

## The Structure of Tetrakis(2-carboxypyridinium) Octacyanomolybdate(IV)

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### Abstract

$[\text{C}_6\text{H}_6\text{NO}_2]_4[\text{Mo}(\text{CN})_8]$ , which is isomorphous with the W analogue, crystallizes in the monoclinic space group  $P2/n$  with  $a = 9.167$  (6),  $b = 18.514$  (12),  $c = 10.149$  (6) Å,  $\beta = 90.16$  (8)°,  $Z = 2$ . The final  $R$  for 1936 observed reflections was 0.042. Eight cyanide ligands are bonded to the Mo atom in the form of a  $4m2$  dodecahedron. Average Mo–C and  $\text{C}\equiv\text{N}$  distances are 2.159 and 1.150 Å respectively. Four of the eight cyanide ligands are hydrogen bonded to carboxylic acid O atoms [2.542 (7) Å] and the other four to pyridinium N atoms [2.786 (7) Å].

### Introduction

The stereochemical configuration of octacyano-metallate ions in the solid state and in solution is a much debated subject. Electronic, vibrational and/or electron spin resonance spectral data (Garner & Mabbs, 1979, and references therein) are apparently unable to give a clear-cut answer as to the type of eight-coordination polyhedron for a specific cyano complex.

The flexible framework of  $M(\text{CN})_8^{n-}$  ions ( $M = \text{Mo}$  or  $\text{W}$ ;  $n = 3$  or  $4$ ) has resulted in at least three definite stereochemical configurations, found by crystal-structure determinations. The more frequently occurring ones are the  $D_{2d}(4m2)$  dodecahedron in  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  (Hoard, Hamor & Glick, 1968) and  $[n\text{-Bu}_4\text{N}]_3\text{Mo}(\text{CN})_8$  (Corden, Cunningham & Eisenberg, 1970) and the  $D_{4d}(8m2)$  square antiprism in  $\text{H}_4\text{W}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$  (Basson, Bok & Leipoldt, 1970) and  $\text{H}_4\text{W}(\text{CN})_8 \cdot 4\text{HCl} \cdot 12\text{H}_2\text{O}$  (Bok, Leipoldt & Basson, 1972). Anion geometries of  $\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$  (Bok, Leipoldt & Basson, 1970) and  $[\text{HN}(\text{C}_2\text{H}_5)_3]_2[\text{H}_3\text{O}]_2\text{Mo}(\text{CN})_8$  (Leipoldt, Basson & Bok, 1980) are about halfway between those of a square antiprism or dodecahedron and a  $C_{2v}(mm)$  4,4-bicapped trigonal prism respectively. The latter type of configuration, although not as favourable as the previous ones on steric grounds alone (Burdett, Hoffmann & Fay, 1978) has been established for the  $\text{Mo}(\text{CN})_8^{3-}$  ion in  $\text{Cs}_3\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  (Basson, Leipoldt, Bok, van Vollenhoven & Cilliers, 1980).

The present compound, like  $[n\text{-Bu}_4\text{N}]_3\text{Mo}(\text{CN})_8$  but in contrast to the others, crystallized without water of crystallization. Since lattice water fulfilled an important role in either completing the coordination shell of the cation or stabilizing small cations like the proton in the immediate vicinity of CN ligands, a structure determination in the absence of this effect was considered worthwhile. The possible relative effect of a polar OH group and cation on the charge distribution on CN ligands could also result in different  $M\text{—C}\equiv\text{N}$  bond lengths.

### Experimental

$\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_4\text{W}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  were prepared by published methods (Leipoldt, Bok & Cilliers, 1974*a,b*). A solution of  $\text{K}_4\text{M}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  (1 g in 20 ml water) was mixed with 10 ml of a 10% (*v/v*) hydrochloric acid solution containing about 0.6 g of 2-picolinic acid. Orange and wine-red tablets of the respective Mo and W compounds crystallized overnight. Table 1 contains the crystal data. Photographs taken with the Weissenberg equi-inclination technique confirmed isomorphism for the two compounds. It also showed systematic absences for  $h0l$  ( $h + l \neq 2n$ ) reflections corresponding to the monoclinic space group  $P2/n$ .

Intensities were recorded for the Mo compound on a Philips four-circle X-ray diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  radiation ( $\lambda = 0.7107$  Å) for  $\theta \leq 23^\circ$ . A cube-like crystal  $0.24 \times 0.26 \times 0.30$  mm

Table 1. Crystal data for isomorphous complexes

	$(\text{C}_6\text{H}_6\text{NO}_2)_4\text{Mo}(\text{CN})_8$	$(\text{C}_6\text{H}_6\text{NO}_2)_4\text{W}(\text{CN})_8$
Molecular mass	800.6	888.5
$a$ (Å)	9.167 (6)	9.19
$b$ (Å)	18.514 (12)	18.72
$c$ (Å)	10.149 (6)	10.18
$\beta$ (°)	90.16 (8)	90.0
$V$ (Å <sup>3</sup> )	1722.5	1751.3
$D_m$ (Mg m <sup>-3</sup> )	1.54	1.72
$D_c$ (Mg m <sup>-3</sup> )	1.54	1.68
$Z$	2	2

Table 2. Atomic coordinates ( $\times 10^4$ ) with their *e.s.d.*'s in parentheses

	x	y	z		x	y	z
Mo	2500	2497 (0)	2500	N(5)	6618 (5)	303 (2)	9251 (5)
C(1)	1236 (6)	1544 (3)	2976 (6)	C(7)	7604 (7)	124 (3)	10185 (6)
C(2)	3072 (6)	3445 (3)	3639 (5)	C(8)	8322 (7)	666 (4)	10877 (7)
C(3)	3202 (6)	2169 (3)	4439 (6)	C(9)	8020 (7)	1384 (4)	10586 (7)
C(4)	388 (7)	2827 (3)	3189 (6)	C(10)	6993 (7)	1557 (3)	9592 (6)
N(1)	649 (5)	1022 (3)	3283 (5)	O(3)	7899 (5)	3243 (2)	-59 (5)
N(2)	3422 (6)	3966 (3)	4178 (5)	O(4)	7791 (6)	4424 (2)	10348 (5)
N(3)	3533 (7)	1992 (3)	5479 (5)	C(11)	8209 (6)	3918 (3)	-286 (6)
N(4)	-743 (6)	3011 (3)	3543 (6)	C(12)	9169 (6)	4021 (3)	-1454 (6)
O(1)	4660 (7)	586 (3)	7345 (6)	N(6)	9457 (5)	4718 (2)	-1767 (5)
O(2)	4928 (5)	1760 (2)	7601 (4)	C(13)	10304 (7)	4899 (4)	-2793 (6)
C(5)	5190 (7)	1092 (3)	7877 (6)	C(14)	10904 (8)	4366 (4)	-3587 (7)
C(6)	6310 (6)	997 (3)	8955 (5)	C(15)	10622 (8)	3641 (4)	-3285 (7)
				C(16)	9735 (7)	3467 (3)	-2201 (6)

( $\mu R = 0.13$ ) was used for data collection. Three reflections were chosen as standards and remeasured after every 60 reflections. No decomposition was detected. Of 2479 reflections measured, 1936 were classed as observed:  $I > 2\sigma(I)$ . They were corrected only for Lorentz and polarization effects. The structure was solved with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a Univac 1100 computer.

The Patterson function confirmed point symmetry 2 for the Mo atoms. The coordinates of the remaining non-hydrogen atoms were located in a subsequent Fourier map. Full-matrix least-squares refinement of positional and isotropic temperature parameters resulted in  $R = 0.082$ , which decreased to 0.042 with anisotropic temperature factors. The mean parameter shift in the last cycle was  $< 0.1\sigma$  with a maximum shift of about  $0.3\sigma$  in one of the thermal parameters. The scattering factors for Mo were from Cromer & Waber (1965) and for the remaining atoms from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates are listed in Table 2.\*

### Description of structure and discussion

The [001] projection of the structure is given in Fig. 1 illustrating a three-dimensional framework stabilized by strong hydrogen bonds  $N(3)\cdots O(2)$  [2.538 (7) Å] and  $N(4)\cdots O(3^V)$  [2.545 (7) Å] between four N atoms of one  $Mo(CN)_8$  group and adjacent carboxylic acid groups. Each 2-carboxypyridinium cation serves as a link between two  $Mo(CN)_8$  polyhedra by way of the aforementioned hydrogen bonds and short cation-anion contacts of  $N(1)\cdots N(5^{IV})$  [2.786 (7) Å]

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35204 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

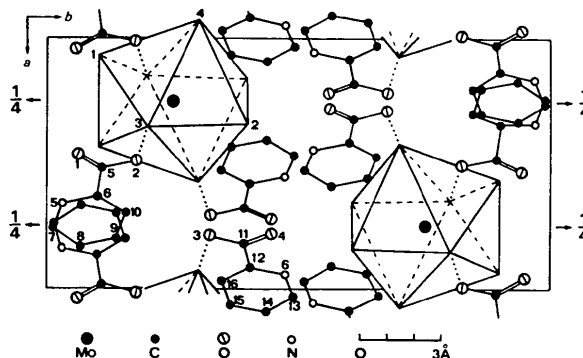


Fig. 1. Projection of the structure along *c*. Dotted lines: hydrogen bonds. Double lines: keto groups. Numbering of atoms is according to Table 2.

and  $N(2)\cdots N(6^V)$  [2.785 (7) Å]. The latter values compare well with the 2.83 Å in  $[HN(C_2H_5)_3]_2\cdot[H_2O]_2Mo(CN)_8$  (Leipoldt, Basson & Bok, 1980).

Least-squares planes through the six atoms of each of the crystallographically different pyridinium rings show a maximum deviation of 0.005 (4) Å for an individual atom whilst carboxylic acid C and O atoms deviate by at most 0.07 (1) Å from this plane. The 2-picolinic acid cation is thus considered to be planar. Bond distances and angles (Table 3) within the two independent cations compare well with similar structures, *e.g.* tris(pyridine-2-carboxylato)manganese(III) monohydrate (Figgis, Raston, Sharma & White, 1978).

The Mo atom is bonded to eight CN ligands in the form of a theoretical  $D_{2d}(4m2)$  dodecahedron but in fact possesses only  $C_2(2)$  symmetry as required by the space group. The approach to ideal  $D_{2d}$  geometry for the  $Mo(CN)_8^{4-}$  ion in the present structure was calculated by two methods. One involves calculation of the angle between the four-atom interpenetrating trapezoidal planes bisecting in the quasi-4-axis of the polyhedron (Lippard & Russ, 1968). Least-squares

planes through C(4), C(1), C(1<sup>1</sup>), C(4<sup>1</sup>) and C(3), C(2), C(2<sup>1</sup>), C(3<sup>1</sup>) form an angle of 89.1°. These correspond to the two *BAAB* planes in the labelling procedure of Hoard, Hamor & Glick (1968) for edge types and corners of the ideal dodecahedron which will also be used in this text. The latter angle compares well with the theoretical value of 90° as opposed to 77.4° in a square antiprism.

Any distortion of the ideal dodecahedron leading to either a square antiprism or bicapped trigonal prism involves a twisting of the *BAAB* planes resulting in non-planarity. Muetterties & Guggenberger (1974) utilized this distortion in the form of a shape parameter ( $\varphi$ ) to describe the ideal  $\varphi$  angle for different eight-coordinate geometries. These are 0, 14.1 and 24.5° for the  $D_{2d}$ ,  $C_{2v}$  and  $D_{4d}$  models respectively. A second shape parameter,  $\delta$ , concerning the dihedral angle between certain shape-determining faces has values of 29.5° ( $D_{2d}$ ), 0, 21.8, 48.2° ( $C_{2v}$ ) and 0, 52.4° ( $D_{4d}$ ).

Table 3. Bond distances (Å) and angles (°) for the two independent cations (e.s.d.'s in parentheses)

Cation 1			
O(1)–C(5)	1.184 (8)	O(1)–C(5)–O(2)	125.7 (6)
O(2)–C(5)	1.290 (7)	O(1)–C(5)–C(6)	121.0 (6)
C(5)–C(6)	1.507 (8)	C(5)–C(6)–N(5)	114.5 (5)
C(6)–N(5)	1.349 (7)	C(6)–N(5)–C(7)	122.0 (5)
N(5)–C(7)	1.350 (8)	N(5)–C(7)–C(8)	119.5 (6)
C(7)–C(8)	1.388 (9)	C(7)–C(8)–C(9)	119.4 (6)
C(8)–C(9)	1.390 (9)	C(8)–C(9)–C(10)	119.9 (6)
C(9)–C(10)	1.415 (9)	C(9)–C(10)–C(6)	117.9 (5)
C(10)–C(6)	1.371 (8)	C(10)–C(6)–N(5)	121.3 (5)
Cation 2			
O(4)–C(11 <sup>II</sup> )	1.200 (8)	O(3)–C(11)–O(4 <sup>III</sup> )	125.8 (6)
O(3)–C(11)	1.303 (7)	O(4 <sup>III</sup> )–C(11)–C(12)	121.1 (5)
C(11)–C(12)	1.491 (8)	C(11)–C(12)–N(6)	115.1 (5)
C(12)–N(6)	1.356 (7)	C(12)–N(6)–C(13)	122.2 (5)
N(6)–C(13)	1.342 (8)	N(6)–C(13)–C(14)	120.2 (6)
C(13)–C(14)	1.389 (9)	C(13)–C(14)–C(15)	118.7 (6)
C(14)–C(15)	1.400 (9)	C(14)–C(15)–C(16)	119.8 (6)
C(15)–C(16)	1.407 (9)	C(15)–C(16)–C(12)	118.6 (6)
C(16)–C(12)	1.377 (8)	C(16)–C(12)–N(6)	120.4 (5)
Symmetry code			
(I)	$\frac{1}{2} - x, y, \frac{1}{2} - z$	(IV)	$x - \frac{1}{2}, -y, z - \frac{1}{2}$
(II)	$x, y, 1 + z$	(V)	$x - \frac{1}{2}, 1 - y, \frac{1}{2} + z$
(III)	$x, y, z - 1$		

We calculated  $\varphi = 2.8^\circ$  and  $\delta = 30.3$  and  $34.2^\circ$  for the present structure. Both shape-determining methods thus confirm an almost perfect dodecahedral geometry for the  $\text{Mo}(\text{CN})_8^{4-}$  ion in this structure.

Dimensions of Mo–C≡N chains and the dodecahedron are presented in Tables 4 and 5 respectively. The mean values compare well with those of other octacyano complexes. The ideal dodecahedron, as a result of two interpenetrating bisphenoids, can have two symmetry-equivalent sets of metal–ligand bonds, namely  $M-L_A$  or  $M-L_B$  types. The bond ratio  $M-L_A/M-L_B$ , angles  $\theta_A$  and  $\theta_B$  which  $M-L_A$  and  $M-L_B$  form with the quasi-4-axis and edge lengths referred to a unit length in  $M-L$  distances can also serve in identifying a hard sphere (HSM) or most favorable (MFP) polyhedron type (Hoard & Silverton, 1963; Lippard, 1967).

We calculated  $\theta_A = 35.6(2)$ ,  $\theta_B = 73.6(2)^\circ$ ,  $M-L_A/M-L_B = 1.01(1)$ ,  $a \approx m = 1.16(1)$ ,  $g = 1.24(1)$  and  $b = 1.47(1)$ . The theoretical MFP values together with those of  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  (in parentheses) are:  $\theta_A = 35.2(36.0)$ ,  $\theta_B = 73.5(72.9)^\circ$ ,  $M-L_A/M-L_B = 1.03(1.00)$ ,  $a \approx m = 1.17(1.17)$ ,  $g = 1.24(1.24)$  and  $b = 1.49(1.47)$ . Considering the latter values there is little to choose between the dodeca-

Table 5. Dimensions of coordination polyhedron of the  $\text{Mo}(\text{CN})_8^{4-}$  ion based on C atoms (e.s.d.'s in parentheses)

	Edge length (Å)	Edge type*	C–Mo–C angle (°)
C(1)–C(1 <sup>I</sup> )	2.514 (8)	<i>a</i>	70.9 (2)
C(2)–C(2 <sup>I</sup> )	2.536 (8)	<i>a</i>	71.7 (2)
C(4)–C(1)	2.509 (8)	<i>m</i>	71.1 (2)
C(2)–C(3)	2.500 (8)	<i>m</i>	70.7 (2)
Mean	2.515		71.1
C(4)–C(2)	2.751 (8)	<i>g</i>	79.2 (2)
C(4)–C(2 <sup>I</sup> )	2.600 (8)	<i>g</i>	74.1 (2)
C(3)–C(1)	2.603 (8)	<i>g</i>	74.1 (2)
C(3)–C(1 <sup>I</sup> )	2.760 (8)	<i>g</i>	79.4 (2)
Mean	2.679		76.7
C(4)–C(3)	3.119 (8)	<i>b</i>	92.9 (2)
C(4)–C(3 <sup>I</sup> )	3.207 (8)	<i>b</i>	96.3 (2)
Mean	3.163		94.6

\* See text.

Table 4. Dimensions of the Mo–C≡N chains in the  $\text{Mo}(\text{CN})_8^{4-}$  ion (e.s.d.'s in parentheses)

Chain	M–C (Å)	Bond type*	C≡N (Å)	Mo...N (Å)	M–C≡N (°)
Mo–C(1)–N(1)	2.167 (5)	<i>A</i>	1.150 (7)	3.313 (5)	175.0 (5)
Mo–C(2)–N(2)	2.165 (5)	<i>A</i>	1.155 (7)	3.318 (5)	175.7 (5)
Mo–C(3)–N(3)	2.156 (6)	<i>B</i>	1.146 (8)	3.301 (6)	178.0 (5)
Mo–C(4)–N(4)	2.149 (6)	<i>B</i>	1.149 (8)	3.298 (6)	179.0 (5)
Mean	2.159		1.150	3.308	176.9

\* See text.

hedral forms of the present structure and  $K_4Mo(CN)_8 \cdot 2H_2O$ . Although  $M-A$  and  $M-B$  bond distances (Table 4) are the same within experimental error, it can also be reasoned that the average values of the two types are on the fringe of significance, especially with regard to  $Mo \cdots N$  separations which must bear full weight equally in view of practically linear  $Mo-C \equiv N$  chains.

It is also noticeable that the hydrogen bonds and pyridinium nitrogen to anion contacts are directed towards the respective  $M-B$  and  $M-A$  bond types in the  $Mo(CN)_8^{4-}$  ion where the  $M-B$  bond distances tend to be the shorter ones. The latter observation cannot be ascribed to a weak  $\pi$ -bond character, following Orgel's (1960) rule and the comparison as well as conclusions drawn between  $d^0$  oxozirconate(IV) complexes and  $d^2$   $Mo(CN)_8^{4-}$  ions by Hoard, Hamor & Glick (1968).

Burdett, Hoffmann & Fay (1978) made the observation, in considering  $\sigma$ - and  $\pi$ -site preferences in  $MX_4Y_4$  molecules containing  $\pi$ -donor and -acceptor ligands, that it was in most cases the more electronegative ligand which occupied the  $B$  sites of the dodecahedron. This was also in accord with a bond-overlap population study. In the  $Mo(CN)_8^{4-}$  ion with eight equivalent ligands, compared to  $MX_4Y_4$  molecules, distinction between  $A$  and  $B$  bond types would be difficult, especially if the packing of the complex anion and surrounding cations are effective in neutralizing the equally distributed negative charge on all CN ligands. This seems to be the case in structures of octacyano complexes because small cations in, for example,  $H_4W(CN)_8 \cdot 6H_2O$  and  $Na_3W(CN)_8 \cdot 4H_2O$  prefer a more flattened version (square antiprism or somewhat deformed) of the complex anion to fit the cation's coordination-shell dimensions. Larger cations in  $K_4Mo(CN)_8 \cdot 2H_2O$  could fit the dodecahedron better whilst still larger ones in  $Cs_3Mo(CN)_8 \cdot 2H_2O$  with a cubic or 4,4,4-tricapped trigonal prismatic shell fit best to a similar 4,4-bicapped trigonal prismatic configuration of the anion.

We suggest that the tendency in dissimilar  $M-A$  and  $M-B$  bonds in this structure is a consequence of the non-spherical cation's influence on the negative-charge distribution of  $M-C \equiv N$  bonds. The greater electron-attracting power of the pyridinium N atom compared with a polar OH group will have a similar effect to that predicted by Orgel's rule or found for  $\sigma$ -site preferences. The preferred anion configuration in the

present structure is the ideal dodecahedron, since it can accommodate relatively different bond lengths compared with the square antiprism.

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