Computer Centre with the programs of Stewart, Kruger, Ammon, Dickinson & Hall (1972). The anisotropic thermal parameters are defined as  $\exp(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j b_i b_j)$ , where  $i, j = 1, 2, 3$  and  $b_i$  is the  $i$ th reciprocal-cell dimension. The isotropic thermal parameter is defined as  $\exp(-8\pi^2 \sin^2 \theta/\lambda^2)$ . In the final cycle of refinement, all shifts were  $< 0.01\sigma$ . A final difference Fourier map showed no significant peaks. Final positional coordinates, population parameters and thermal factors are given in Table 1. Molecular dimensions are given in Table 2.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32583 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances (Å) and angles (°) in the  $[V(CN)_6(NO)]^{4-}$  anion*

V—C(1)	2.121 (15)	C(N3)—V—C(1)	92.7 (7)
V—C(2)	2.155 (18)	C(N3)—V—C(2)	97.9 (7)
V—C(N3)	1.680 (16)	C(N3)—V—C(4)	114.0 (10)
V—C(4)	2.244 (33)	C(N3)—V—C(1 <sup>1</sup> )	92.3 (7)
V—C(1 <sup>1</sup> )	2.117 (15)	C(N3)—V—C(2 <sup>1</sup> )	98.3 (8)
V—C(2 <sup>1</sup> )	2.153 (18)	C(N3 <sup>1</sup> )—V—C(1)	79.9 (6)
V—C(N3 <sup>1</sup> )	2.171 (16)	C(N3 <sup>1</sup> )—V—C(2)	84.8 (6)
C(1)—N(1)	1.184 (18)	C(N3 <sup>1</sup> )—V—C(4)	75.2 (10)
C(2)—N(2)	1.165 (17)	C(N3 <sup>1</sup> )—V—C(1 <sup>1</sup> )	80.3 (6)
C(N3)—N(3)	1.165 (38)	C(N3 <sup>1</sup> )—V—C(2 <sup>1</sup> )	84.5 (6)
C(N3)—O(3)	1.278 (23)	C(1)—V—C(2)	71.3 (6)
C(4)—N(4)	1.155 (46)	C(1)—V—C(4)	136.4 (1)
V—C(1)—N(1)	173.2 (11)	C(1)—V—C(1 <sup>1</sup> )	71.1 (5)
V—C(2)—N(2)	172.3 (11)	C(1)—V—C(2 <sup>1</sup> )	141.2 (6)
V—C(N3)—N(3)	166.4 (23)	C(2)—V—C(4)	71.2 (4)
V—C(N3)—O(3)	164.2 (15)	C(2)—V—C(1 <sup>1</sup> )	141.3 (7)
V—C(4)—N(4)	170.6 (20)	C(2)—V—C(2 <sup>1</sup> )	142.2 (5)
V—C(1 <sup>1</sup> )—N(1 <sup>1</sup> )	173.4 (11)	C(4)—V—C(1 <sup>1</sup> )	136.6 (10)
V—C(2 <sup>1</sup> )—N(2 <sup>1</sup> )	173.7 (11)	C(4)—V—C(2 <sup>1</sup> )	71.0 (9)
C(N3)—V—C(N3 <sup>1</sup> )	170.9 (7)	C(1 <sup>1</sup> )—V—C(2 <sup>1</sup> )	71.4 (6)

## Discussion

In Fig. 1 we show the refined model of the disordered  $[V(CN)_6(NO)]^{4-}$  anion. This model can be separated into two distinct orientations of the anion. It is easy to see which atoms belong to the anion around V (and which to V<sup>1</sup>) with the exception of C(4), N(4) and C(4<sup>1</sup>), N(4<sup>1</sup>). These are the atoms close to the twofold axis which have refined to positions slightly off it [C(4)···C(4<sup>1</sup>) 0.96 Å]. It is not certain whether C(4) or C(4<sup>1</sup>) is bonded to V. Dimensions involving both are shown in Table 3 and neither set gives any unreasonable angles. We slightly favour the set with C(4) because the C(N3)—V—C(4) and C(N3<sup>1</sup>)—V—C(4) angles are respectively greater and less than 90°; this is what would be expected because of the *trans* effect of the V—N bond. These angles at 114.0 (10) and 75.2 (10)° respectively are more distorted from 90° than the other  $L_{ax}$ —V— $C_{eq}$  angles. However, the angles involving C(4) are much more dependent upon the  $Vy$  coordinate than are the others and this coordinate is particularly inaccurate because of the close proximity of V and V<sup>1</sup> (0.49 Å). However, it may be that one should not expect a regular geometry for  $[V(CN)_6(NO)]^{4-}$  for as we showed in our structure determination of  $K_5[Mo(CN)_7] \cdot H_2O$  (Drew, Mitchell & Pygall, 1977), the ideal pentagonal bipyramid is easily distorted by packing effects. In this latter example, one cyanide group in the equatorial girdle was pushed out of the equatorial plane by over 1 Å. Thus in the present molecule the positions of C(4) and N(4) could be irregular for that very reason, though this is not obvious from the intermolecular contacts (Table 4).

Given this proviso the structure of the anion approximates to a pentagonal bipyramid with the nitrosyl group in an axial position. This geometry is expected as it occurs in nearly all examples of seven-coordinate complexes containing multiple-bonded groups such as O, NO, NS and N; these groups occupy the axial positions of pentagonal bipyramids. The one exception established by an X-ray study is  $(CN_3H_6)_3^-(NbOF_6)$  (Pakhomov, Kaidalovo & Davidovich, 1974), in which the O atom of the anion is in an equatorial position of a pentagonal bipyramid. However, this exception could be a result of the strong hydrogen-bond pattern found in the unit cell.

Table 3. *Angles subtended at V by C(4) and C(4<sup>1</sup>)*

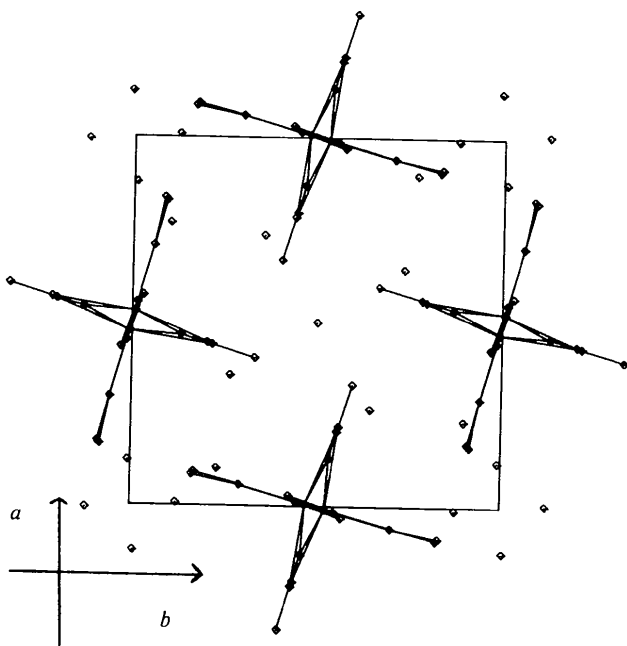
	$X = C(4)$	$X = C(4^1)$
V—X	2.244 (33) Å	2.137 (33) Å
C(N3)—V—X	114.0 (10)°	88.9 (10)°
C(N3 <sup>1</sup> )—V—X	75.2 (10)	100.2 (10)
C(1)—V—X	136.4 (11)	144.2 (11)
C(2)—V—X	71.2 (9)	73.1 (10)
C(1 <sup>1</sup> )—V—X	136.6 (10)	144.6 (11)
C(2 <sup>1</sup> )—V—X	71.0 (9)	73.4 (10)
V—X—N(4) <sup>(a)</sup>	170.6 (20)	173.6 (34)

(a) N(4) when  $X = C(4)$ , N(4<sup>1</sup>) when  $X = C(4^1)$ .

Table 4. Intermolecular contacts  $<3.2 \text{ \AA}$ 

K(1)···C(N3)	3.174	C(4)···O(4 <sup>xii</sup> )	3.054
K(1)···C(2)	3.197	K(2)···N(1)	2.789
K(1)···N(2)	3.178	K(2)···N(2 <sup>vi</sup> )	2.909
K(1)···O(3), N(3)	2.953, 3.025	K(2)···N(4 <sup>vi</sup> ), N(4 <sup>vii</sup> )	2.953, 2.827
K(1)···O(3 <sup>ii</sup> ), N(3 <sup>ii</sup> )	2.774, 2.805	K(2)···N(2 <sup>viii</sup> )	3.119
K(1)···O(3 <sup>iii</sup> )	2.876	K(2)···N(3 <sup>iii</sup> )	2.973
K(1)···O(4 <sup>iii</sup> )	3.114	K(2)···N(2 <sup>v</sup> )	3.041
K(1)···N(4 <sup>iv</sup> )	3.121	K(2)···C(4 <sup>vii</sup> )	3.188
K(1)···N(1 <sup>v</sup> )	3.147	K(2)···C(2 <sup>v</sup> )	3.092
N(3)···O(4 <sup>x</sup> )	3.034	K(3)···N(1)	2.841
N(3)···O(4 <sup>xi</sup> )	2.992	K(3)···N(1 <sup>ix</sup> )	2.841
N(4)···O(4 <sup>xii</sup> )	2.794	K(3)···N(1 <sup>viii</sup> )	2.841
O(4)···O(4 <sup>ii</sup> )	2.224	K(3)···N(1 <sup>v</sup> )	2.841
O(4)···O(4 <sup>xiii</sup> )	1.625		
O(4)···O(4 <sup>xiv</sup> )	1.625		

Symmetry code: superscripts refer to the following equivalent positions with respect to those at  $x, y, z$  (Table 1). (i)  $-x, 1-y, z$ ; (ii)  $-x, -y, z$ ; (iii)  $y, -x, 1-z$ ; (iv)  $1-y, x, 2-z$ ; (v)  $1-y, x, 1-z$ ; (vi)  $x, y, -1+z$ ; (vii)  $-x, 1-y, -1+z$ ; (viii)  $y, 1-x, 1-z$ ; (ix)  $1-x, 1-y, z$ ; (x)  $x, y, 1+z$ ; (xi)  $-y, x, 1-z$ ; (xii)  $-x, 1-y, 1+z$ ; (xiii)  $y, -x, -z$ ; (xiv)  $-y, x, -z$ .

Fig. 2. The unit cell in the  $c$  projection.

The structural features of the nitrosyl group bonded to transition metals have been reviewed by Frenz & Ibers (1972). Two types of bonding pattern have been distinguished. In the first, the nitrosyl group (formally  $\text{NO}^+$ ) acts as a  $\sigma$  donor. The  $M-N$  bond is relatively short and the  $M-N-O$  angle is *ca*  $180^\circ$ . In the second, the nitrosyl group is formally  $\text{NO}^-$ , the  $M-N$  bond is longer and the  $M-N-O$  angle is *ca*  $120^\circ$ . Examples of this second type are found mainly for complexes of the later transition metals such as Co, Ir and Os. Some cases with angles intermediate between  $120$  and  $180^\circ$  are also well known. In the present example,  $[\text{V}(\text{CN})_6-$

$(\text{NO})]^{4-}$ , the nitrosyl group is clearly of the first type with a short  $M-N$  bond and a large  $M-N-O$  angle. This is expected for this part of the periodic table and is comparable with that found in  $\text{K}_3[\text{V}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$  (Jagner & Vannerberg, 1970), in which  $V-N$  is  $1.66(4) \text{ \AA}$  and  $V-N-O$  is  $171(3)^\circ$ . In this structure also a nitrosyl and cyanide group are disordered. The mean  $V-C$  distance of the four ordered bonds is  $2.16 \text{ \AA}$ , and in  $[\text{V}(\text{CN})_7]^{4-}$  it is  $2.15 \text{ \AA}$  (Levenson & Towns, 1974) – values which are comparable with those found in the present anion.

The packing of the structure in the  $c$  projection is shown in Fig. 2. The environment of the K ions in the unit cell is shown in Table 4. All have the expected pattern with short  $K \cdots O$  and  $K \cdots N$  contacts from  $2.77 \text{ \AA}$  upwards. As stated under *Experimental*, the positions of the hydroxyl group and the water molecule could not be distinguished and were refined together as O(4). There are four positions in the unit cell for O(4), of which two are occupied in any unit cell. It is clear that these must have coordinates  $(x, y, z)$  and  $(\bar{x}, \bar{y}, z)$  but even so these are  $2.22 \text{ \AA}$  apart (other pairs are  $1.62 \text{ \AA}$  apart). This distance is less than the shortest  $O \cdots O$  distances known (*ca*  $2.45 \text{ \AA}$ ). This suggests that our treatment of the disorder is too simple and that the electron density in this region cannot be averaged as just one position. However, our approximation is an adequate description of the electron density and we could not find a refinable alternative.

One further point should be mentioned: the structures of several heptacyanides belong to a triclinic space group  $I1$  with  $a, b$ , and  $c$  all *ca*  $9.0 \text{ \AA}$  and with  $\alpha, \beta$ , and  $\gamma$  all *ca*  $90^\circ$ . The list includes  $\text{K}_5[\text{Mo}(\text{CN})_7] \cdot \text{H}_2\text{O}$ ,  $\text{K}_4[\text{V}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ , and  $\text{K}_4[\text{Re}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ . If  $0.5$  is added to the  $y$  and  $0.3$  to the  $z$  coordinates of the present compound (given in Table 1)  $(x, y, z)$  is transposed into  $(z, x, y)$ ; then the coordinates of the atoms are comparable to those obtained in the

triclinic unit cells. However, because of the fourfold axes, the two anions in the unit cell have different orientations, unlike the triclinic case. This is shown in Fig. 3, which is a projection of the unit cell down  $a$ . Note the similarity to body-centring of the contents of the unit cell. This diagram can be compared with Fig. 1 of Drew, Mitchell & Pygall (1977), which shows the  $K_5[Mo(CN)_7] \cdot H_2O$  structure.

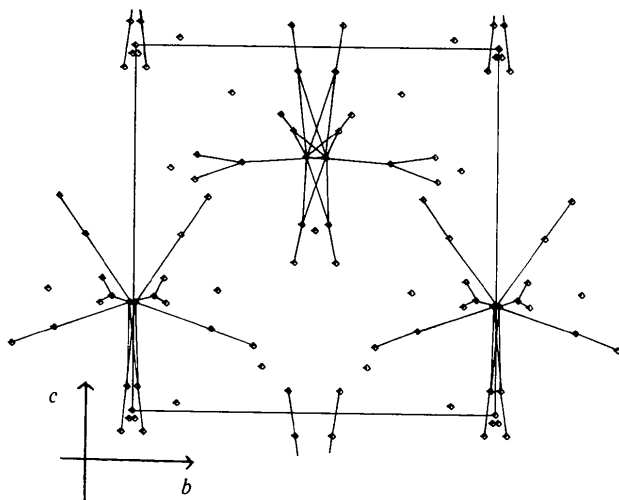


Fig. 3. The unit cell in the  $a$  projection.

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## The Crystal Structure of the Low-Temperature Phase of Poly[1,2-bis(*p*-tolylsulphonyloxymethylene)-1-buten-3-ynylene]

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The title compound ( $C_{20}H_{18}O_6S_2$ )<sub>n</sub> undergoes a phase change below 170 K. The space group of the low-temperature phase is  $P2_1/c$ ,  $a = 14.93$  (1),  $b = 4.910$  (5),  $c = 25.56$  (2) Å,  $\beta = 92$  (1)°,  $Z = 4$ . The crystal structure has been determined and refined by full matrix least-squares analysis of intensities obtained from equi-inclination Weissenberg photographs taken at 120 K. Intensities were estimated visually. The final  $R$  index was 0.10. The phase transition is characterized by the torsions of the side groups attached to the polymer backbone. The phenyl rings in adjacent rows of polymer chains turn in opposite directions. This movement creates two different species of polymer chains in the unit cell. The splitting of levels observed in the optical spectra taken at low temperatures can be attributed to this phase change.

#### Introduction

Many substituted diacetylenes undergo solid-state polymerization by 1:4 addition of adjacent molecules

(Wegner, 1972). Polymerization takes place by annealing or exposure to UV, X-ray or  $\gamma$ -ray radiation and leads to polymers containing fully conjugated polymer chains. In this way large, nearly defect-free polymer