

A Second Configuration for the Octacyanide Group. The Crystal Structure of $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$

BY L. D. C. BOK, J. G. LEIPOLDT AND S. S. BASSON

Department of Chemistry, University of the O.F.S., P.O.Box 339 Bloemfontein, South Africa

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The crystal structure of the compound $\text{C}_8\text{H}_8\text{N}_8\text{O}_4\text{Na}_3\text{W}$ 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 $a=6.126$, $b=16.13$, $c=17.42$ Å, $\beta=94^\circ 45'$, 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 $\text{W}(\text{CN})_8^{3-}$ anion has approximate antiprismatic D_{4d} symmetry. The average distances for the octacyanide ion are: $\text{W}-\text{C}=2.139$, $\text{C}-\text{N}=1.164$, and $\text{W}-\text{N}=3.302$ Å. The carbon atoms form an angle of 59.1° with the tetragonal axis of the anion.

Introduction

The octa-coordinated $\text{Mo}(\text{CN})_8^{3-}$, $\text{W}(\text{CN})_8^{3-}$, and $\text{Re}(\text{CN})_8^{2-}$ 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 $\text{Mo}(\text{CN})_8^{4-}$ 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

$\text{K}_4\text{W}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ 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, and were oxidized to the pentavalent state with cerium sulphate using *N*-phenylanthranilic acid as indicator. From the insoluble $\text{Ag}_3\text{W}(\text{CN})_8$ and $\text{Ag}_3\text{Mo}(\text{CN})_8$ complexes which were precipitated, $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_3\text{Mo}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ 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 $\text{Cu K}\alpha$ 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	$\text{Na}_3\text{Mo}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$	$\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$
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 ($0.21 \times 0.20 \times 0.61$ mm) of $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ 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 $\text{Cu K}\alpha$ radiation [$(\mu(\text{Cu K}\alpha)) = 162.9 \text{ cm}^{-1}$]. 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, $\alpha_1-\alpha_2$ 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.

$H = U$, $K = U$	3 - 2790 - 1145	2 - 704 - 476	15 - 2361 - 2171	-5 - 9668 - 7813	-6 - 8775 - 7019	-1 - 9267 - 9330
4 - 2713 - 2564	4 - 3522 - 4364	5 - 9226 - 9174	-6 - 6939 - 4420	-7 - 1022 - 1276	-1 - 1616 - 1898	-2 - 1007 - 1079
4 - 1120 - 1104	4 - 4595 - 4420	5 - 2529 - 2229	-6 - 4203 - 4292	-8 - 1702 - 1701	-1 - 1616 - 1898	-2 - 1007 - 1079
4 - 508 - 3743	7 - 1075 - 903	6 - 1701 - 774	1 - 1029 - 1013	-9 - 849 - 1015	-10 - 8682 - 7760	-3 - 8180 - 8877
10 - 7855 - 7145	9 - 6064 - 5929	8 - 703 - 44	4 - 2674 - 2245	-11 - 1335 - 1256	-12 - 2336 - 2427	-5 - 3730 - 3833
12 - 2483 - 2365	10 - 5501 - 4434	10 - 1522 - 1049	2 - 2676 - 2659	-13 - 1065 - 1579	-14 - 2592 - 2555	-6 - 545 - 495
14 - 5817 - 5317	12 - 3107 - 2700	11 - 1522 - 1141	3 - 1067 - 1009	-15 - 1065 - 1579	-16 - 2592 - 2555	-7 - 545 - 495
16 - 4825 - 4269	14 - 1775 - 1678	13 - 2370 - 2192	4 - 1212 - 1141	-17 - 4763 - 3850	-18 - 615 - 577	-10 - 1607 - 714
22 - 673 - 595	16 - 4271 - 3829	17 - 1522 - 1302	5 - 1271 - 1302	-19 - 1100 - 1100	-20 - 4098 - 2913	-11 - 4428 - 4322
$H = O$, $K = 1$	17 - 1518 - 719	18 - 1188 - 717	11 - 1415 - 1212	-22 - 726 - 1262	-23 - 1500 - 1484	-15 - 1507 - 1316
1 - 1034 - 1024	19 - 2250 - 2019	20 - 515 - 19	10 - 3402 - 3402	-24 - 1000 - 1000	-25 - 1620 - 1782	-16 - 2013 - 1865
2 - 784 - 231	21 - 1022 - 775	22 - 677 - 469	14 - 1540 - 1664	5 - 4889 - 3873	3 - 3029 - 3185	-17 - 883 - 2090
4 - 1117 - 951	$H = O$, $K = 11$	$H = O$, $K = 11$	7 - 4653 - 4468	9 - 5182 - 5202	$H = 1$, $K = 8$	
5 - 4654 - 4664	$H = O$, $K = 6$	1 - 5706 - 6093	1 - 1805 - 1815	9 - 1248 - 1454	8 - 7854 - 7594	
6 - 9225 - 8725	2 - 2557 - 2727	3 - 2093 - 2601	2 - 2558 - 2746	10 - 1285 - 1377	8 - 6092 - 5528	1 - 4742 - 262
8 - 952 - 120	3 - 7154 - 8294	4 - 3110 - 3120	4 - 1141 - 1379	12 - 1010 - 1040	10 - 2930 - 3211	3 - 374 - 3719
10 - 1245 - 1203	5 - 1709 - 1929	6 - 1347 - 1304	6 - 2182 - 2103	14 - 6777 - 6447	13 - 4114 - 1492	5 - 1220 - 1794
11 - 2125 - 2061	7 - 1709 - 1929	8 - 1347 - 1304	7 - 1157 - 1152	15 - 645 - 527	11 - 2979 - 3114	7 - 1142 - 7041
13 - 930 - 85	9 - 4065 - 4101	10 - 1585 - 1591	9 - 2175 - 1790	16 - 645 - 527	14 - 2979 - 3114	11 - 1142 - 7041
14 - 1945 - 1854	8 - 1722 - 1598	9 - 4627 - 4502	8 - 218 - 1744	17 - 1451 - 1544	15 - 1820 - 1938	9 - 1011 - 873
15 - 2040 - 1945	10 - 5419 - 4679	11 - 4174 - 3501	11 - 1142 - 1117	18 - 509 - 50	17 - 2269 - 2141	12 - 2471 - 2187
16 - 4406 - 3959	12 - 4710 - 4710	17 - 2482 - 2197	12 - 2097 - 1957	20 - 2342 - 2419	18 - 1571 - 1748	12 - 615 - 168
18 - 2470 - 2420	19 - 1704 - 1704	20 - 2482 - 2197	21 - 2097 - 1957	22 - 2342 - 2419	19 - 1571 - 1748	12 - 615 - 168
19 - 1213 - 978	21 - 1672 - 2113	22 - 174 - 314	23 - 1142 - 1117	24 - 2097 - 1957	21 - 1571 - 1748	12 - 615 - 168
20 - 2470 - 2420	22 - 1704 - 1704	23 - 174 - 314	24 - 1142 - 1117	25 - 2097 - 1957	22 - 1571 - 1748	12 - 615 - 168
21 - 800 - 478	23 - 1367 - 1404	24 - 1098 - 560	25 - 2097 - 1618	26 - 5964 - 5926	27 - 1019 - 1119	18 - 7010 - 3287
22 - 2744 - 2715	25 - 2556 - 1821	26 - 544 - 353	27 - 1652 - 1065	28 - 5756 - 6119	29 - 3076 - 3085	17 - 3742 - 3578
$H = O$, $K = 2$	2 - 1204 - 1113	3 - 1705 - 893	4 - 3712 - 2681	-5 - 16197 - 14135	-6 - 3429 - 3474	19 - 340 - 400
1 - 2409 - 3062	20 - 1248 - 1241	$H = O$, $K = 12$	6 - 2193 - 1968	-7 - 810 - 816	-8 - 6576 - 7229	20 - 247 - 247
2 - 3495 - 4474	21 - 1417 - 1555	7 - 272 - 772	8 - 804 - 511	11 - 192 - 2021	12 - 5921 - 6493	1 - 2933 - 3170
3 - 3504 - 3524	22 - 1704 - 1704	13 - 1142 - 1117	14 - 2176 - 1744	15 - 1704 - 1704	16 - 2176 - 1744	17 - 1794 - 1948
4 - 7074 - 7524	$H = O$, $K = 7$	1 - 3729 - 3554	2 - 1370 - 1302	-5 - 1919 - 1815	-7 - 2784 - 2983	-1 - 2933 - 3170
5 - 6726 - 5801	1 - 5524 - 6641	4 - 1558 - 1262	11 - 541 - 521	12 - 1726 - 1704	13 - 2176 - 2151	14 - 347 - 347
7 - 4553 - 4613	2 - 2100 - 1748	9 - 1570 - 1168	10 - 540 - 461	11 - 1741 - 1711	12 - 2176 - 2151	13 - 347 - 347
9 - 5159 - 5248	3 - 2600 - 2962	7 - 1570 - 1570	8 - 524 - 556	9 - 1000 - 1344	10 - 2015 - 2293	11 - 347 - 347
9 - 5159 - 5248	4 - 2600 - 2962	7 - 1570 - 1570	8 - 524 - 556	9 - 1000 - 1344	10 - 2015 - 2293	11 - 347 - 347
10 - 2753 - 2753	11 - 3521 - 3521	12 - 1570 - 1570	13 - 524 - 556	14 - 1084 - 1344	15 - 2015 - 2293	16 - 347 - 347
11 - 2782 - 2770	13 - 3521 - 3521	14 - 1570 - 1570	15 - 524 - 556	16 - 1084 - 1344	17 - 2015 - 2293	18 - 347 - 347
12 - 2782 - 2770	15 - 3521 - 3521	16 - 1570 - 1570	17 - 524 - 556	18 - 1084 - 1344	19 - 2015 - 2293	20 - 347 - 347
$H = O$, $K = 3$	1 - 2790 - 2564	2 - 1570 - 1570	3 - 393 - 393	4 - 4552 - 4260	5 - 3076 - 3085	1 - 3471 - 4820
1 - 2782 - 2770	3 - 2557 - 2727	4 - 1570 - 1570	5 - 4552 - 4260	6 - 3076 - 3085	7 - 8993 - 8756	1 - 3471 - 4820
12 - 1294 - 247	13 - 271 - 2214	14 - 1570 - 1570	15 - 521 - 521	16 - 1019 - 12042	17 - 577 - 611	12 - 614 - 268
13 - 2782 - 2770	15 - 2556 - 2556	16 - 1570 - 1570	17 - 521 - 521	18 - 1019 - 12042	19 - 577 - 611	13 - 614 - 268
14 - 6083 - 5447	16 - 1570 - 1570	17 - 521 - 521	18 - 1019 - 12042	19 - 577 - 611	20 - 1019 - 12042	14 - 614 - 268
15 - 5122 - 3479	17 - 4773 - 5618	18 - 1570 - 1570	19 - 521 - 521	20 - 1019 - 12042	21 - 577 - 611	15 - 614 - 268
16 - 5122 - 3479	18 - 4773 - 5618	19 - 1570 - 1570	20 - 521 - 521	21 - 1019 - 12042	22 - 577 - 611	16 - 614 - 268
17 - 2165 - 1757	19 - 3473 - 4375	20 - 1570 - 1570	21 - 521 - 521	22 - 1019 - 12042	23 - 577 - 611	17 - 614 - 268
18 - 1645 - 1959	21 - 1257 - 1257	22 - 1570 - 1570	23 - 521 - 521	24 - 1019 - 12042	25 - 577 - 611	18 - 614 - 268
19 - 1645 - 1959	22 - 1257 - 1257	23 - 1570 - 1570	24 - 521 - 521	25 - 1019 - 12042	26 - 577 - 611	19 - 614 - 268
20 - 1791 - 1655	23 - 1257 - 1257	24 - 1570 - 1570	25 - 521 - 521	26 - 1019 - 12042	27 - 577 - 611	20 - 614 - 268
21 - 1791 - 1655	24 - 1257 - 1257	25 - 1570 - 1570	26 - 521 - 521	27 - 1019 - 12042	28 - 577 - 611	21 - 614 - 268
22 - 1791 - 1655	25 - 1257 - 1257	26 - 1570 - 1570	27 - 521 - 521	28 - 1019 - 12042	29 - 577 - 611	22 - 614 - 268
23 - 1791 - 1655	26 - 1257 - 1257	27 - 1570 - 1570	28 - 521 - 521	29 - 1019 - 12042	30 - 577 - 611	23 - 614 - 268
24 - 1791 - 1655	27 - 1257 - 1257	28 - 1570 - 1570	29 - 521 - 521	30 - 1019 - 12042	31 - 577 - 611	24 - 614 - 268
25 - 1791 - 1655	28 - 1257 - 1257	29 - 1570 - 1570	30 - 521 - 521	31 - 1019 - 12042	32 - 577 - 611	25 - 614 - 268
26 - 1791 - 1655	29 - 1257 - 1257	30 - 1570 - 1570	31 - 521 - 521	32 - 1019 - 12042	33 - 577 - 611	26 - 614 - 268
27 - 1791 - 1655	30 - 1257 - 1257	31 - 1570 - 1570	32 - 521 - 521	33 - 1019 - 12042	34 - 577 - 611	27 - 614 - 268
28 - 1791 - 1655	31 - 1257 - 1257	32 - 1570 - 1570	33 - 521 - 521	34 - 1019 - 12042	35 - 577 - 611	28 - 614 - 268
29 - 1791 - 1655	32 - 1257 - 1257	33 - 1570 - 1570	34 - 521 - 521	35 - 1019 - 12042	36 - 577 - 611	29 - 614 - 268
30 - 1791 - 1655	33 - 1257 - 1257	34 - 1570 - 1570	35 - 521 - 521	36 - 1019 - 12042	37 - 577 - 611	30 - 614 - 268
31 - 1791 - 1655	34 - 1257 - 1257	35 - 1570 - 1570	36 - 521 - 521	37 - 1019 - 12042	38 - 577 - 611	31 - 614 - 268
32 - 1791 - 1655	35 - 1257 - 1257	36 - 1570 - 1570	37 - 521 - 521	38 - 1019 - 12042	39 - 577 - 611	32 - 614 - 268
33 - 1791 - 1655	36 - 1257 - 1257	37 - 1570 - 1570	38 - 521 - 521	39 - 1019 - 12042	40 - 577 - 611	33 - 614 - 268
34 - 1791 - 1655	37 - 1257 - 1257	38 - 1570 - 1570	39 - 521 - 521	40 - 1019 - 12042	41 - 577 - 611	34 - 614 - 268
35 - 1791 - 1655	38 - 1257 - 1257	39 - 1570 - 1570	40 - 521 - 521	41 - 1019 - 12042	42 - 577 - 611	35 - 614 - 268
36 - 1791 - 1655	39 - 1257 - 1257	40 - 1570 - 1570	41 - 521 - 521	42 - 1019 - 12042	43 - 577 - 611	36 - 614 - 268
37 - 1791 - 1655	40 - 1257 - 1257	41 - 1570 - 1570	42 - 521 - 521	43 - 1019 - 12042	44 - 577 - 611	37 - 614 - 268
38 - 1791 - 1655	41 - 1257 - 1257	42 - 1570 - 1570	43 - 521 - 521	44 - 1019 - 12042	45 - 577 - 611	38 - 614 - 268
39 - 1791 - 1655	42 - 1257 - 1257	43 - 1570 - 1570	44 - 521 - 521	45 - 1019 - 12042	46 - 577 - 611	39 - 614 - 268
40 - 1791 - 1655	43 - 1257 - 1257	44 - 1570 - 1570	45 - 521 - 521	46 - 1019 - 12042	47 - 577 - 611	40 - 614 - 268
41 - 1791 - 1655	44 - 1257 - 1257	45 - 1570 - 1570	46 - 521 - 521	47 - 1019 - 12042	48 - 577 - 611	41 - 614 - 268
42 - 1791 - 1655	45 - 1257 - 1257	46 - 1570 - 1570	47 - 521 - 521	48 - 1019 - 12042	49 - 577 - 611	42 - 614 - 268
43 - 1791 - 1655	46 - 1257 - 1257	47 - 1570 - 1570	48 - 521 - 521	49 - 1019 - 12042	50 - 577 - 611	43 - 614 - 268
44 - 1791 - 1655	47 - 1257 - 1257	48 - 1570 - 1570	49 - 521 - 521	50 - 1019 - 12042	51 - 577 - 611	44 - 614 - 268
45 - 1791 - 1655	48 - 1257 - 1257	49 - 1570 - 1570	50 - 521 - 521	51 - 1019 - 12042	52 - 577 - 611	45 - 614 - 268
46 - 1791 - 1655	49 - 1257 - 1257	50 - 1570 - 1570	51 - 521 - 521	52 - 1019 - 12042	53 - 577 - 611	46 - 614 - 268
47 - 1791 - 1655	50 - 1257 - 1257	51 - 1570 - 1570	52 - 521 - 521	53 - 1019 - 12042	54 - 577 - 611	47 - 614 - 268
48 - 1791 - 1655	51 - 1257 - 1257	52 - 1570 - 1570	53 - 521 - 521	54 - 1019 - 12042	55 - 577 - 611	48 - 614 - 268
49 - 1791 - 1655	52 - 1257 - 1257	53 - 1570 - 1570	54 - 521 - 521	55 - 1019 - 12042	56 - 577 - 611	49 - 614 - 268
50 - 1791 - 1655	53 - 1257 - 1257	54 - 1570 - 1570	55 - 521 - 521	56 - 1019 - 12042	57 - 577 - 611	50 - 614 - 268
51 - 1791 - 1655	54 - 1257 - 1257	55 - 1570 - 1570	56 - 521 - 521	57 - 1019 - 12042	58 - 577 - 611	51 - 614 - 268
52 - 1791 - 1655	55 - 1257 - 1257	56 - 1570 - 1570	57 - 521 - 521	58 - 1019 - 12042	59 - 577 - 611	52 - 614 - 268
53 - 1791 - 1655	56 - 1257 - 1257	57 - 1570 - 1570	58 - 521 - 521	59 - 1019 - 12042	60 - 577 - 611	53 - 614 - 268
54 - 1791 - 1655	57 - 1257 - 1257	58 - 1570 - 1570	59 - 521 - 521	60 - 1019 - 12042	61 - 577 - 611	54 - 614 - 268
55 - 1791 - 1655	58 - 1257 - 1257	59 - 1570 - 1570	60 - 521 - 521	61 - 1019 - 12042	62 - 577 - 611	55 - 614 - 268
56 - 1791 - 1655	59 - 1257 - 1257	60 - 1570 - 1570	61 - 521 - 521	62 - 1		

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 $\text{Mo}(\text{CN})_8^{4-}$ 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 $K_4Mo(CN)_8 \cdot 2H_2O$ (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

Table 2 (cont.)

111	403	3758	-8	2669	2516	16	551	268	-12	1529	1285	7	1514	1715	-1	422	161	1	2542	2246	
122	900	867	-9	3100	1049	16	680	525	-12	1062	1029	7	304	3559	-1	3288	3122	-10	159	159	
123	740	779	-11	1593	1462	19	337	-184	-1	N = 3, E = 6	N = 3, E = 6	9	6191	6726	-1	4557	4155	-7	1593	159	
124	545	2049	-11	1593	1462	19	337	-184	-1	N = 3, E = 6	N = 3, E = 6	10	1453	810	-1	525	525	-7	1593	159	
H = 2, E = 14																					
1	5142	3205	-2	752	815	16	269	2410	-12	9522	9955	7	1207	712	-1	538	356	1	468	160	
2	1293	1295	-2	2584	1558	16	269	2410	-12	1980	2465	7	1207	712	-1	5297	5700	-10	1628	1582	
3	1294	1295	-2	2584	1558	16	2700	11175	-12	5473	4726	17	1527	1656	-1	297	272	-1	7070	1058	
4	1295	1295	-2	2584	1558	16	2700	11175	-12	5473	4726	17	1527	1656	-1	297	272	-1	2579	2711	
5	1296	1295	-2	2584	1558	16	2700	11175	-12	5473	4726	17	1527	1656	-1	297	272	-1	2645	2717	
6	575	612	-2	1961	1853	19	2944	2295	-9	1849	2869	12	584	297	-2	1072	510	-6	692	857	
7	1247	1341	-2	2448	204	16	599	173	-12	2622	2299	12	2949	1057	-1	3221	5700	-10	1628	1582	
8	522	552	-2	2026	2001	16	599	173	-12	1521	1656	1	4454	4787	-1	5284	3074	-10	1442	1532	
9	1134	1149	-1	1465	1516	14	402	503	-14	1417	1073	7	4768	4677	-1	2014	2290	-10	1628	1582	
10	1248	1184	-1	3112	2864	2	6119	5077	-16	503	363	-10	1676	1578	-1	2469	2179	-10	1628	1582	
11	1464	1700	-1	873	840	16	3475	3771	-18	1489	1293	-8	802	950	-1	9124	3198	-10	1189	1245	
12	1464	1700	-1	873	840	16	3475	3771	-18	1489	1293	-8	802	950	-1	9124	3198	-10	1189	1245	
13	1464	1700	-1	873	840	16	3475	3771	-18	1489	1293	-8	802	950	-1	9124	3198	-10	1189	1245	
14	1248	1184	-1	3112	2864	2	6119	5077	-16	503	363	-10	1676	1578	-1	2469	2179	-10	1628	1582	
15	1464	1700	-1	873	840	16	3475	3771	-18	1489	1293	-8	802	950	-1	9124	3198	-10	1189	1245	
16	1464	1700	-1	873	840	16	3475	3771	-18	1489	1293	-8	802	950	-1	9124	3198	-10	1189	1245	
H = 2, E = 19																					
1	1778	1825	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
2	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
3	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
4	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
5	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
6	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
7	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
8	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
9	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
10	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
11	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
12	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
13	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
14	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
15	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
16	1429	1552	-1	2944	2945	16	2927	2945	-9	5799	4476	14	1165	1548	-1	2577	2577	-10	1628	1582	
H = 2, E = 19																					
1	1004	1106	-1	228	287	15	558	648	-1	1201	1121	12	545	211	-1	4450	4408	1	921	904	
2	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
3	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
4	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
5	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
6	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
7	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
8	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
9	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
10	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
11	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
12	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
13	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
14	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
15	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
16	1293	2753	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
H = 2, E = 19																					
1	1004	1106	-1	19	347	20	1994	2059	11	4764	5155	-8	1074	1165	-1	992	1047	-10	2975	2992	
2	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
3	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
4	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
5	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
6	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
7	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
8	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
9	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
10	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
11	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
12	1293	1789	-1	204	199	16	3080	3047	-12	5295	5272	15	1095	2502	-2	1029	887	-10	1628	1582	
13	1293	1789	-1	204	199	16	3080	3047	-12												

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 Muettterties & 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 $\theta = 59.0^\circ$. (Hoard, Martin, Smith & Whitney, 1954). This structure was only determined two-dimensionally. $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ 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.*)

M = 2, E = M	N = 3, E = 18	-2	1414	1752	112	1802	1111	1	175	2057	301	17	1207	3848
O 0446 - 3550	Q 1592 1511	-2	1675	1926	113	1921	1125	1	177	2027	291	17	1211	3848
E = 2, E = 9	N = 3, E = 15	-3	727	927	114	1247	1195	7	4411	477	657	17	1203	1933
O 0224 - 3519	O 1224 - 1477	-3	1345	1485	115	1481	1205	7	4411	477	657	17	1211	1933
E = 2, E = 10	M = 4, E = 0	-3	521	5855	116	5855	116	7	3123	329	5025	17	224	1595
O 0350 - 1452	E 1247 - 2449	-3	1847	2448	117	1928	1143	11	2477	2477	3025	17	1211	1933
E = 2, E = 11	M = 4, E = 0	-3	521	5855	118	5855	118	7	3123	329	5025	17	224	1595
O 0571 - 315	H 2217 - 2820	-4	551	625	119	597	1149	1	175	2057	301	17	1207	3848
E = 2, E = 12	M = 4, E = 0	-4	727	927	120	895	1149	1	175	2057	301	17	1207	3848
O 1022 - 1341	M 1071 - 1536	-5	245	245	121	1420	1420	1	175	2057	301	17	1207	3848
E = 2, E = 13	M = 4, E = 0	-5	845	845	122	1705	1705	1	175	2057	301	17	1207	3848
O 0307 - 695	M 1240 - 4922	-6	845	845	123	1705	1705	1	175	2057	301	17	1207	3848
E = 2, E = 14	M = 4, E = 0	-6	597	5707	124	1051	1051	1	175	2057	301	17	1207	3848
O 1743 - 1778	M = 4, E = 1	-7	320	261	125	2566	2721	1	175	2057	301	17	1207	3848
E = 2, E = 15	M = 4, E = 1	-7	9794	9315	126	1371	1371	1	175	2057	301	17	1207	3848
O 3086 - 2725	M = 4, E = 2	-7	1047	1047	127	1242	1242	1	175	2057	301	17	1207	3848
E = 2, E = 17	M = 4, E = 2	-7	2554	2577	128	220	214	1	175	2057	301	17	1207	3848
O 1256 - 1350	M = 4, E = 3	-7	8607	8607	129	1053	1053	1	175	2057	301	17	1207	3848
E = 2, E = 18	M = 4, E = 3	-7	778	780	130	1053	1053	1	175	2057	301	17	1207	3848
O 0953 - 1942	M = 4, E = 4	-7	1723	1723	131	1723	1723	1	175	2057	301	17	1207	3848
M = 2, E = 19	S 3163 - 3211	-8	1295	1295	132	1295	1295	1	175	2057	301	17	1207	3848
O 1066 - 1095	M = 4, E = 5	-8	591	591	133	1295	1295	1	175	2057	301	17	1207	3848
E = 2, E = 20	M = 4, E = 5	-8	5719	5707	134	1295	1295	1	175	2057	301	17	1207	3848
O 1889 - 1941	M = 4, E = 6	-8	331	331	135	1561	1561	1	175	2057	301	17	1207	3848
M = 3, E = 1	O 1797 - 1905	-9	1797	1797	136	1797	1797	1	175	2057	301	17	1207	3848
O 5179 - 4585	M = 4, E = 7	-9	6307	5651	137	676	676	1	175	2057	301	17	1207	3848
E = 3, E = 2	O 2984 - 3095	-9	158	158	138	1425	1425	1	175	2057	301	17	1207	3848
O 6520 - 5542	M = 4, E = 8	-9	158	158	139	1425	1425	1	175	2057	301	17	1207	3848
E = 3, E = 3	O 423 - 444	-9	178	178	140	1425	1425	1	175	2057	301	17	1207	3848
O 4549 - 4476	M = 4, E = 9	-9	178	178	141	1425	1425	1	175	2057	301	17	1207	3848
E = 3, E = 4	O 801 - 1023	-9	1532	1532	142	1245	1245	1	175	2057	301	17	1207	3848
O 4580 - 4559	M = 4, E = 10	-9	1575	1575	143	1245	1245	1	175	2057	301	17	1207	3848
E = 3, E = 5	O 449 - 894	-9	1575	1575	144	1245	1245	1	175	2057	301	17	1207	3848
O 3762 - 3981	M = 4, E = 11	-9	1642	1642	145	1627	1627	1	175	2057	301	17	1207	3848
E = 3, E = 6	O 451 - 547	-9	116	116	146	1627	1627	1	175	2057	301	17	1207	3848
O 2979 - 3390	M = 4, E = 12	-9	2274	2274	147	2274	2274	1	175	2057	301	17	1207	3848
E = 3, E = 7	O 844 - 1299	-9	1740	1740	148	2028	2028	1	175	2057	301	17	1207	3848
O 1827 - 2521	M = 4, E = 13	-9	2141	2141	149	2127	2127	1	175	2057	301	17	1207	3848
E = 3, E = 8	O 913 - 1136	-9	478	478	150	2127	2127	1	175	2057	301	17	1207	3848
O 1344 - 1762	M = 4, E = 14	-10	112	1482	151	1600	1600	1	175	2057	301	17	1207	3848
E = 3, E = 9	O 404 - 700	-10	112	112	152	1600	1600	1	175	2057	301	17	1207	3848
O 1010 - 202	M = 4, E = 15	-10	4557	5029	153	1488	1778	1	175	2057	301	17	1207	3848
E = 3, E = 10	O 1777 - 1902	-10	112	112	154	1625	1625	1	175	2057	301	17	1207	3848
O 604 - 178	M = 4, E = 16	-10	4181	4127	155	1018	1018	1	175	2057	301	17	1207	3848
E = 3, E = 11	G 1212 - 1211	-10	4181	4127	156	1018	1018	1	175	2057	301	17	1207	3848
O 619 - 512	M = 4, E = 17	-10	4109	5248	157	788	1755	1	175	2057	301	17	1207	3848
E = 3, E = 12	O 1816 - 1749	-10	4107	5248	158	567	567	1	175	2057	301	17	1207	3848
O 625 - 211	M = 4, E = 18	-10	934	1566	159	1447	2524	1	175	2057	301	17	1207	3848
E = 3, E = 13	1 901 - 1323	-10	2013	2013	160	1014	1014	1	175	2057	301	17	1207	3848
O 2094 - 8218	7 185 - 187	-10	423	421	161	984	984	1	175	2057	301	17	1207	3848
E = 3, E = 15	10 3584 - 3511	-10	1871	2080	162	682	4178	1	175	2057	301	17	1207	3848
O 1726 - 1748	12 1842 - 2363	-10	820	917	163	2105	1965	1	175	2057	301	17	1207	3848
E = 3, E = 16	14 2014 - 2454	-10	4415	4415	164	241	85	1	175	2057	301	17	1207	3848
O 1855 - 1890	15 269 - 269	-10	4488	1009	165	1009	1009	1	175	2057	301	17	1207	3848
E = 3, E = 17	17 193 - 197	-10	5444	5982	166	1009	1009	1	175	2057	301	17	1207	3848
O 2007 - 2037	19 2195 - 2195	-10	4860	5205	167	5765	5955	1	175	2057	301	17	1207	3848

Table 2 (*cont.*)

N	=	S	, E	=	16
O	-	326	-	346	
N	=	S	, E	=	15
-	-	1600	-	1600	
-	-	263	-	263	
-	-	1163	-	1163	
-	-	3200	-	3200	
-	-	320	-	320	
-	-	1093	-	1100	
-	-	1896	-	1884	
-	-	245	-	245	
-	-	4755	-	5310	
-	-	941	-	1100	
-	-	1745	-	1745	
-	-	205	-	205	
-	-	857	-	857	
-	-	2551	-	2724	
-	-	227	-	227	
-	-	565	-	427	
-	-	11	-	11	
-	-	1717	-	2279	
-	-	11	-	11	
-	-	650	-	309	
-	-	11	-	11	
-	-	2493	-	2925	
-	-	11	-	11	
-	-	2742	-	2872	
-	-	11	-	11	
-	-	1745	-	2032	
-	-	11	-	11	
-	-	271	-	271	
-	-	2957	-	2959	
-	-	11	-	11	
-	-	3100	-	3131	
-	-	11	-	11	
-	-	1717	-	1826	
-	-	11	-	11	
-	-	2811	-	2905	
-	-	11	-	11	
-	-	2933	-	3376	
-	-	11	-	11	
-	-	2730	-	2734	
-	-	11	-	11	
-	-	1075	-	1800	
-	-	11	-	11	
-	-	4177	-	4177	
-	-	11	-	11	
-	-	1167	-	1114	
-	-	11	-	11	
-	-	3493	-	3633	
-	-	11	-	11	
-	-	563	-	563	
-	-	11	-	11	
-	-	2687	-	2841	
-	-	11	-	11	
-	-	655	-	147	
-	-	11	-	11	
-	-	2677	-	2795	
-	-	11	-	11	
-	-	1659	-	1697	
-	-	11	-	11	
-	-	2087	-	1456	
-	-	11	-	11	
-	-	3507	-	2658	
-	-	11	-	11	
-	-	2485	-	1977	
-	-	11	-	11	
-	-	1912	-	1936	
-	-	11	-	11	
-	-	1750	-	1750	
-	-	11	-	11	
-	-	2350	-	2350	
-	-	11	-	11	
-	-	2087	-	2155	
-	-	11	-	11	
-	-	549	-	945	
-	-	11	-	11	
-	-	1093	-	1527	
-	-	11	-	11	
-	-	2590	-	7516	
-	-	11	-	11	
-	-	5245	-	5145	
-	-	11	-	11	
-	-	193	-	193	
-	-	11	-	11	
-	-	1926	-	1883	
-	-	11	-	11	
-	-	617	-	617	
-	-	11	-	11	
-	-	475	-	1393	
-	-	11	-	11	
-	-	2727	-	2859	
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-	-	2829	-	2770	
-	-	11	-	11	
-	-	341	-	876	
-	-	11	-	11	
-	-	851	-	1176	
-	-	11	-	11	
-	-	244	-	1644	
-	-	11	-	11	
-	-	2525	-	3145	
-	-	11	-	11	
-	-	2653	-	2624	
-	-	11	-	11	
-	-	2761	-	2761	
-	-	11	-	11	
-	-	3511	-	2959	
-	-	11	-	11	
-	-	564	-	847	
-	-	11	-	11	
-	-	3209	-	2441	
-	-	11	-	11	
-	-	641	-	504	
-	-	11	-	11	
-	-	3317	-	853	
-	-	11	-	11	
-	-	3318	-	7215	
-	-	11	-	11	
-	-	294	-	1644	
-	-	11	-	11	
-	-	1442	-	3220	
-	-	11	-	11	
-	-	3687	-	3620	
-	-	11	-	11	
-	-	2529	-	1074	
-	-	11	-	11	
-	-	3056	-	2970	
-	-	11	-	11	
-	-	1504	-	1418	
-	-	11	-	11	
-	-	2357	-	2326	
-	-	11	-	11	
-	-	3292	-	3111	
-	-	11	-	11	
-	-	2525	-	2525	
-	-	11	-	11	
-	-	1091	-	858	
-	-	11	-	11	
-	-	3149	-	2749	
-	-	11	-	11	
-	-	3149	-	3149	
-	-	11	-	11	
-	-	3149	-	2749	
-	-	11	-	11	
-	-	3149	-	3149	
-	-	11	-	11	
-	-	3149	-	2749	
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-	-	3149	-	3149	
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-	-	3149	-	3149	
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-	-	3149	-	2749	
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-	-	3149	-	3149	
-	-	11	-	11	
-	-	3149	-	2749	
-	-	11	-	11	
-	-	3149	-	3149	
-	-	11	-	11	
-	-	3149	-	2749	
-	-	11	-	11	
-	-	3149	-	3149	
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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 (\AA^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 Å² 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				

$\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ 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 <i>s</i> 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 <i>l</i> 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 $\text{W}(\text{CN})_8^{3-}$ ion

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

Atoms in plane	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	Deviation
C(1)	0.9992	0.0213	0.0336	1.3573	0.077 Å
C(2)					-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.

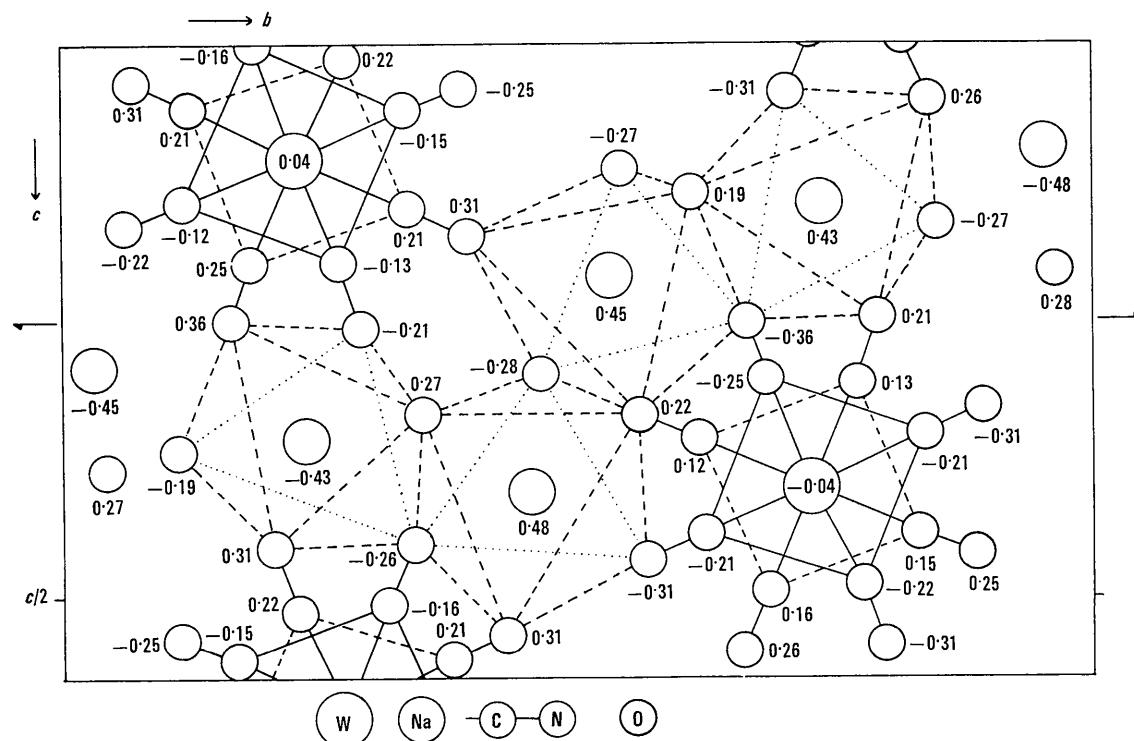


Fig. 1. The structure of $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ viewed along the a axis showing the link up of the different polyhedra. The figures in each circle represent the fractional x coordinate of the atom.

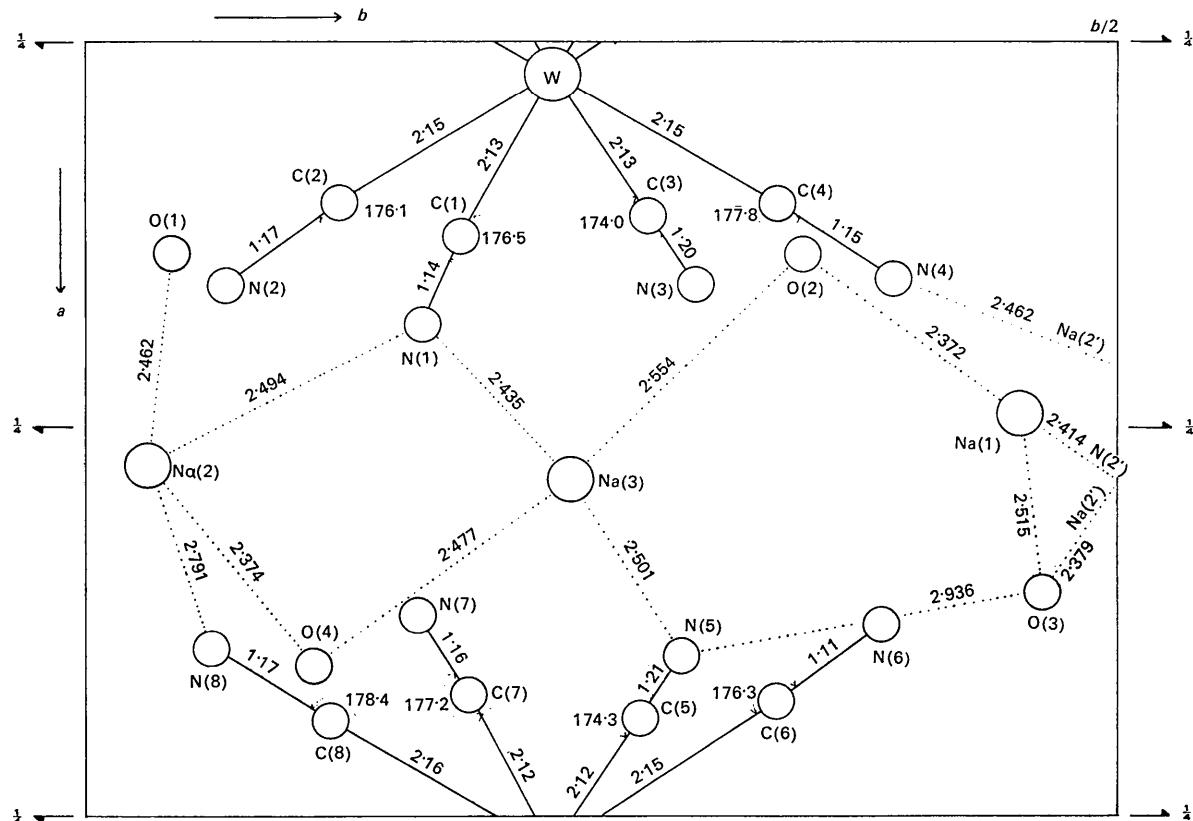


Fig. 2. The structure viewed along half of the unit-cell in the z direction. Bond lengths and angles are indicated.

Table 7. Shape parameters for the square antiprism

HSM	MFP	$\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$
$l=s=1.215$	$l=1.258, s=1.190$	$l=2.620, s=2.592$
$l/s=1.00$	$l/s=1.057$	$l/s=1.011$
$\theta=59.25^\circ$	$\theta=57.3^\circ$	$\theta=59.1^\circ$

Table 8. Bond lengths and angles at the sodium atoms

$\text{N}(2)-\text{Na}(1)^a$	2.414	$\text{N}(1)-\text{Na}(3)$	2.435	$\text{N}(1)-\text{Na}(2)$	2.494
$\text{N}(2)-\text{Na}(1)^b$	2.554	$\text{N}(3)-\text{Na}(3)^b$	2.500	$\text{N}(4)-\text{Na}(2)^a$	2.462
$\text{N}(7)-\text{Na}(1)^b$	2.505	$\text{N}(5)-\text{Na}(3)$	2.501	$\text{N}(8)-\text{Na}(2)$	2.791
$\text{N}(8)-\text{Na}(1)^a$	2.615	$\text{N}(7)-\text{Na}(3)^b$	2.528	$\text{O}(1)-\text{Na}(2)$	2.462
$\text{O}(2)-\text{Na}(1)$	2.372	$\text{O}(2)-\text{Na}(3)$	2.554	$\text{O}(3)^a-\text{Na}(2)$	2.379
$\text{O}(3)-\text{Na}(1)$	2.515	$\text{O}(4)-\text{Na}(3)$	2.477	$\text{O}(4)-\text{Na}(2)$	2.374
$\text{N}(7)^b-\text{Na}(1)-\text{N}(8)^a$	169.5	$\text{N}(2)^b-\text{Na}(1)-\text{O}(2)$	95.2		
$\text{N}(7)^b-\text{Na}(1)-\text{O}(2)$	85.7	$\text{N}(2)^b-\text{Na}(1)-\text{O}(3)$	168.6		
$\text{N}(7)^b-\text{Na}(1)-\text{O}(3)$	84.2	$\text{O}(2)-\text{Na}(1)-\text{O}(3)$	89.1		
$\text{N}(8)^a-\text{Na}(1)-\text{O}(2)$	87.4	$\text{N}(1)-\text{Na}(3)-\text{N}(3)^b$	97.3		
$\text{N}(8)^a-\text{Na}(1)-\text{O}(3)$	87.7	$\text{N}(1)-\text{Na}(3)-\text{N}(5)$	84.6		
$\text{N}(1)-\text{Na}(2)-\text{N}(4)^a$	174.5	$\text{N}(1)-\text{Na}(3)-\text{N}(7)^b$	166.7		
$\text{N}(1)-\text{Na}(2)-\text{N}(8)$	82.7	$\text{N}(1)-\text{Na}(3)-\text{O}(2)$	86.7		
$\text{N}(1)-\text{Na}(2)-\text{O}(1)$	79.4	$\text{N}(1)-\text{Na}(3)-\text{O}(4)$	86.0		
$\text{N}(1)-\text{Na}(2)-\text{O}(3)^a$	86.9	$\text{N}(3)^b-\text{Na}(3)-\text{N}(5)$	170.3		
$\text{N}(1)-\text{Na}(2)-\text{O}(4)$	87.0	$\text{N}(3)^b-\text{Na}(3)-\text{N}(7)^b$	85.8		
$\text{N}(4)^a-\text{Na}(2)-\text{N}(8)$	98.8	$\text{N}(3)^b-\text{Na}(3)-\text{O}(2)$	75.3		
$\text{N}(4)^a-\text{Na}(2)-\text{O}(1)$	98.9	$\text{N}(3)^b-\text{Na}(3)-\text{O}(4)$	101.0		
$\text{N}(4)^a-\text{Na}(2)-\text{O}(3)^a$	88.0	$\text{N}(5)-\text{Na}(3)-\text{N}(7)^b$	90.3		
$\text{N}(4)-\text{Na}(2)-\text{O}(4)$	98.4	$\text{N}(5)-\text{Na}(3)-\text{O}(2)$	95.3		
$\text{N}(8)-\text{Na}(2)-\text{O}(1)$	161.9	$\text{N}(8)-\text{Na}(2)-\text{O}(4)$	88.4		
$\text{N}(8)-\text{Na}(2)-\text{O}(3)^a$	86.5	$\text{O}(1)-\text{Na}(2)-\text{O}(3)^a$	90.3		
$\text{N}(2)^a-\text{Na}(1)-\text{N}(2)^b$	88.4	$\text{O}(1)-\text{Na}(2)-\text{O}(4)$	92.8		
$\text{N}(2)^a-\text{Na}(1)-\text{N}(7)^b$	97.5	$\text{O}(3)^a-\text{Na}(2)-\text{O}(4)$	172.5		
$\text{N}(2)^a-\text{Na}(1)-\text{N}(8)^a$	88.9	$\text{N}(5)-\text{Na}(3)-\text{O}(4)$	88.7		
$\text{N}(2)^a-\text{Na}(1)-\text{O}(2)$	175.3	$\text{N}(7)^b-\text{Na}(3)-\text{O}(2)$	81.6		
$\text{N}(2)^a-\text{Na}(1)-\text{O}(3)$	87.9	$\text{N}(7)^b-\text{Na}(3)-\text{O}(4)$	106.2		
$\text{N}(2)^b-\text{Na}(1)-\text{N}(7)^b$	85.6	$\text{O}(2)-\text{Na}(3)-\text{O}(4)$	171.3		
$\text{N}(2)^b-\text{Na}(1)-\text{N}(8)^a$	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 $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ they have the ability [unlike the case in $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$] 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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