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A Second Configuration for the Octacyanide Group. The Crystal Structure of $Na_3W(CN)_8.4H_2O$

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The crystal structure of the compound $C_8H_8N_8O_4Na_3W$ has been determined by means of a three-dimensional X-ray analysis. The space group is $P2_1/c$ (C_{2h}^5), and the cell dimensions are $a=6{\cdot}126$, $b=16{\cdot}13$, $c=17{\cdot}42$ Å, $\beta=94°45'$, with 4 molecules per unit cell. The corresponding Mo compound is isomorphous with the W compound. The atoms all lie in general positions, while the $W(CN)_8^{3-}$ anion has approximate antiprismatic D_{4d} symmetry. The average distances for the octacyanide ion are: W–C = 2·139, C–N = 1·164, and W–N = 3·302 Å. The carbon atoms form an angle of 59·1° with the tetragonal axis of the anion.

Introduction

The octa-coordinated $Mo(CN)_8^{3-}$, $W(CN)_8^{3-}$, and $Re(CN)_8^{2-}$ complex anions are the only transition-metal cyanide compounds with a d^1-electron configuration that have been well characterized. Since Hoard & Nordsieck (1939) determined the dodecahedral configuration of the complex $Mo(CN)_8^{4-}$ anion, it has been postulated that all Mo and W octacyano complexes have the same structural anion configuration since there is a partial correspondence of the distribution of intensities and frequencies in the infrared and Raman spectra. For further evidence in this connexion an X-ray study has been made of the pentavalent octacyanocomplexes of Mo and W.

Experimental

$K_4W(CN)_8.2H_2O$ and $K_4Mo(CN)_8.2H_2O$ were prepared by the methods of Kosinska & Stasicka (1957) and of Furman & Miller (1960) respectively, and were oxidized to the pentavalent state with cerium sulphate using *N*-phenylanthranilic acid as indicator. From the insoluble $Ag_3W(CN)_8$ and $Ag_3Mo(CN)_8$ complexes which were precipitated, $Na_3W(CN)_8.4H_2O$ and $Na_3Mo(CN)_8.4H_2O$ were prepared by the method of Baadsgaard & Treadwell (1955). Prismatic a-needles of both complexes were grown from aqueous solution by evaporation over anhydrous $ZnCl_2$ in the dark.

The crystal data (Table 1) were determined from oscillation and Weissenberg photos with Cu $K\alpha$ radiation. The W and Mo compounds were found to be isomorphic. The camera was standardized with NaCl. Densities were determined by flotation. The isomorphic compounds showed systematic absences for $0k0$, $k\neq 2n$, $h0l$, $l\neq 2n$, giving a unique determination of the space group $P2_1/c$.

Optical investigation in polarized light showed extinction parallel to the needle axis for both compounds. No twinning or peculiar extinction effects were observed.

Table 1. *Crystal data*

Compound	$Na_3Mo(CN)_8.4H_2O$	$Na_3W(CN)_8.4H_2O$
M.W.	445·12	533·02
a (Å)	6·126	6·126
b (Å)	16·14	16·13
c (Å)	17·53	17·42
β	94°27′	94°45′
Z	4	4
V (Å)^3	1728	1715·4
D_x (g.cm^{-3})	1·71	2·06
D_m (g.cm^{-3})	1·71	2·05

It was found that the Mo^V complex decomposed more rapidly in X-radiation than the corresponding W^V compound, and thus the structure investigation was carried out on the W compound.

A suitable crystal (0·21 × 0·20 × 0·61 mm) of $Na_3W(CN)_8.4H_2O$ was covered with Canada balsam, as it otherwise begins to lose water of crystallization after about two days. The crystal was rotated about the a axis. Integrated multiple-film equi-inclination Weissenberg photographs were taken for layers 0 to 5, with Cu $K\alpha$ radiation [μ(Cu $K\alpha$) = 162·9 cm^{-1}]. The intensities of about 87% of a total of 3081 reflexions could be determined visually using a standard calibrated scale, and were corrected with the usual factors, Lorentz, polarization, spot shape, α_1–α_2 splitting, and absorption.

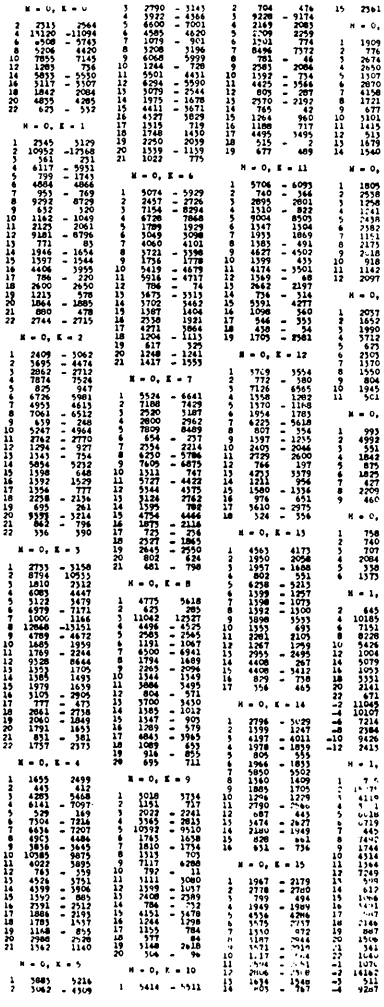
Structure determination and refinement

A three-dimensional Patterson synthesis gave the coordinates of the tungsten atom. The large difference in atomic number between W and the lighter elements caused false peaks so that the other atomic coordinates could not be determined.

A Fourier synthesis was next made in three dimensions with only the W atoms placed in the general positions. The expected peaks for the lighter elements could be determined without great difficulty. The R value was at this stage 0·374. A second three-dimensional Fourier synthesis was carried out with all the

Table 2. *Observed and calculated structure factors*

The data are separated into groups having common values of h and k. The three columns in each group list values of l, F_o and F_c, in that order.



atoms placed in the asymmetrical unit. Well developed symmetrical peaks resulted while the R value decreased further to 0·30, which was considered satisfactory for starting a refinement.

The coefficient for the general isotropic temperature factor of the atoms was taken as 3·0 Å^2. After the first refinement cycle in which only the scale factors were refined by the least-squares method, R was 0·284, where

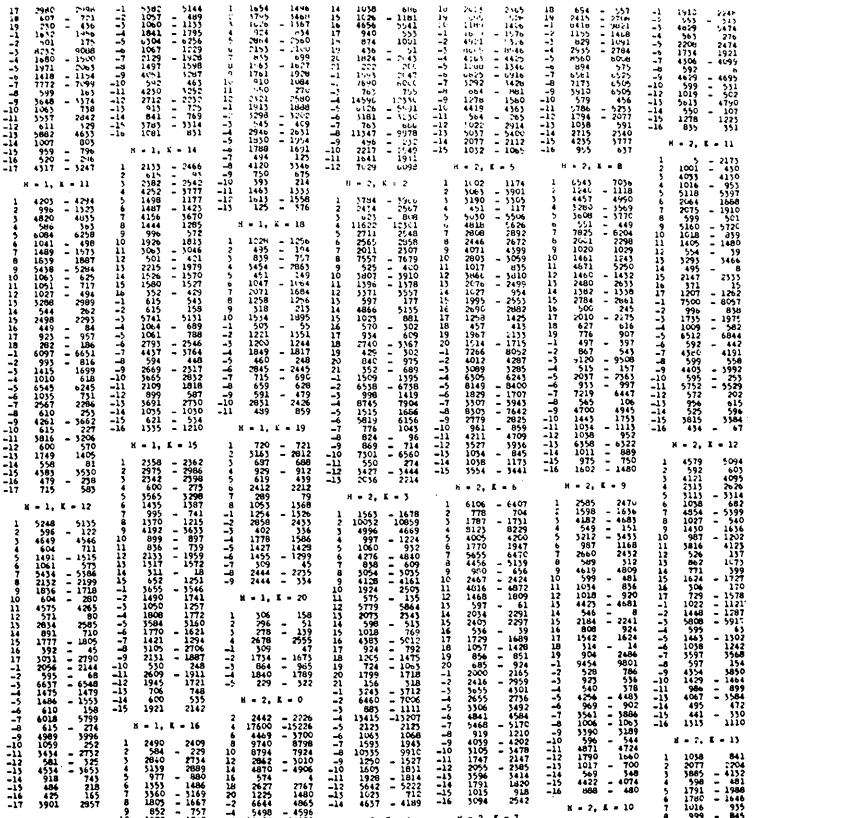
$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} .$$

In the second cycle, in which the atomic coordinates were refined isotropically, the discrepancy index decreased to 0·184.

Two more full-matrix least-squares cycles reduced the R value to 0·1415 and 0·1349 respectively. Both the final weighted and unweighted R index (including unobserved reflexions) was reduced to 0·1323 in one more cycle. Analysis of the observed and calculated structure factors showed that for the F_o range from 0 to 1000 the average R index was 0·39 for 1002 reflexions, whilst an average value of 0·094 was calculated for the remaining intensity data. Omitting the unobserved reflexion data should thus give a much lower R index. At this stage the maximum shift in atomic coordinates for most of the atoms was far less than 0·95 of the estimated standard deviations, except for W, C(3), C(5), and C(8), where only a few of the fractional coordinates could be shifted appreciably. However, the coordinates and temperature factors, as well as subsequent distances and angles reported here, confirm the reliability of the structure.

The atomic scattering factors of Na^+, C, and O, as well as extrapolated values for W^{5+} were obtained from the work of Cromer & Waber (1965), while those for

Table 2 (*cont.*)

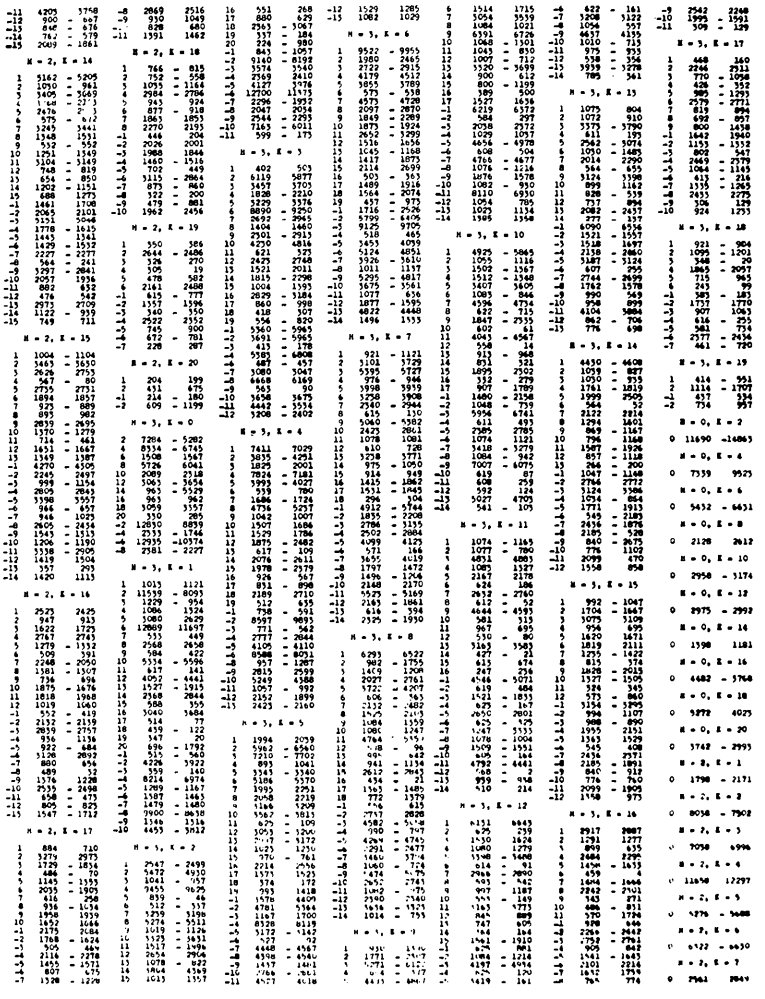


N^- were taken from *International Tables for X-ray Crystallography* (1962). The final observed and calculated structure factors are given in Table 2. Final parameters and standard deviations are listed in Table 3.

Discussion

The (100) projection of the structure is illustrated in Fig. 1. It shows that the octacyano ion for pentavalent Mo and W has the antiprismatic configuration in the salts investigated here. The calculation of interatomic distances within the anion (Table 4) shows that the average W–C separations are 2·139 Å, the W–N separations 3·302 Å, and the C–N separations 1·164 Å. These distances agree well with the values 2·163, 3·314 and 1·152 Å which were redetermined by Hoard, Hamor & Glick (1968) for the dodecahedral $Mo(CN)_8^{4-}$ ion. By subtracting the covalent radius (Pauling, 1960) of the carbon atoms from the experimentally observed metal–ligand distances, it is calculated from the above data that the 'effective metal radii' of W^V and Mo^{IV} are 1·37 and 1·39 Å respectively. The smaller radius of the tungsten atom is to be expected due to its higher formal positive charge. The W–C≡N chains depart by not more than 6° from linearity (the average being 176·3°) and no W–N distance is more than 0·004 Å shorter or longer than the sum of the W–C and C≡N bond lengths. A closer inspection of the W–C≡N chain dimensions seems to indicate that the average W–C distances are shorter by 0·022 Å and the average C≡N distances longer by 0·012 Å, with a net shortening of 0·01 Å for the W–N distances, compared with the corresponding values for $K_4Mo(CN)_8.2H_2O$ (Hoard *et al.*, 1968). The W–C bond lengths (Table 4) can be grouped into two categories: the atoms C(1), C(3), C(5), and C(7) having an average W–C length of 2·124 Å, and the remaining four averaging 2·155 Å. Two of the atoms in each category are accompanied by longer C≡N distances and two by shorter ones compared with the average value. The mean dimensions of the coordination polyhedron (Table 5) are in excellent agreement with what would be expected for

Tab e 2 (*cont.*)



the antiprism. The *s* and *l* edges, averaging 2·592 and 2·620 Å respectively, are of the same magnitude; the angles at atoms on the corners of the two square faces normal to the $\bar{8}$ axis average 89·9°. Table 6 shows the least-squares equations for the best mean planes through the carbon and nitrogen atoms. It is evident that the planes containing the atoms C(1), C(2), C(3), C(4) and their corresponding nitrogen analogues exhibit the greatest mean deviation of about 0·079 and 0·086 Å respectively. These planes lie approximately normal to the [100] direction. The maximum estimated standard deviation for these atoms in the latter direction is approximately 0·025 Å. The former deviations exceed the latter by a factor 3. It seems, subject to the accuracy of the structure, that some disorder of the atoms in these planes must be present.

The shape of the square antiprism of maximum symmetry D_{4d}–$\bar{8}2m$ is determined by two parameters: the ratio *l*/*s* and the angle θ made by a bond M–*A* with the $\bar{8}$ axis. Table 7 compares our generalized experimental data with those of the 'most favourable' polyhedra (MFP) and the hard sphere model (HSM) as reported by Hoard & Silverton (1963), where the valence shell of the central atom is free from non-bonding electrons and surrounded by neon-shell ligands.

Kepert (1965) and Muetterties & Wright (1967) showed that most of the square antiprismatic molecules exhibited distortion with the effect of decreasing the bond angle, θ, approximating the MFP-model. The only monomeric compound with a monodentate ligand listed was Na_3TaF_8 with $\theta = 59{\cdot}0°$. (Hoard, Martin, Smith & Whitney, 1954). This structure was only determined two-dimensionally. $Na_3W(CN)_8 . 4H_2O$ is the first of the square antiprismatic monomeric types to be subjected to a full three-dimensional analysis. The latter compound, together with Na_3TaF_8, seems to give the highest θ value, approximating to the HSM model.

The bond lengths and angles at the sodium atoms are given in Table 8. Each of the sodium atoms is surrounded octahedrally by a group consisting of four

Table 2 (*cont.*)

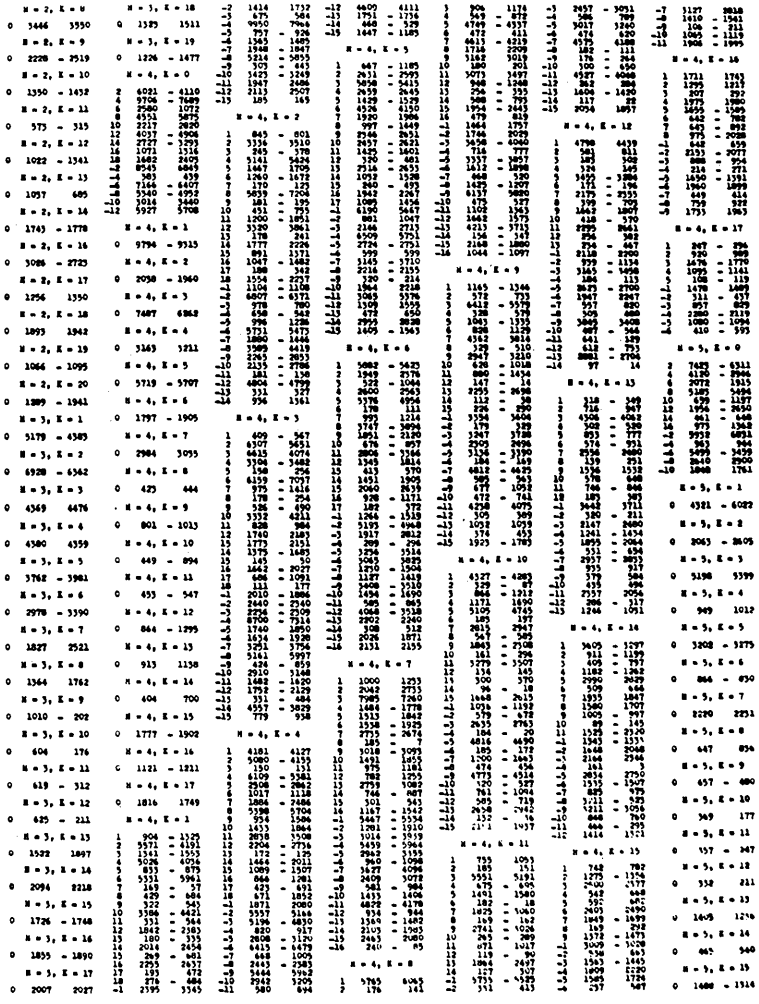


Table 2 (*cont.*)

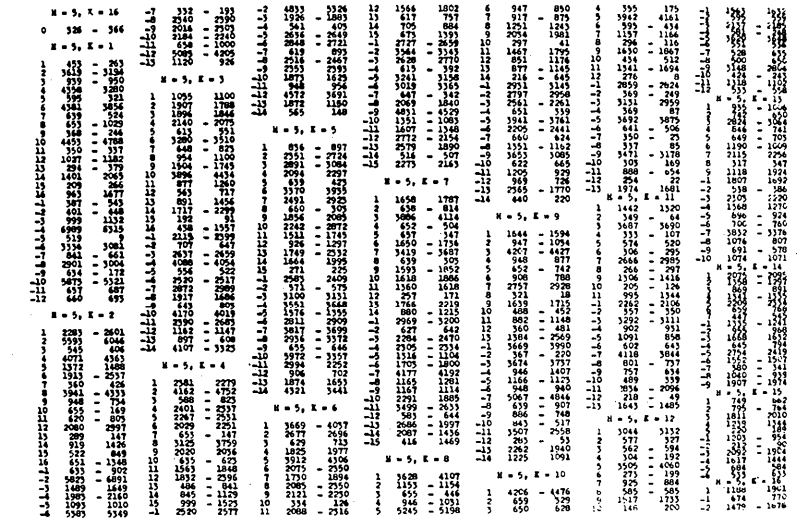


Table 3. *Final atomic coordinates and respective isotropic thermal parameters*

Estimated standard deviations of the last two figures are given in parentheses.

	x/a ($\times 10^4$)	y/b ($\times 10^4$)	z/c ($\times 10^4$)	B (Å^2)
W	424 (2)	2263 (1)	1036 (1)	3·47 (4)
C(1)	2519 (42)	1825 (14)	1987 (14)	3·58 (51)
C(2)	2100 (46)	1226 (16)	572 (15)	4·53 (60)
C(3)	2216 (47)	2736 (17)	135 (16)	3·69 (62)
C(4)	2108 (44)	3352 (15)	1485 (15)	3·68 (55)
C(5)	−1260 (40)	2685 (14)	1975 (13)	2·62 (49)
C(6)	−1455 (46)	3311 (16)	590 (15)	4·11 (59)
C(7)	−1570 (46)	1854 (16)	57 (15)	3·87 (59)
C(8)	−1234 (69)	1179 (26)	1432 (24)	4·48 (110)
N(1)	3635 (39)	1629 (14)	2514 (13)	4·38 (53)
N(2)	3116 (41)	677 (15)	347 (14)	4·41 (57)
N(3)	3110 (40)	2956 (14)	−418 (13)	4·48 (54)
N(4)	3065 (43)	3918 (16)	1728 (15)	5·02 (62)
N(5)	−2075 (41)	2895 (15)	2550 (14)	4·71 (56)
N(6)	−2467 (43)	3858 (16)	398 (15)	5·26 (61)
N(7)	−2605 (46)	1603 (17)	−481 (16)	5·40 (67)
N(8)	−2170 (39)	605 (14)	1649 (13)	4·31 (52)
Na(1)	4811 (17)	4534 (6)	4070 (6)	4·07 (23)
Na(2)	−4541 (19)	299 (7)	2920 (6)	4·58 (25)
Na(3)	−4331 (18)	2351 (6)	3573 (6)	4·19 (24)
O(1)	2725 (49)	410 (19)	3875 (17)	9·40 (84)
O(2)	2738 (36)	3477 (13)	3403 (12)	5·96 (53)
O(3)	−2840 (35)	4631 (13)	2956 (12)	5·56 (51)
O(4)	−1941 (45)	1111 (17)	3676 (16)	8·32 (75)

nitrogen and two oxygen atoms of the water molecules for Na(1) and Na(3), and three nitrogen and three oxygen atoms for Na(2). The mean separations for Na(1), Na(2), and Na(3) in each octahedron are 2·495, 2·493 and 2·499 Å respectively. All the octahedra are regular within the accuracy of the structure, and adjacent ones are linked by a common edge comprising a nitrogen and an oxygen atom. (Fig. 1.). The sodium atoms all occur at about the same height in the [100] direction (Fig. 2). Na(1) and Na(3) link four square antiprisms in the [010] and [001] directions respectively by means of one nitrogen atom on the square face of each polyhedron, the four nitrogen atoms being part of the octahedron. Na(2), with one extra oxygen atom incorporated in the octahedron, connects three different antiprisms in the above-mentioned way. The oxygen atoms occupy two different planes in pairs on both sides of the sodium atoms and occur approximately at the same height as the four nitrogen atoms of each of the two adjacent antiprisms in the [100] direction. No atoms occupy positions directly above or below the square vat of the antiprism. The closest nitrogen–oxygen separations are N(3)···O(1) (2·910 Å), N(5)···O(3) (2·936 Å) and N(6)···O(1) (2·817 Å). All the nitrogen atoms of one square antiprism are part of an octahedron around the sodium atoms, excepting N(6). The N(6)···O(1) distance is less than the sum of the van der Waals radii of the two atoms, and suggests a weak hydrogen bond to stabilize this nitrogen atom.

Table 3 shows relatively high B factors of 9·40 and 8·32 Å^2 for O(1) and O(4) respectively. Although these atoms are subjected to electrostatic interactions with the sodium atoms (being part of the octahedra) their positions are not so uniquely fixed relative to the remaining oxygen atoms considering the packing of the structure as a whole. Their thermal movement in the [001] direction might be appreciably larger, since they occupy the brim of a hole between adjacent antiprisms in the [010] direction.

Blight & Kepert (1968) stress the point that factors like ligand–ligand repulsion, crystal field stabilization, bond strength, π-bonding, and solvation energies could not be successfully correlated to the preferred stereochemistry of eight-coordinated compounds, and that the lattice energy in the solid state appears to be the most important factor in deciding the configurational type. Hoard & Silverton (1963) stated that the shape of a complex is affected to some degree by the packing relations. Such is the case for Na_3TaF_8, K_2TaF_7 and $CsTaF_6$, where the configurational type and even the chemical constitution minimizes the crystal energy and the structure is mainly determined by the choice of the cation.

Table 4. *Dimensions* (Å) *of the* W–C≡N *chains within the anion*

Estimated standard deviations of bond lengths in parentheses.

W–C(1)	2·129 (0·026)	C(1)–N(1)	1·144 (0·035)	W–N(1)	3·271 (0·024)
W–C(2)	2·154 (0·028)	C(2)–N(2)	1·169 (0·038)	W–N(2)	3·321 (0·025)
W–C(3)	2·129 (0·029)	C(3)–N(3)	1·201 (0·038)	W–N(3)	3·326 (0·024)
W–C(4)	2·151 (0·027)	C(4)–N(4)	1·147 (0·038)	W–N(4)	3·297 (0·026)
W–C(5)	2·118 (0·025)	C(5)–N(5)	1·205 (0·035)	W–N(5)	3·320 (0·025)
W–C(6)	2·154 (0·028)	C(6)–N(6)	1·114 (0·038)	W–N(6)	3·267 (0·026)
W–C(7)	2·119 (0·028)	C(7)–N(7)	1·160 (0·040)	W–N(7)	3·279 (0·028)
W–C(8)	2·163 (0·042)	C(8)–N(8)	1·168 (0·048)	W–N(8)	3·332 (0·024)

Averaged distances (Å)

W–C	2·139	C—N	1·164	W–N	3·302

Bond angle (degrees) at carbon atoms in the chains

W–C(1)–N(1)	176·5	W–C(5)–N(5)	174·3
W–C(2)–N(2)	176·1	W–C(6)–N(6)	176·3
W–C(3)–N(3)	174·0	W–C(7)–N(7)	177·2
W–C(4)–N(4)	177·8	W–C(8)–N(8)	178·4
Averaged value	176·3		

$Na_3W(CN)_8.4H_2O$ in the solid state can be described as a salt-like structure consisting of almost parallel sheets normal to (100) containing atoms in the order W, O, Na, O, W, the coordination polyhedra being linked by highly electrostatic interactions with sodium ions, thus maximizing the crystal energy.

Table 5. *Dimensions of the coordination polyhedron*

Edge length			
	Edges of *s* type		
C(1)–C(2)	2·640 Å	C(5)–C(6)	2·608 Å
C(2)–C(3)	2·554	C(6)–C(7)	2·526
C(3)–C(4)	2·558	C(7)–C(8)	2·623
C(4)–C(1)	2·618	C(8)–C(5)	2·608
Mean	2·592		
	Edges of *l* type		
C(1)–C(5)	2·697 Å	C(3)–C(7)	2·715 Å
C(5)–C(4)	2·537	C(7)–C(2)	2·559
C(4)–C(6)	2·575	C(2)–C(8)	2·632
C(6)–C(3)	2·615	C(8)–C(1)	2·634
Mean	2·620		
Angles			
C(1)–W–C(2)	76·1°	C(2)–C(1)–C(4)	91·9°
C(2)–W–C(3)	73·2	C(3)–C(2)–C(1)	85·7
C(3)–W–C(4)	73·4	C(4)–C(3)–C(2)	95·4
C(4)–W–C(1)	75·4	C(1)–C(4)–C(3)	86·1
C(5)–W–C(6)	75·3	C(6)–C(5)–C(8)	91·5
C(6)–W–C(7)	72·5	C(7)–C(6)–C(5)	88·7
C(7)–W–C(8)	75·5	C(8)–C(7)–C(6)	93·0
C(8)–W–C(5)	75·1	C(5)–C(8)–C(7)	86·7
Mean	74·6	Mean	89·9
C(5)–C(1)–C(4)	57·0	C(7)–C(3)–C(2)	58·0
C(1)–C(5)–C(4)	59·9	C(3)–C(7)–C(2)	57·8
C(4)–C(5)–C(6)	60·0	C(2)–C(7)–C(8)	61·0
C(5)–C(4)–C(6)	61·4	C(7)–C(2)–C(8)	60·7
C(6)–C(4)–C(3)	61·3	C(8)–C(2)–C(1)	60·0
C(4)–C(6)–C(3)	59·0	C(2)–C(8)–C(1)	60·2
C(7)–C(6)–C(3)	63·7	C(1)–C(8)–C(5)	61·9
C(6)–C(3)–C(7)	56·5	C(8)–C(1)–C(5)	58·6
		Mean	59·8

Table 6. *Analysis of the planarity of the* $W(CN)_8^{3-}$ *ion*

Equation of plane referring to orthogonal axes: $Ax+By+Cz=D$.

Atoms in plane	Coefficients *A*	*B*	*C*	*D*	Deviation
C(1)					0·077 Å
C(2)	0·9992	0·0213	0·0336	1·3573	−0·079
C(3)					0·082
C(4)					−0·079
*W**					−1·109
N(1)					0·085
N(2)	0·9991	0·0294	0·0321	1·9944	−0·086
N(3)					0·086
N(4)					−0·086
*W**					−1·719
C(5)					−0·021
C(6)	0·9997	0·0132	0·0209	−0·9064	0·022
C(7)					−0·022
C(8)					0·021
*W**					1·102
N(5)					−0·007
N(6)	0·9998	0·0079	0·0183	−1·5139	0·007
N(7)					−0·007
N(8)					0·007
*W**					1·686

* These atoms were not included in the calculation of the plane.

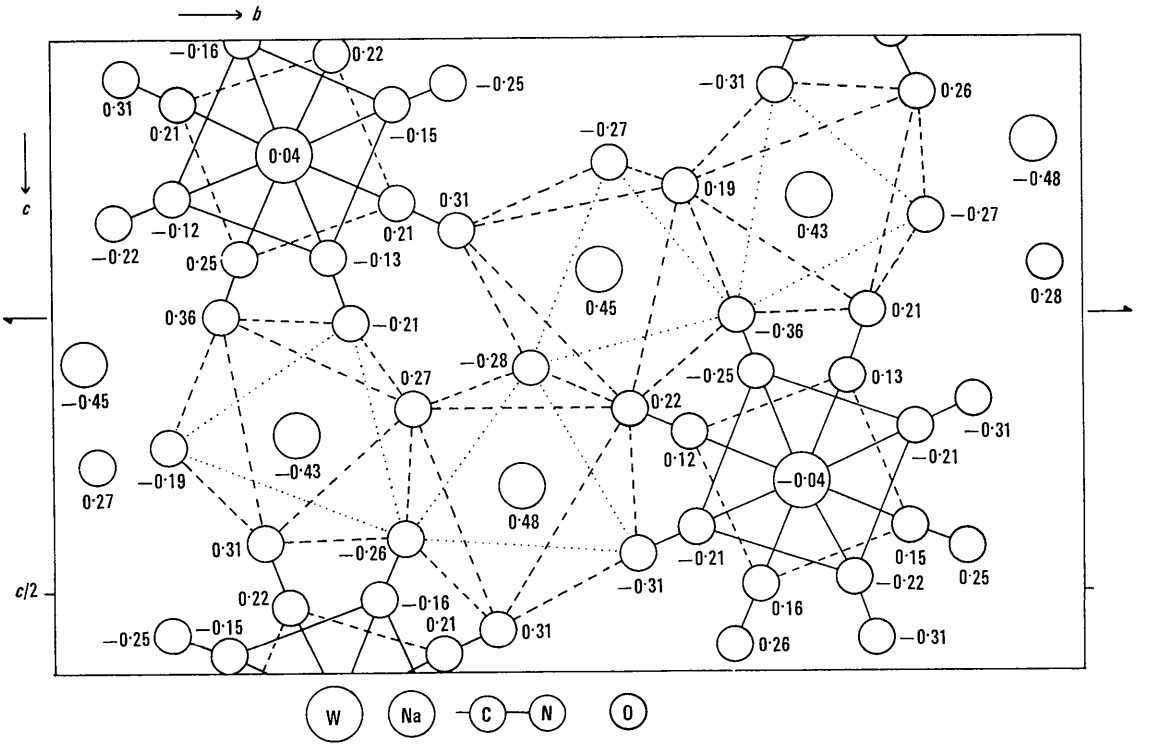


Fig. 1. The structure of $Na_3W(CN)_8.4H_2O$ viewed along the *a* axis showing the link up of the different polyhedra. The figures in each circle represent the fractional *x* coordinate of the atom.

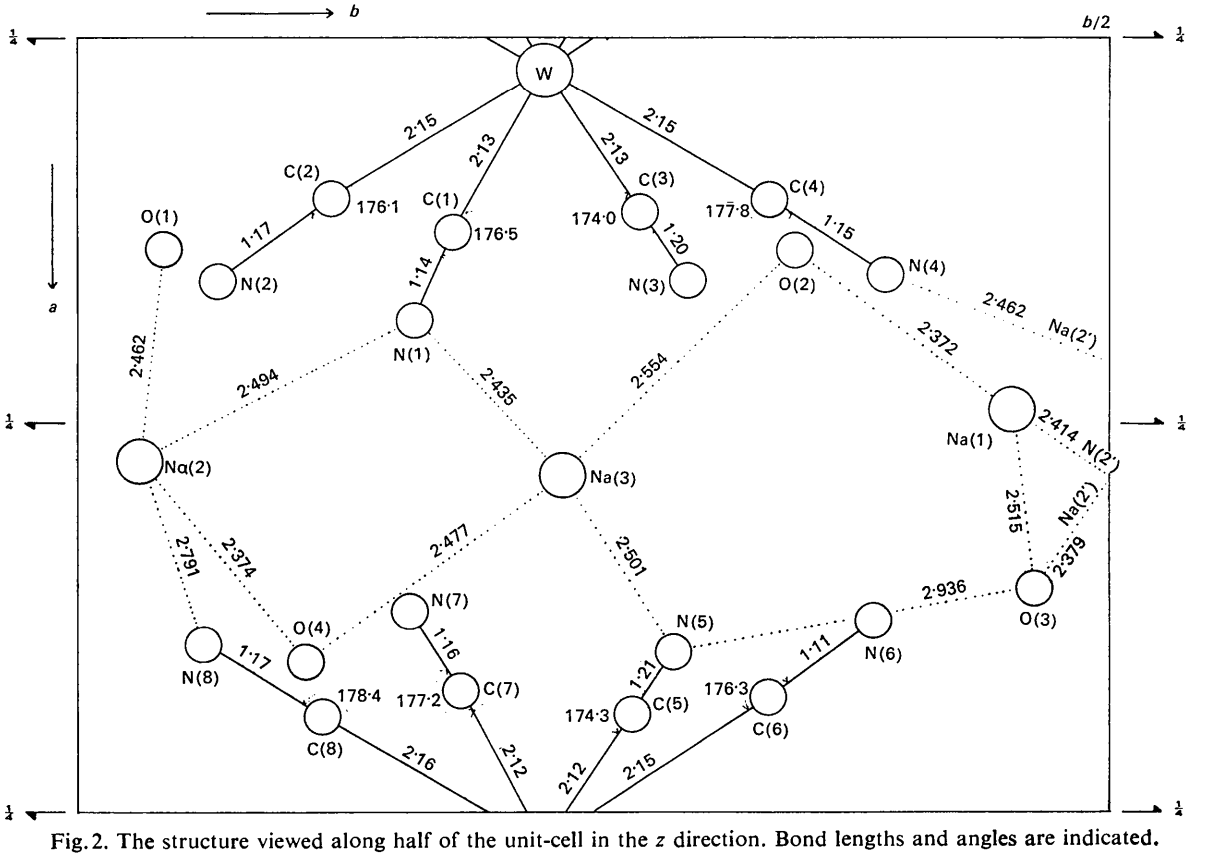


Fig. 2. The structure viewed along half of the unit-cell in the *z* direction. Bond lengths and angles are indicated.

Table 7. *Shape parameters for the square antiprism*

HSM	MFP	$Na_3W(CN)_8.4H_2O$
$l=s=1\cdot215$	$l=1\cdot258$, $s=1\cdot190$	$l=2\cdot620$, $s=2\cdot592$
$l/s=1\cdot00$	$l/s=1\cdot057$	$l/s=1\cdot011$
$\theta=59\cdot25°$	$\theta=57\cdot3°$	$\theta=59\cdot1°$

Table 8. *Bond lengths and angles at the sodium atoms*

N(2)–Na(1)[a]	2·414	N(1)–Na(3)	2·435	N(1)—Na(2)	2·494
N(2)–Na(1)[b]	2·554	N(3)–Na(3)[b]	2·500	N(4)—Na(2)[a]	2·462
N(7)–Na(1)[b]	2·505	N(5)–Na(3)	2·501	N(8)—Na(2)	2·791
N(8)–Na(1)[a]	2·615	N(7)–Na(3)[b]	2·528	O(1)—Na(2)	2·462
O(2)–Na(1)	2·372	O(2)–Na(3)	2·554	O(3)[a]–Na(2)	2·379
O(3)–Na(1)	2·515	O(4)–Na(3)	2·477	O(4)—Na(2)	2·374
N(7)[b]–Na(1)–N(8)[a]	169·5	N(2)[b]–Na(1)–O(2)	95·2		
N(7)[b]–Na(1)–O(2)	85·7	N(2)[b]–Na(1)–O(3)	168·6		
N(7)[b]–Na(1)–O(3)	84·2	O(2)—Na(1)–O(3)	89·1		
N(8)[a]–Na(1)–O(2)	87·4	N(1)—Na(3)–N(3)[b]	97·3		
N(8)[a]–Na(1)–O(3)	87·7	N(1)—Na(3)–N(5)	84·6		
N(1)—Na(2)–N(4)[a]	174·5	N(1)—Na(3)–N(7)[b]	166·7		
N(1)—Na(2)–N(8)	82·7	N(1)—Na(3)–O(2)	86·7		
N(1)—Na(2)–O(1)	79·4	N(1)—Na(3)–O(4)	86·0		
N(1)—Na(2)–O(3)[a]	86·9	N(3)[b]–Na(3)–N(5)	170·3		
N(1)—Na(2)–O(4)	87·0	N(3)[b]–Na(3)–N(7)[b]	85·8		
N(4)[a]–Na(2)–N(8)	98·8	N(3)[b]–Na(3)–O(2)	75·3		
N(4)[a]–Na(2)–O(1)	98·9	N(3)[b]–Na(3)–O(4)	101·0		
N(4)[a]–Na(2)–O(3)[a]	88·0	N(5)—Na(3)–N(7)[b]	90·3		
N(4)—Na(2)–O(4)	98·4	N(5)—Na(3)–O(2)	95·3		
N(8)—Na(2)–O(1)	161·9	N(8)—Na(2)–O(4)	88·4		
N(8)—Na(2)–O(3)[a]	86·5	O(1)—Na(2)–O(3)[a]	90·3		
N(2)[a]–Na(1)–N(2)[b]	88·4	O(1)—Na(2)–O(4)	92·8		
N(2)[a]–Na(1)–N(7)[b]	97·5	O(3)[a]–Na(2)–O(4)	172·5		
N(2)[a]–Na(1)–N(8)[a]	88·9	N(5)—Na(3)–O(4)	88·7		
N(2)[a]–Na(1)–O(2)	175·3	N(7)[b]–Na(3)–O(2)	81·6		
N(2)[a]–Na(1)–O(3)	87·9	N(7)[b]–Na(3)–O(4)	106·2		
N(2)[b]–Na(1)–N(7)[b]	85·6	O(2)—Na(3)–O(4)	171·3		
N(2)[b]–Na(1)–N(8)[a]	103·0				

[a, b] The general positions $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$ and x, $\frac{1}{2}-y$, $\frac{1}{2}+z$ respectively.

Considering the prediction of Hoard *et al.* (1968), it seems that one of the decisive factors in determining the stereochemical form of an octacyanide group (or groups containing monodentate ligands) must be sought in the particular physical environment, in which the water molecules seem to play a dominant part, whether in solution or in the solid state. In $Na_3W(CN)_8.4H_2O$ they have the ability [unlike the case in $K_4Mo(CN)_8.2H_2O$] to fill the vacant positions of the polyhedra around the cation, thus completing its normal ligancy. The small cation can then undergo strong interaction with the ligand atoms of the anion situated or orientated in favourable positions forming part of the octahedra, resulting in a tighter packing.

Calculations until completion of the first two refinement cycles were carried out on an IBM 360 computer, and further refinements on the KDF9 computer.

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