

The Square Antiprismatic Configuration for the Octacyanotungstate(IV) Ion. The Crystal Structure of $\text{H}_4\text{W}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$

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The crystal structure of the compound $\text{C}_8\text{H}_{16}\text{N}_8\text{O}_6\text{W}$ has been determined by means of a three-dimensional X-ray analysis. The space group is *Pmma*, and the cell dimensions are $a=14.30$, $b=9.881$, $c=6.267$ Å, with 2 molecules per unit cell. The corresponding Mo compound is isomorphous with the W compound. The $\text{W}(\text{CN})_8^{4-}$ anion has only *mm* symmetry and an approximate square antiprismatic D_{4d} configuration. The average dimensions for the octacyanotungstate(IV) ion are: W–C, 2.180; C–N, 1.127; W–N, 3.306 Å, and the angle W–C≡N, 177.5°. The σ bonds form an angle of 57.6° with the theoretical $\bar{3}$ axis of the anion. Possible evidence for partial π -bond character and N···N contacts of 2.55 Å between adjacent anions has been found. It is concluded that the structure consists of a three-dimensional hydrogen-bonded framework.

Introduction

The crystal structure of $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ (and that of the isomorphous tungsten analogue) was determined by Hoard & Nordsieck (1939) and was redetermined by Hoard, Hamor & Glick (1968). This proved the D_{2d} dodecahedral configuration for octacyanometalate ions with a d^2 -electronic configuration. Since then the geometry of the d^1 and d^2 octacyano-ions has become a speculative subject because spectral, magnetic, and other evidence has suggested an intramolecular distortion from D_{2d} to antiprismatic D_{4d} geometry. The infrared and Raman spectra of $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ in the solid state have been examined by many authors and interpreted on the basis of D_{2d} geometry only, but solution studies like those of Stammreich & Sala (1960, 1961), and of Kettle & Parish (1965), indicated the D_{4d} configurational type for the anion. The same result was found by Muetterties (1965) from a ^{13}C nuclear magnetic resonance spectrum of isotopically enriched $\text{Mo}(\text{CN})_8^{4-}$ in CS_2 . McGarvey (1966) and Hayes (1966) concluded that the electron spin resonance spectra could be interpreted only in terms of a D_{4d} coordination polyhedron. Muetterties & Wright (1967) stated that these ambiguous results could be explained *via* an isomerization process between the D_{2d} and D_{4d} configurations, since the energy barriers as a function of shape are qualitatively relatively small for these two polyhedra. The basic analyses of Hoard & Silverton (1963) and of Hoard, Hamor & Glick (1968) suggested that there is not much to choose between the antiprismatic and dodecahedral configurations for the $\text{X}(\text{CN})_8^{y-}$ ions ($\text{X} = \text{W}, \text{Mo}$; $y = 3, 4$), and that the observable form is mainly determined by localized stabilizing interactions of atoms in the immediate physical environment of the anion. This assumption seems to be true in regard to the crystal structure of $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ (Bok, Leipoldt & Basson, 1969). It seems as though the water content and the size of the

cation in the latter structure play an important role in determining the packing and linkage of the surrounding antiprisms. In contrast, in the structure of $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ no regular coordination polyhedra could be found for the potassium atoms. In view of the importance of the water content, it was decided to determine the crystal structure of an acid like $\text{H}_4\text{W}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$ to observe the influence of the physical environment on the anion.

Experimental

$\text{K}_4\text{W}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ and $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ were prepared by the methods of Kosinska & Stasicka (1957) and of Furman & Miller (1960) respectively. Both salts were purified by precipitating the Cd salt, adding less than the stoichiometric amount of K_2CO_3 , removing CdCO_3 by filtration, and precipitating the potassium salt by adding ethyl alcohol. Addition of AgNO_3 to the potassium salt gave the insoluble silver salt, from which $\text{H}_4\text{W}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$ and $\text{H}_4\text{Mo}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$ were obtained by adding less than the equivalent amount of dilute hydrochloric acid, removing AgCl by filtration, and slowly evaporating the resultant solutions over anhydrous ZnCl_2 in the dark. Yellow-orange prismatic needles elongated along [001] were obtained. It was found, in agreement with Olsson (1914), that the crystals deliquesce when in contact with the atmosphere after about half an hour.

The crystal data (Table 1) were determined from oscillation and Weissenberg photographs using $\text{Cu K}\alpha$ radiation ($\lambda_{\text{Cu K}\alpha} = 1.542$ Å). The W and Mo compounds were found to be isomorphous. The camera was standardized with NaCl. Densities were determined by flotation in a diiodomethane–chloroform mixture. The isomorphous compounds exhibited the following systematic absences for rotation about the c and b axes respectively: $hk0$, $h \neq 2n$, $h00$, $h \neq 2n$. These data corresponded to the orthorhombic space groups *Pmma*,

Table 2 (cont.)

2	9	7.3	12.2	6	7	8.0	15.1	10	6	4.6	- 8.2	0	7	12.7	- 4.0	3	4	46.0	- 52.8	7	6	27.0	- 33.4	
2	10	9.9	- 12.7	6	8	11.4	- 15.2	11	1	54.0	- 46.8	0	8	11.7	- 5.7	3	9	51.6	- 54.9	7	7	23.9	- 29.3	
2	11	69.5	- 61.8	6	9	6.0	- 9.4	11	2	42.8	- 42.2	0	9	9.2	- 5.7	3	7	28.0	- 29.2	8	1	21.0	- 11.5	
2	12	74.8	- 64.3	6	10	6.7	- 8.3	11	3	41.9	- 46.1	0	0	56.0	- 58.6	3	8	17.8	- 24.0	8	2	13.2	- 16.4	
3	1	65.3	- 57.7	7	3	46.7	- 55.9	11	4	30.1	- 35.6	0	1	15.1	- 11.5	3	5	19.1	- 16.4	8	3	15.1	- 4.9	
3	2	57.8	- 57.9	7	2	45.3	- 47.8	11	5	25.4	- 28.4	0	0	11.5	- 3.1	4	1	18.5	- 14.3	8	4	12.3	- 12.4	
3	3	35.2	- 40.7	7	3	56.1	- 57.9	11	6	19.5	- 20.1	0	4	0	43.5	- 47.6	4	2	19.3	- 14.3	8	5	11.5	- 6.1
3	4	35.3	- 40.7	7	4	46.7	- 55.9	11	7	18.0	- 17.8	0	5	20.2	- 16.4	4	3	15.1	- 16.4	8	6	11.5	- 6.1	
3	5	35.9	- 40.4	7	5	36.2	- 40.0	12	1	15.8	- 27.8	0	6	20.2	- 16.4	4	4	15.0	- 16.4	8	7	9.5	- 7.9	
3	6	51.0	- 30.5	7	6	28.8	- 35.7	12	2	13.5	- 17.0	0	7	0	44.8	- 44.8	4	5	15.1	- 5.7	8	8	9.4	- 4.5
3	7	17.7	- 23.5	7	7	23.5	- 30.7	12	3	18.6	- 20.4	0	8	0	13.5	- 4.8	4	6	15.0	- 10.6	9	1	95.1	- 50.4
3	8	51.1	- 30.5	7	8	28.8	- 35.7	12	4	12.6	- 15.4	0	9	0	12.8	- 6.5	4	7	12.2	- 6.5	9	2	50.6	- 47.2
3	9	17.7	- 23.5	7	9	23.5	- 30.7	12	5	0	11.2	0	10	0	50.9	- 40.6	4	8	10.7	- 5.7	9	3	34.0	- 39.1
4	1	28.8	- 26.1	7	9	13.4	- 18.3	12	6	9.4	- 10.6	0	11	0	11.2	- 5.3	4	9	7.9	- 5.8	9	4	40.5	- 44.2
4	2	35.9	- 32.2	8	1	45.5	- 36.5	12	6	8.4	- 10.6	0	12	0	12.8	- 6.5	4	10	10.7	- 5.7	9	5	34.0	- 39.1
4	3	29.5	- 30.9	8	2	29.3	- 29.3	12	6	40.5	- 37.7	0	13	0	39.1	- 36.4	5	1	48.0	- 51.7	9	6	29.1	- 32.5
4	4	19.7	- 15.9	8	3	25.6	- 27.8	13	1	35.5	- 33.5	0	1	72.0	- 70.6	5	2	44.9	- 40.1	9	7	12.8	- 12.8	
4	5	14.5	- 12.8	8	4	29.6	- 32.2	13	2	29.1	- 30.1	0	2	58.5	- 61.3	5	3	46.1	- 45.2	10	1	46.9	- 41.2	
4	6	20.9	- 21.5	8	5	29.2	- 24.6	13	3	24.1	- 28.8	0	3	49.6	- 49.6	5	4	42.1	- 42.1	10	2	12.5	- 9.2	
4	7	14.5	- 18.3	8	6	24.2	- 29.2	13	4	18.4	- 24.1	0	4	34.9	- 44.6	5	5	41.9	- 43.6	10	3	12.2	- 10.1	
4	8	13.6	- 18.4	8	7	17.0	- 15.1	13	5	11.9	- 22.6	0	5	46.8	- 46.7	5	6	20.2	- 32.7	10	4	11.7	- 6.2	
4	9	12.0	- 10.5	8	8	11.1	- 12.1	14	1	15.0	- 15.8	0	6	36.3	- 40.1	5	7	18.8	- 22.7	10	5	10.6	- 6.7	
4	10	5.1	- 6.4	8	9	8.1	- 12.9	14	2	9.8	- 10.6	0	7	34.8	- 36.5	5	8	10.1	- 17.3	10	6	8.8	- 6.7	
5	1	70.2	- 69.8	9	1	55.2	- 49.0	14	3	17.0	- 14.6	0	8	26.1	- 29.6	5	9	11.0	- 17.5	11	1	46.9	- 41.2	
5	2	64.1	- 62.5	9	2	49.0	- 45.0	14	4	22.9	- 26.9	0	9	15.9	- 11.9	6	2	13.0	- 10.7	11	2	16.1	- 24.8	
5	3	71.1	- 69.2	9	3	46.7	- 47.0	14	5	8.9	- 15.0	0	10	11.0	- 10.8	6	3	13.2	- 9.1	11	3	23.4	- 26.8	
5	4	60.6	- 59.4	9	4	38.6	- 45.4	15	1	28.9	- 29.1	0	11	20.6	- 24.1	6	4	15.2	- 11.5	11	4	20.1	- 29.7	
5	5	44.1	- 48.4	9	5	31.7	- 33.7	15	2	22.9	- 26.9	0	12	12.8	- 5.4	6	5	13.0	- 12.1	11	5	19.1	- 23.6	
5	6	33.0	- 40.1	9	6	23.2	- 29.3	15	3	19.6	- 27.9	0	13	13.2	- 10.2	6	6	12.4	- 11.5	11	6	11.0	- 8.6	
5	7	32.0	- 39.7	9	7	24.3	- 26.7	15	4	17.0	- 14.6	0	14	12.8	- 9.5	6	7	11.2	- 4.5	12	1	10.6	- 9.1	
5	8	25.0	- 28.7	9	8	8.4	- 17.3	15	5	0	0	0	15	12.6	- 3.4	6	8	9.2	- 4.5	12	2	9.8	- 5.7	
5	9	16.1	- 20.5	9	9	8.4	- 17.3	15	6	0	0	0	16	11.5	- 4.2	7	1	62.7	- 55.2	12	3	8.6	- 5.0	
6	1	11.3	- 10.4	10	1	25.6	- 21.2	0	1	24.4	- 18.8	0	17	12.6	- 9.5	6	9	9.2	- 4.5	12	4	10.6	- 9.1	
6	2	42.3	- 36.7	10	2	29.4	- 25.5	0	2	16.4	- 17.5	0	18	11.5	- 4.2	7	2	63.1	- 57.8	13	1	35.5	- 33.8	
6	3	19.7	- 19.5	10	3	25.1	- 22.5	0	3	11.7	- 6.1	0	19	8.9	- 6.2	7	3	59.7	- 52.6	13	2	31.2	- 24.6	
6	4	8.1	- 9.5	10	4	20.0	- 22.5	0	4	12.6	- 13.4	0	20	69.1	- 68.5	7	4	41.7	- 45.3	13	3	21.0	- 28.4	
6	5	14.4	- 19.9	10	5	19.2	- 19.6	0	5	20.9	- 17.3	0	21	65.8	- 64.4	7	5	40.4	- 41.5	13	4	13.3	- 25.3	
6	6	20.9	- 25.8	10	6	20.0	- 13.4	0	6	13.2	- 8.5	0	22	48.1	- 47.8	7	6	40.4	- 41.5	13	5	13.3	- 25.3	
6	7	5.4	- 17.8	10	7	10.7	- 11.2	0	7	0	0	0	23	0	0	0	0	0	0	0	0	0	0	0

without heavy metal additives. Solutions of Canada balsam in alcohols or ethers were unsatisfactory because of solution effects. The crystal was rotated about the c axis. Integrated multiple-film equi-inclination Weissenberg photographs were taken for layers 0 to 5, using Cu $K\alpha$ radiation [$\mu(\text{Cu } K\alpha) = 128.8 \text{ cm}^{-1}$]. The intensities of 837 reflexions were determined visually using a standard calibrated scale. A value of $I_{\text{unobs}} = \frac{1}{3}I_{\text{min}}$ was assigned to 74 additional unobserved reflexions (Hamilton, 1955). The intensity data were corrected by the usual factors, Lorentz, polarization, spot shape, $\alpha_1 - \alpha_2$ splitting, and absorption.

Structure determination and refinement

The observed intensity data revealed strong reflexions for $l=0-2$ if $h=2n$, while for layers 4 and 5 strong reflexions were obtained for $h \neq 2n$. Since the W atom is the only heavy atom in the molecule and the unit cell only contains two molecules of the acid, it appeared that the W atom should be placed in either of the twofold positions: $f(\frac{1}{4} \frac{1}{2} z; \frac{3}{4} \frac{1}{2} \bar{z})$ or $e(\frac{1}{4} 0 z; \frac{3}{4} 0 \bar{z})$. The notation used here is that of *International Tables for X-ray Crystallography* (1952) for space group No. 51, $Pm\bar{m}a$. The other twofold positions in the space group require a centre of symmetry which is not compatible with any of the common eight-coordination polyhedra found in practice.

From the corrected intensities (program written by E. G. Boonstra) a three-dimensional Patterson synthesis was calculated using a centrosymmetric Fourier program compiled by P. Gantzel and H. Hope. The above-mentioned twofold positions give rise to the Harker peaks $\frac{1}{2}, 0, \pm 2z$ which were satisfied in $P(uvw)$ for $z = \frac{4}{5}$. Since the point symmetry of both twofold positions was the same, it was decided to place the W atoms in the symmetry related sets at $y = \frac{1}{2}$. A three-dimensional Fourier synthesis was next computed with only the heavy atoms placed in the unit cell. The peaks for the lighter elements could be determined without great difficulty. The residual, $R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$,

was 0.26 at this stage. A least-squares full-matrix refinement of the atomic parameters (with only half the number of oxygen positions placed) and a general isotropic temperature factor of 3.0 \AA^2 , using the Fortran program *ORFLS* (Busing, Martin & Levy, 1962) terminated after one cycle with a residual, $R = 0.164$. The quantity minimized by this program is $\sum w(F_o - F_c)^2$. A weighting scheme for the structure factors with $w = 1$ was used for all observed and unobserved reflexions. At this stage a three-dimensional difference Fourier synthesis was computed which revealed the positions of the remaining oxygen atoms with certainty. The number of reflexions was now reduced to 895 due to Laue streaks and other film factors resulting in inaccurate intensity measurements. Recalculation with all the atoms placed gave a residual R of 0.149, and four more cycles of isotropic least-squares refinement reduced this value to 0.138, which was considered complete with parameter shifts less than 0.1 of their standard deviations. The Debye-Waller factors for O(3) (11.05 \AA^2), O(2) (9.7 \AA^2) and O(1) (9.5 \AA^2) are exceptionally high and can be attributed to disorder in the structure. The difference Fourier synthesis showed that O(3) (placed in the mirror plane at $\frac{1}{4} 0 z$) had a broad elliptical peak elongated along the $[100]$ direction with two maxima 0.43 \AA away from the plane. This was an indication of a disordering effect. It was also substantiated in a subsequent conversion of isotropic to anisotropic temperature factors and in computing one cycle of refinement, in which the term b_{22} became negative.

The O(2) \cdots O(3) separation (2.461 \AA) is the shortest presumably non-bonded distance in the structure, and as the estimated standard deviations have a maximum value of 0.05 \AA (Table 4), it is comparable with the shortest O \cdots O separations (2.55 \AA) found for inorganic acids (Pimentel & McClellan, 1960). O(4) is more firmly bound than other O atoms in the structure as it is tetrahedrally hydrogen bonded to two N and two O atoms, while O(2) and O(3) are each hydrogen bonded in only two directions. The close contact and

less firm bonding could lead to excessive vibration of O(2) and O(3). O(1) is on the edge of the tetrahedron and is presumably hydrogen bonded in only three directions so that it would still vibrate more than O(4) but less than O(2) and O(3).

When layer lines were not scaled experimentally, Lingafelter & Donohue (1966) stated that a full anisotropic refinement would be meaningless because of complete degeneracy between b_{ii} and the scale factors. However, the introduction of anisotropic thermal motion in this structure determination is justified in the overall accuracy of the structure. The number of reflexions was further reduced to 879 followed by three cycles of anisotropic refinement keeping the thermal coefficients of O(3) constant. The final R index terminated at 0.091 including observed and unobserved reflexions. The maximum parameter shifts were all less than 0.1 of the standard deviations and refinement was considered complete.

The above scattering factors for W, C, N, and O were obtained from the work of Cromer & Waber (1965). The final observed and calculated structure factors are given in Table 2. The system of nomenclature is given in Table 3, final parameters and standard deviations are listed in Table 4 and the isotropic and anisotropic thermal coefficients with standard deviations in Table 5.

Table 3. System of nomenclature for atoms relating Roman numerals and positions in the space group

I	$\frac{1}{2}$	\bar{y}	z	VI	$\frac{1}{2}$	y	$\frac{1}{2}$
II	$\frac{1}{2}-x$	$\frac{1}{2}$	z	VII	$\frac{1}{2}+x$	0	\bar{z}
III	$\frac{1}{2}-x$	y	z	VIII	$\frac{1}{2}+x$	y	\bar{z}
IV	$\frac{1}{2}-x$	\bar{y}	z	IX	$\frac{1}{2}+x$	$\frac{1}{2}$	\bar{z}
V	$\frac{1}{2}-x$	0	z				

' = $1+z$

" = \bar{y} in adjacent cell

Description of the structure

[010] and [001] projections of the structure are given in Fig. 2 and 3. It is shown that the configuration of the anion is an approximate square antiprism formed by eight CN-ligands around the W atom (Table 6). The anions in the crystal are stacked in linear columns approximately 2.65 Å apart normal to (001). They also form nearly linear zigzag chains in the [100] direction, the difference in height between two W atoms in adjoining unit cells being 0.55 Å. The anion possesses only mm symmetry which is also the required point symmetry for the heavy atom in the space group. The four cyanide groups originating from C(3) and N(3) approximate symmetry 4, the difference in the s lengths (see Fig. 1) being only 0.052 and 0.083 Å respectively (Table 6). The other four cyanide groups originating from C(1) and C(2) on the mirror planes at $x = \frac{1}{2}$ and

Table 4. Final fractional coordinates ($\times 10^4$) and their estimated standard deviations obtained from the anisotropic refinement

	Wyckoff notation	Point symmetry	x/a	y/b	z/c	$\delta(x)$	$\delta(y)$	$\delta(z)$
W	f	mm	2500	5000	437	—	—	0.0013 Å
C(1)	k	m	2500	3102	2348	—	0.0227 Å	0.0301
C(2)	j	m	1284	5000	2423	0.0215 Å	—	0.0257
C(3)	l	1	1581	3696	8582	0.0143	0.0160	0.0226
N(1)	k	m	2500	2144	3161	—	0.0188	0.0244
N(2)	j	m	638	5000	3578	0.0186	—	0.0213
N(3)	l	1	1123	2999	7596	0.0143	0.0160	0.0175
O(1)	i	m	709	0	1614	0.0272	—	0.0320
O(2)	e	mm	2500	0	9423	—	—	0.0401
O(3)	e	mm	2500	0	5497	—	—	0.0508
O(4)	h	2	0	1697	5000	—	0.0217	—

Table 5. Anisotropic thermal parameters with estimated standard deviations (in parentheses) ($\times 10^4$)

The b_{ij} are defined by:

$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{13}hl + 2b_{23}kl)]$$

	B_j^*	$\delta(B_j^*)$	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
W	2.82 Å ²	0.05 Å	24	100 (1)	167 (5)	—	—	—
C(1)	3.26	0.60	43 (11)	73 (23)	318 (104)	—	—	2 (39)
C(2)	3.12	0.58	40 (11)	82 (20)	182 (88)	—	18 (24)	—
C(3)	3.75	0.46	27 (6)	102 (17)	526 (89)	-15 (9)	-69 (19)	-69 (33)
N(1)	3.74	0.55	49 (10)	80 (19)	323 (86)	—	—	-10 (35)
N(2)	3.74	0.56	43 (9)	121 (22)	154 (71)	—	13 (21)	—
N(3)	4.84	0.48	55 (8)	154 (19)	259 (61)	15 (11)	-8 (18)	1 (29)
O(1)	9.50	1.12	81 (16)	355 (55)	578 (123)	—	22 (38)	—
O(2)	9.68	1.69	182 (42)	275 (69)	334 (151)	—	—	—
O(3)†	11.05	1.98	358 (35)	-6 (73)	241 (215)	—	—	—
O(4)	6.36	0.72	83 (14)	171 (28)	426 (94)	—	-113 (29)	—

* After final isotropic refinement ($R=0.138$).

† After one cycle of anisotropic refinement.

$y = \frac{1}{2}$ show a mean out-of-plane displacement of ± 0.03 and ± 0.13 Å at the C and N atoms respectively, accompanied by a $\pm 5^\circ$ deviation for the expected right-angles on the corners of the square vat of the antiprism (Fig. 1).

The oxygen atoms of the water molecules all occupy specialized site symmetries, ranging from a twofold axis to the maximum molecular symmetry mm . Although the positions of the hydrogen atoms could not be found from the difference Fourier synthesis, the whole structure can be considered as a hydrogen bonded one with the water molecules stacked between the anionic sheets

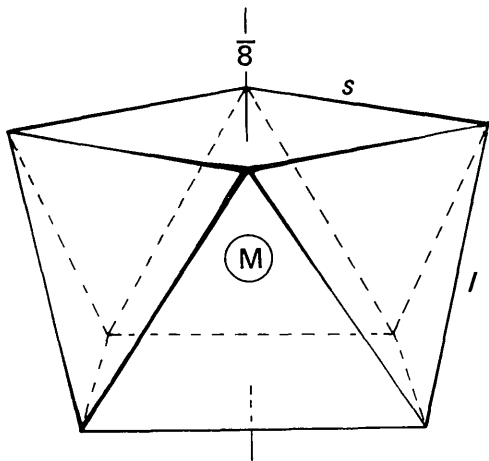


Fig. 1. The Archimedean antiprism with $D_{4d}-\bar{8}m2$ symmetry.

The metal atom M is situated at the centre and each of the eight ligands are directed towards the corners of the polyhedron. The 16 edges are equally divided between two symmetry types, s and l . The vertical axis and four horizontal axes of symmetry 2 intersect at M . Each of the latter symmetry elements passes through the midpoints of two opposed l edges. The four vertical mirror planes bisect the angles between the twofold axes.

with a $[010]$ repeat distance. Each of the symmetry-related atoms O(4) is surrounded tetrahedrally by two nitrogen and two oxygen atoms with presumably O—H---N, 2.62 Å, and O—H---O, 2.89 Å (Table 7). The hydrogen bonding of the O(4) tetrahedra is such that all the nitrogen atoms in the general positions of two adjacent anions in the unit cell are linked across the oxygen atom (Fig. 2). Each of these tetrahedra shares a common edge, for example between O(1) (V) and O(1) (VII), with the corresponding one in the adjoining unit cell (Fig. 3). It is only O(3) of the remaining water molecules which participates in the bonding scheme between anions in the $[010]$ direction. The O(3)—H---N distance of 2.58 Å and the other similar distances reported here are typical for O—H---N hydrogen bonds in inorganic compounds (Pimentel & McClellan, 1960). The O(2) water molecule links the oxygen atoms of two O(4) tetrahedra on both sides of the mirror plane in the $[001]$ repeat distance of the adjoining unit cell with an O(1)—H---O(2') distance of 2.905 Å. The bonding angles at O(2) and O(3) are 123.6 and 110.7° respectively, and it is assumed that the hydrogen atoms of these water molecules are situated in the mirror planes at $x = \frac{1}{4}$ and $y = 0$.

Discussion

The dimensions of the $W(CN)_8^{4-}$ ion are given in Tables 6 and 8. It is interesting to compare the mean bond lengths in the W—C≡N chain with the reported data of Hoard, Hamor & Glick (1968) and of Bok, Leipoldt & Basson (1969). We then note a decrease of about 0.02 Å in the metal-carbon bond lengths in the series $W(CN)_8^{4-}$ (2.177 Å) > $Mo(CN)_8^{4-}$ (2.163 Å) > $W(CN)_8^{3-}$ (2.139 Å) and a corresponding increase of about 0.015 Å in the carbon-nitrogen bond lengths

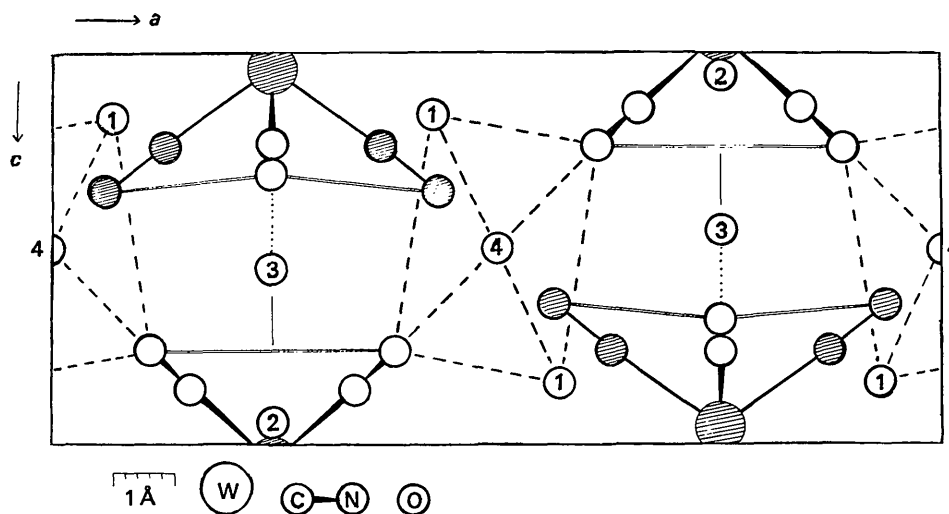


Fig. 2. Projection of the structure along b , seen up to $y = \frac{1}{2}$. Shaded atoms refer to W, C(2) and N(2) situated in the mirror plane at $y = \frac{1}{2}$. All non-shaded atoms must be seen as superposed on an identical group(s) due to the same mirror plane. Dashed lines outline the O(4) tetrahedra. Dotted lines refer to H-bonding between O(3) and N(1) of the CN-groups. The numbering of the O atoms is the same as in Table 4. Atom numbers 1, 2 and 3 are situated on the mirror plane at $y = 0$.

(1.133 < 1.152 < 1.164 Å). The metal–nitrogen separations remained practically the same. The $\text{W}(\text{CN})_8^{4-}$ ion shows an increase of 1.8% in the metal–carbon bond length compared with the $\text{W}(\text{V})$ analogue. This value is much smaller than the ~5% increase over the expected value for the Mo–C bond length in the $\text{MoO}_2(\text{CN})_4^{2-}$ ion (Day & Hoard, 1968). The average estimated standard deviations for the above mentioned bond lengths are about 0.02 Å for the W compounds and 0.01 Å for the Mo compound. It remains to be decided whether these changes are due to experimental error or are significant. The average metal–carbon length for the $\text{W}(\text{CN})_8^{4-}$ ion is almost the same as the W–C(3) bond length. W–C(3) represents four of the possible eight different W–C bond lengths possible for the anion according to the point symmetry mm of the space group. The W–C(1) and W–C(2) bond lengths as found deviate by up to 0.05 Å from the mean value of 2.177 Å, but if the experimental error is taken into account they could be nearly the same. If, however, the difference is significant, it is possible that the

shortening and lengthening of these bonds over the mean value may be attributed to the considerations given below.

The square antiprism of $D_{4d}\bar{8}m2$ symmetry is illustrated in Fig. 1. The calculation of the bonding angle θ between the metal–carbon bond and the $\bar{8}$ axis of the antiprism yielded the following values: C(1), 57.5°; C(2), 54.4°; C(3), 57.7°; mean = 56.5°. If the d^4sp^3 hybrid valence orbitals of Duffey (1950) with $l/s = 1.049$, $\theta = 57.6^\circ$ are considered (see Fig. 1 for l and s), then the mean value of 57.6° for C(1) and C(3) must be representative for the anion. The average l/s ratio is 1.069, but considering only the C(3)–C(3) (III) and C(3) (III)–C(3) (IV) edge lengths, this ratio becomes 1.062. The values $\theta = 57.6^\circ$, $l/s = 1.062$ also approximate well to the Hoard–Silverton model with $\theta = 57.3^\circ$, $l/s = 1.057$ (Hoard & Silverton, 1963). The stereochemistry of the $\text{W}(\text{CN})_8^{4-}$ ion thus clearly differs from that of the $\text{W}(\text{CN})_8^{3-}$ ion, where the latter follows the hard sphere model with $l \approx s = 2.60$ Å and $\theta = 59.1^\circ$ (Bok, Leipoldt & Basson, 1969).

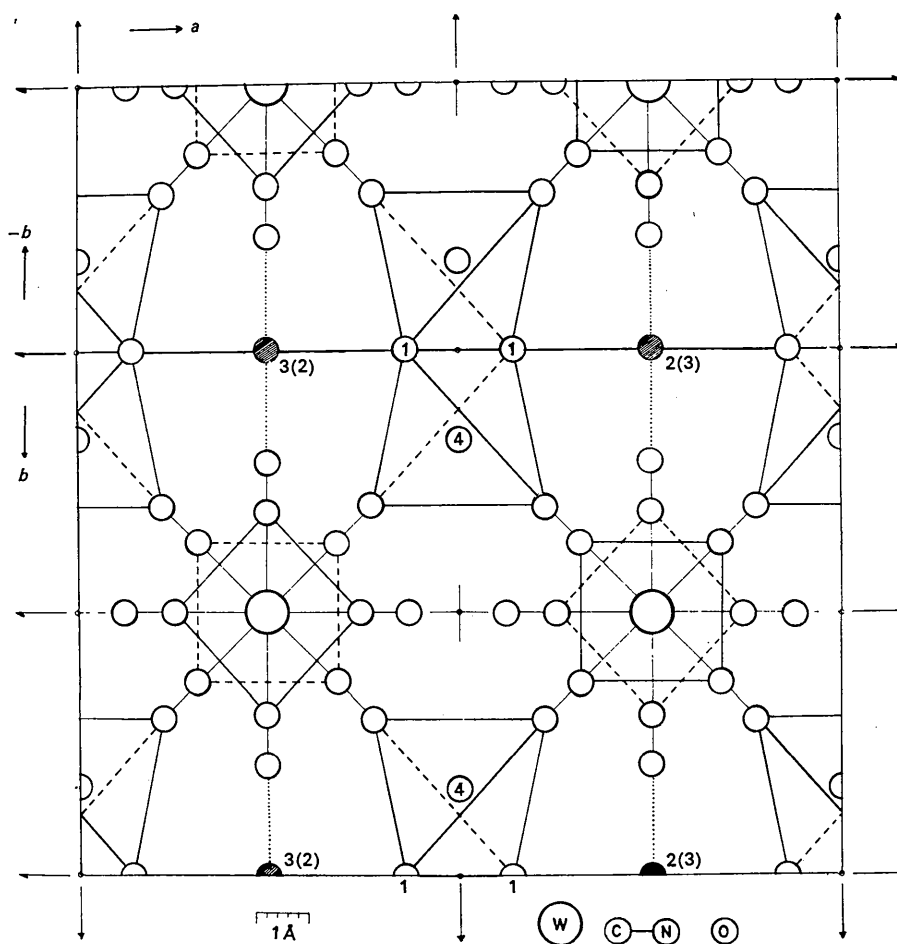


Fig. 3. Projection of the structure along c . Thick solid and dashed lines outline the polyhedra around the W and O atoms. Dotted lines indicate H-bonding between O(3) and N(1) atoms. Shaded circles refer to O(3) on top of O(2) and *vice versa*. The numbering for oxygen atoms is the same as in Fig. 2.

The W–C(1) and W–C(2) bond lengths are peculiar in that a shortening of the metal–carbon bond length is accompanied by a lengthening of the C≡N length, and *vice versa*. The shortened W–C(2) bond also has the smallest bonding angle with the $\bar{8}$ axis of the anion. This effect is accompanied by a N(2)···N(2) (IX) contact of 2.55 Å between two adjacent anions in the unit cell. This anion–anion contact is to be expected since the cation/anion radius ratio is much less than 0.414 (Pauling, 1960). The same effect was also observed by

Pierrot, Kern & Weiss (1966) for $H_4Fe(CN)_6$ with N···N contacts of 2.68 Å and 2.88 Å. The above-mentioned van der Waals contact makes an angle of 134.4° with the W–C≡N chains and corresponds to a van der Waals radius of 1.28 Å for nitrogen. This decrease of approximately 0.20 Å from the several values listed in the literature for the van der Waals radius of nitrogen (Britton, in Dunitz & Ibers, 1967) must be attributed to the partial negative charge on the nitrogen atom, which is further substantiated by

Table 6. *Dimensions of the coordination polyhedron*

Distances		Edges of <i>s</i> type	
C(1)——C(2)	2.557 Å	N(1)——N(2)	3.889 Å
C(3)——C(3) (III)	2.629	N(3)——N(3) (III)	3.937
C(3) (III)–C(3) (IV)	2.577	N(3) (III)–N(3) (IV)	3.954
Mean	2.587	Mean	3.926
		Edges of <i>l</i> type	
C(1')–C(3)	2.764	N(1')–N(3)	4.093
C(2')–C(3)	2.763	N(2')–N(3)	4.296
Mean	2.764	Mean	4.195
Diagonally across square faces			
C(3)–C(3) (IV)	3.682	N(3)–N(3) (IV)	5.580
C(1)–C(1) (I)	3.751	N(1)–N(1) (I)	5.643
C(2)–C(2) (II)	3.476	N(2)–N(2) (II)	5.326
Mean	3.636	Mean	5.516
Angles			
C(2)——C(1)——C(2) (II)	85.63°	N(2)——N(1)——N(2) (II)	86.43°
C(1)——C(2)——C(1) (I)	94.33	N(1)——N(2)——N(1) (I)	93.03
C(3) (III)–C(2) (II')–C(3) (IV)	55.60	N(3) (III)–N(2) (II')–N(3) (IV)	54.81
C(1')——C(3)——C(2')	55.1	N(1')——N(3)——N(2')	55.20
C(3)——C(1')——C(2')	62.40	N(3)——N(1')——N(2')	65.05
C(2') (II)–C(3) (III)–C(3) (IV)	62.20	N(2') (II)–N(3) (III)–N(3) (IV)	62.60
C(1)——W——C(2)	71.75	N(1)——W——N(2)	72.08
C(1)——W——C(1) (I)	114.90	N(1)——W——N(1) (I)	117.66
C(2)——W——C(2) (II)	108.79	N(2)——W——N(2) (II)	107.05
C(3)——W'——C(3) (III)	74.63	N(3)——W'——N(3) (III)	72.99
C(3)——W'——C(3) (IV)	116.23	N(3)——W'——N(3) (IV)	114.91
C(3) (III)–W'——C(3) (IV)	72.56	N(3) (III)–W'——N(3) (IV)	73.36

Table 7. *Interatomic distances and angles between atoms adjacent to the $W(CN)_6^{4-}$ ions*

Oxygen tetrahedra			
O(4)–O(1)	2.889 Å	N(3) (III)–N(3) (VIII)	4.573 Å
O(4)–N(3)	2.623	O(1) (VII)–O(1) (V)	4.704
O(1)–N(3)	4.815	N(3) (III)–O(1) (VII)	3.987
N(3)——O(1)——O(4)	27.63°	N(3) (VIII)–O(1) (V)——O(4) (VI)	41.10°
O(1)——O(4)——N(3)	121.66	O(1) (VII)–O(1) (V)——O(4) (VI)	35.50
N(3) (III)–O(4) (VI)–N(3) (VIII)	121.26	N(3) (III)–N(3) (VIII)–O(4) (VI)	29.35
O(1) (V)–O(4) (VI)–O(1) (VII)	109.00	N(3) (III)–O(1) (V)——O(1) (VII)	49.50
N(3) (III)–O(4) (VI)–O(1) (VII)	92.53	N(3) (III)–N(3) (VIII)–O(1) (VII)	50.18
Other dimensions			
O(1)–O(2')	2.905 Å	N(2) (II)–N(2) (IX)	2.551 Å
O(3)–O(2)	2.461	N(1)——O(2)	4.460
O(3)–N(1)	2.576	O(1)——O(2)	5.524
O(3)–O(1)	3.532	O(4)——O(3)	3.961
O(1)–N(1)	3.462	N(2) (II)–N(3) (VIII)	3.285
N(2)–N(3)	3.276		
N(1)–O(3)–O(2)	124.63°	O(1)–O(3)——O(1) (V)	92.90°
O(1)–O(3)–O(2)	133.55	N(1)–O(3)–N(1') (I)	110.74
O(1)–O(3)–N(1)	66.95	O(1)–N(1)–O(1) (V)	95.38
O(4)–O(3)–O(4) (VI)	128.98	O(1)–O(2')–O(1) (V)	123.60

Table 8. Dimensions of the $\text{W}-\text{C}\equiv\text{N}$ chains in the $\text{W}(\text{CN})_8^{4-}$ ion

Bond lengths					
W-C(1)	2.225 Å	C(1)-N(1)	1.074 Å	W-N(1)	3.296 Å
W-C(2)	2.138	C(2)-N(2)	1.174	W-N(2)	3.312
W'-C(3)	2.177	C(3)-N(3)	1.133	W'-N(3)	3.311
Mean	2.180	Mean	1.127	Mean	3.306
Bond angles					
W-C(1)-N(1)	176.3°	W-C(2)-N(2)	177.9°		
W'-C(3)-N(3)	178.4	Mean	177.5		

the partial double-bond character for the $\text{W}-\text{C}(2)$ bond. It seems as though the anion-anion contact forces the $\text{W}-\text{C}\equiv\text{N}$ chain towards a smaller bonding angle of 54.4° (instead of 57.6°). The d_{z^2} orbital of the W atom has its principal lobes directed along $\pm z$ parallel to the crystallographic [001] direction, and makes a nodal angle of 54.7° with the $\bar{8}$ axis of the anion. This gives an overlap of 0.3° with the $\text{W}-\text{C}(2)$ bond direction and permits an electron flow towards the empty $p\pi^*$ orbitals of the cyanide groups. This 'back-donation' avoids the accumulation of a large negative charge on the metal atom and consequently weakens the carbon-nitrogen bond. As pointed out by Hoard, Hamor & Glick (1968), the equatorial doughnut of the d_{z^2} orbital is centred on the xy plane and any σ bond with an angle of approximately 33° is especially favourable for π overlap. This is illustrated in the lengthening of the $\text{W}-\text{C}(1)$ bond length over the mean value. The partial π -bond character of the $\text{W}-\text{C}(2)$ bond minimizes the electron density in the environment of the $\text{W}-\text{C}(1)$ bond and consequently loosens the σ bond. This also results in a shortening of the $\text{C}\equiv\text{N}$ bond. Thus when the angle θ between the σ bond and the $\bar{8}$ axis of the anion is greater than 57° normal bond lengths are expected, but when θ is smaller, π bonding can shorten the metal-carbon bond.

In comparing the hard-sphere approximation of $\text{W}(\text{CN})_8^{3-}$ with the model given by Hoard & Silverton (1963) for $\text{W}(\text{CN})_8^{4-}$, it is found that the closed-shell repulsive energy will be reduced by 2.2% in going from the $\text{W}(\text{V})$ to the $\text{W}(\text{IV})$ species. This may be due to the smaller 'effective metallic radius' of 1.37 Å for $\text{W}(\text{V})$ compared with 1.41 Å for $\text{W}(\text{IV})$.

The structure found does not enable us to predict definitely when an octacyano complex will choose the antiprismatic or the dodecahedral coordination. Although the four acidic protons could not be found in the difference Fourier synthesis, the structure shows, however, that the packing of the ions in both $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ and $\text{H}_4\text{W}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$ is layer-like, and that the water molecules and/or cations are interstitially positioned in an orderly array to bring about close electrostatic interactions to stabilize all or part of the CN^- groups.

Calculations were carried out on an I.B.M. 360 model 65 computer.

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References

- BOK, L. D. C., LEIPOLDT, J. G. & BASSON, S. S. (1970). *Acta Cryst.* B26, 684.
- BUSING, W. R., MARTIN, K. D. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104.
- DAY, V. W. & HOARD, J. L. (1968). *J. Amer. Chem. Soc.* 90, 3374.
- DUFFEY, G. H. (1950). *J. Chem. Phys.* 18, 746.
- DUNITZ, J. D. & IBERS, J. A. (1967). *Perspectives in Structural Chemistry*, Vol. I, p. 143. New York, London, Sydney: John Wiley.
- FURMAN, N. H. & MILLER, C. O. (1950). *Inorganic Synthesis*, Vol. 3, p. 160. New York: McGraw Hill.
- HAMILTON, W. C. (1955). *Acta Cryst.* 8, 185.
- HAYES, R. G. (1966). *J. Chem. Phys.* 44, 2210.
- HOARD, J. L., HAMOR, T. A. & GLICK, M. D. (1968). *J. Amer. Chem. Soc.* 90, 3177.
- HOARD, J. L. & NORDSIECK, H. H. (1939). *J. Amer. Chem. Soc.* 61, 2853.
- HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* 2, 235.
- KETTLE, S. F. A. & PARISH, R. V. (1965). *Spectrochim. Acta*, 21, 1087.
- KOSINSKA, A. & STASICKA, J. W. (1957). *Roczniki Chem.* 31, 1029.
- LINGAFELTER, E. C. & DONOHUE, J. (1966). *Acta Cryst.* 20, 321.
- MCGARVEY, B. R. (1966). *Inorg. Chem.* 5, 476.
- MUETTERTIES, E. L. (1965). *Inorg. Chem.* 4, 769.
- MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Quart. Rev.* 21, 109.
- OLSSON, O. (1914). *Z. anorg. Chem.* 88, 49.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. p. 520. Ithaca: Cornell Univ. Press.
- PIERROT, M., KERN, R. & WEISS, R. (1966). *Acta Cryst.* 20, 425.
- PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*, p. 285. London: Freeman.
- STAMMREICH, H. & SALA, O. (1960). *Z. Electrochem.* 64, 741.
- STAMMREICH, H. & SALA, O. (1961). *Z. Electrochem.* 65, 149.