

## The Crystal Structure of Bis(triethylammonium)dihydroniumoctacyanomolybdate(IV)

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### Introduction

Crystal structure determinations of octacyano-metalate complexes indicate that the dodecahedron ( $D_{2d}$ ) and square antiprism ( $D_{4d}$ ) are the most favourable polyhedra for  $M(CN)_8^{n-}$  ions ( $M = Mo(IV), Mo(V), W(IV), W(V)$  and  $Nb(IV)$  [1–5]). In contrast to this, a recent crystal structure determination of  $Cs_3Mo(CN)_8 \cdot 2H_2O$  showed that the  $Mo(CN)_8^{3-}$  ion exhibited a bicapped trigonal prismatic ( $C_{2v}$ ) geometry (to be published). In systematic molecular orbital analyses [6], it was concluded that whatever the desires of p and d electronic interactions, the equilibrium geometry will be nearer to the sterically determined one than any other. One of the factors influencing this stereochemistry is believed to be the physical environment of the  $M(CN)_8^{n-}$  ion. A knowledge of this geometry of these ions in the solid state for a variety of cations can thus be considered as a prerequisite for spectroscopic analyses of the solids and solutions as a result of the fluctuating nature in the geometry of the  $M(CN)_8^{n-}$  ion. The structure determination of  $[H-N(C_2H_5)_3]_2 [H_3O]_2 [Mo(CN)_8]$  can be considered as a contribution to this much debated stereochemical aspect.

### Experimental

A solution of  $K_4Mo(CN)_8 \cdot 2H_2O$  (1 g in 15 cm<sup>3</sup> water) was mixed with a equal volume of triethylamine which was acidified with concentrated hydrochloric acid. Yellow well-formed crystals were obtained after about 30 minutes. *Crystal data*:  $C_{20}H_{38}N_{10}O_2Mo$ , molecular weight 546.53, monoclinic space group  $C2/c$ ,  $a = 17.946 \text{ \AA}$ ,  $b = 10.832 \text{ \AA}$ ,  $c = 16.155 \text{ \AA}$ ,  $\beta = 113.4^\circ$ ,  $d_{exp} = 1.27 \text{ g cm}^{-3}$ ,  $d_{calc} = 1.26 \text{ g cm}^{-3}$ ,  $Z = 4$ ,  $\mu(MoK\alpha) = 4.8 \text{ cm}^{-1}$ . The corresponding tungsten compound is isomorphous with the molybdenum complex with  $a = 18.00 \text{ \AA}$ ,  $b = 10.83 \text{ \AA}$ ,  $c = 16.16 \text{ \AA}$ ,  $\beta = 113.5^\circ$ .

The three dimensional intensity data were collected with a Philips PW1100 four circle X-ray dif-

fractometer using graphite monochromated  $MoK\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) for  $\theta$  values between  $3^\circ$  and  $23^\circ$ . A crystal with dimensions  $0.2 \times 0.2 \times 0.3 \text{ mm}^3$  was used for the data collection. The crystal remained stable during the data collection. 1862 independent reflections were measured of which 1692 were considered as observed. Only Lorentz and polarization corrections were applied. The structure was solved using the X-ray 72 system of programs on a Univac 1100 computer. The molybdenum atom was located from a three dimensional Patterson function. All the other non-hydrogen atoms were located from successive Fourier analyses. Five cycles of full matrix least squares refinement of all the positional and isotropic thermal parameters resulted in the residual factor, R, of 0.062.

A table of the observed and calculated structure factors may be obtained from the authors. The final positional and isotropic thermal parameters are listed in Table I.

TABLE I. Fractional Atomic Coordinates ( $\times 10^4$ ) and Isotropic Temperature Factors ( $\times 10^3$ ).<sup>a</sup>

Atom	X	Y	Z	$U_{iso}$
Mo	5000	7628(1)	2500	22(1)
C(1)	5054(4)	6349(7)	1522(5)	28(2)
C(2)	3840(4)	6703(7)	1879(5)	27(2)
C(3)	4304(4)	8824(7)	1414(5)	26(2)
C(4)	5802(5)	8557(7)	2001(5)	29(2)
N(1)	5091(5)	5653(7)	994(5)	51(2)
N(2)	3231(4)	6186(6)	1548(5)	40(2)
N(3)	3913(4)	9417(7)	803(5)	41(2)
N(4)	6222(4)	9028(7)	1702(5)	45(2)
N(11)	5932(5)	6600(8)	6146(6)	65(2)
C(11)	6209(7)	6533(12)	7166(8)	76(3)
C(21)	6743(9)	7628(14)	7678(10)	102(4)
C(12)	6619(9)	6571(15)	5810(10)	108(5)
C(22)	6987(10)	5352(17)	5958(12)	124(6)
C(13)	5319(9)	7754(14)	5727(9)	98(4)
C(23)	4575(12)	7585(21)	5874(14)	154(7)
O(1)	2012(3)	4703(5)	733(3)	35(1)

<sup>a</sup>Double digits in the numbering scheme refer to the triethylammonium ion. The second digit of the carbon atoms refers to the three different ethyl groups.

### Results and Discussion

The bond lengths are given in Table I. The mean Mo–C distance (2.149 Å) is in good agreement with the value found in  $K_4Mo(CN)_8 \cdot 2H_2O$  [1]. The mean C–N distance (1.155 Å) agrees with the value found in many other cyanide complexes. The Mo–C≡N chains are nearly linear; no Mo–C–N bond angle departs by more than  $3.4^\circ$  from  $180^\circ$ . Visual inspec-

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TABLE II. Interatomic Distances (Å) and Their e.s.d.s.

Mo-C(1)	2.132(8)
Mo-C(2)	2.165(7)
Mo-C(3)	2.140(7)
Mo-C(4)	2.157(9)
C(1)-N(1)	1.16(1)
C(2)-N(2)	1.15(1)
C(3)-N(3)	1.15(1)
C(4)-N(4)	1.16(1)
N(11)-C(11)	1.52(2)
N(11)-C(12)	1.53(2)
N(11)-C(13)	1.62(2)
C(11)-C(21)	1.54(2)
C(12)-C(22)	1.45(2)
C(13)-C(23)	1.46(3)
O(1)-N(2)	2.61(1)
O(1)-N(3)	2.56(1)
O(1)-N(4)	2.60(1)
N(11)-N(1)	2.83(1)

tion of a model of the  $\text{Mo}(\text{CN})_8^{4-}$  ion, showed that it does not correspond to one of the usual geometries (dodecahedron and square antiprism) found in eight coordinate cyanide complexes. The method of Muetterties and Guggenberger [7] was used to describe the  $\text{Mo}(\text{CN})_8^{4-}$  ion as it offers an unambiguous method for the analyses of the geometry of coordination polyhedra. The ideal and observed angles for a number of cyanide complexes are shown in Table III. It is clear that the coordination polyhedron can be described as about half-way between a dodecahedron and a bicapped trigonal prism. The deviation from an ideal dodecahedron is also reflected by the observed angle ( $87.7^\circ$ ) between the two trapezoidal planes. For an ideal dodecahedron this angle should be  $90^\circ$  [8]. From the results in Table III, it follows that the geometry of the  $\text{M}(\text{CN})_8^{n-}$  ions is determined to a large extent by the particular physical environment such as hydrogen bonding and/or crystal packing.

Two of the eight cyanide ligands are hydrogen bonded to the nitrogen atoms of two neighbouring

triethylammonium ions,  $\text{N} \cdots \text{N} = 2.83(1) \text{ \AA}$ . The other six cyanide ligands are hydrogen bonded to hydronium ions. The oxygen atom is hydrogen bonded to N(2), N(3) and N(4) with distances 2.61(1) Å, 2.55(1) Å and 2.60(1) Å respectively. This is an indication of the existence of the  $\text{H}_3\text{O}^+$  ion although the hydrogen atoms could not be located from a Fourier analyses. The presence of two  $\text{H}_3\text{O}^+$  ions per molecule in the solid state was confirmed by titrating a solution of the compound with sodium hydroxide with bromo thymol blue as indicator.

Each oxygen atom together with its neighbouring nitrogen atoms has an approximately trigonal pyramidal geometry. The oxygen atom is situated 0.71 Å out of the trigonal plane. The N-O-N angles are  $110.6^\circ$ ,  $113.0^\circ$  and  $114.7^\circ$ . N(2), N(3) and N(4), constituting the trigonal plane, forms a slightly distorted equilateral triangle with dimensions of 4.25 Å, 4.39 Å and 4.30 Å for the edges and angles of  $58.5^\circ$ ,  $59.6^\circ$  and  $61.8^\circ$ . If it is assumed that the O-H $\cdots$ N bonds are linear (as was found in a neutron diffraction study of *p*-toluenesulfonic acid monohydrate [9]) then the above description of the trigonal pyramidal moiety can be considered as representative of the geometry of the  $\text{H}_3\text{O}^+$  ion. This is in good agreement with the above mentioned neutron diffraction study. The  $\text{Mo} \cdots \text{N} \cdots \text{O}$  chains depart by not more than  $15^\circ$  from linearity.

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TABLE III. Ideal and Observed Angles (Degrees) for  $\text{ML}_8$  Complexes.

Complex	$\delta'$ Angles	$\phi$ Angles
Ideal dodecahedron [7]	29.5, 29.5, 29.5, 29.5	0.0
Ideal bicapped trigonal prism [7]	0.0, 21.8, 48.2, 48.2	14.1
Ideal square antiprism [7]	0.0, 0.0, 52.4, 52.4	24.5
$\text{H}_4\text{W}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$ [3]	0.0, 2.9, 48.7, 48.7	22.7
$\text{Na}_3\text{W}(\text{CN})_8 \cdot 4\text{H}_2\text{O}$ [2]	2.7, 9.6, 45.7, 48.2	18.5, 19.3
$\text{H}_4\text{W}(\text{CN})_8 \cdot 4\text{HCl} \cdot 12\text{H}_2\text{O}$ [4]	5.2, 5.2, 46.3, 52.5	22.0
$\text{Cs}_3\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}^a$	0.0, 22.7, 47.5, 49.7	17.5
$[\text{H} \cdots \text{N}(\text{C}_2\text{H}_5)_3]_2[\text{H}_3\text{O}]_2\text{Mo}(\text{CN})_8$	17.3, 22.6, 38.9, 38.9	9.2

<sup>a</sup>To be published.

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