The observed high resistance against compression of the γ-brass structure may suggest that the bonding is partly of covalent type. On the basis of the measurements of several electronic properties, Menth (1967) showed that the γ phase in the copper–zinc system should be regarded as a semimetal. If this interpretation is correct, the force which holds the atomic clusters firm will be a direct bonding between atoms. In order to clarify the character of the bonding, however, further investigation, both theoretical and experimental, is necessary.

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The Structure of Tricaesium Octacyanomolybdate(V) Dihydrate, Cs₃Mo(CN)₈.2H₂O — a New Stereochemical Configuration for $[M(CN)_8]^{n-}$ Ions

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Abstract

The crystal structure of Cs₃[Mo(CN)₈].2H₂O has been determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/m$ with two molecules in a unit cell of dimensions $a = 8.682$ (6), $b = 14.198$ (9), $c = 8.477$ (7) Å and $\beta = 117.91$ (10)°. The final R value for all the observed reflections was 0.039. The Mo atom is coordinated to eight cyano groups in a geometric form which can be best described as a 4,4-bicapped trigonal prism. The mean Mo—C and C—N distances are 2.17 (2) and 1.14 (2) Å respectively. Two distinct classes of Cs⁺ ions are present, having cubic and 4,4,4-tricapped trigonal-prismatic environments respectively.

Introduction

Cs₃[Mo(CN)₈].2H₂O and Cs₃[W(CN)₈].2H₂O (in contrast to the other alkali-metal salts) can be used as analytical primary standards as a result of their high stability (Basson, Bok & Grobler, 1974).

The $[M(CN)_8]^{n-}$ ions (M = Mo or W, and n = 3 or 4) are also of great spectroscopic and crystallographic interest (Lippard, 1967). Various spectroscopic investigations, of which the Mössbauer studies have proved to be the most successful (Clark, Gancedo, Maddock & Williams, 1975), have been carried out to determine the geometries of these ions in the solid state and in solution, often with contradictory results. X-ray crystallographic studies have provided examples of dodecahedral (D_{2d}) as well as square-antiprismatic (D_{4d}) configurations for $[M(CN)_8]^{n-}$ ions (Basson, Bok & Leipoldt, 1970; Corden, Cunningham &

Eisenberg, 1970; Bok, Leipoldt & Basson, 1972; Laing, Gafner, Griffith & Kiernan, 1979; Leipoldt, Basson & Bok, 1979). The crystallographic data also show that lattice factors play an important role in the stabilization of the preferred polyhedron for a specific compound of this type. Further structural studies will thus not only help in elucidating these factors, but will also be of great importance as a basis for the spectroscopic work (Garner & Mabbs, 1979) on these compounds.

Experimental

$Cs_3[Mo(CN)_8].2H_2O$ and $Cs_3[W(CN)_8].2H_2O$ were prepared as previously described (Bok, Leipoldt & Basson, 1975). Bright-yellow monoclinic crystals were obtained after recrystallization from water. Since both the crystals and the solution are sensitive to light, all work was carried out in diffuse light. The crystals slowly decompose in X-rays for exposure times longer than 48 h. Table 1 contains the crystal data. Preliminary investigations with the Weissenberg technique yielded the space groups $P2_1$ or $P2_1/m$, of which the latter proved to be correct in the subsequent structure determination.

Three-dimensional intensity data were recorded for the Mo compound by means of a Philips four-circle X-ray diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) for θ values up to 23°. An almost spherical crystal (radius = 0.04 mm, $\mu R = 0.26$) was used for the intensity data collection. Three reflections were chosen as standards which were remeasured after every 60 reflections. No decomposition of the crystal was detected by way of this procedure. The intensity collection comprised 1192 reflections, of which 987 were stronger than the background and were only corrected for Lorentz and polarization effects. The structure was solved utilizing the XRAY 72 system of programs on a Univac 1100 computer.

A three-dimensional Patterson function gave the coordinates of the Cs and Mo atoms. The coordinates of all the other non-hydrogen atoms were then determined from a three-dimensional Fourier analysis. The positional and temperature parameters were refined by means of a full-matrix least-squares program. The final R value (using all the observed

Table 1. *Crystallographic data*

	$Cs_3[Mo(CN)_8].2H_2O$	$Cs_3[W(CN)_8].2H_2O$
M_r	738·86	826·87
a (Å)	8·682 (6)	8·70 (2)
b (Å)	14·198 (9)	14·15 (4)
c (Å)	8·477 (7)	8·46 (2)
β (°)	117·91 (10)	117·90 (50)
D_c (Mg m^{-3})	2·65	2·98
D_e (Mg m^{-3})	2·65	2·95

Table 2. *Fractional atomic coordinates ($\times 10^4$) with corresponding Debye–Waller factors*

The estimated standard deviations of the atomic coordinates (in parentheses) refer to the last digits.

	Point symmetry	x	y	z	B (Å^2)
Mo	m	3804 (2)	7500	2088 (2)	1·4 (1)
Cs(1)	$\bar{1}$	0	5000	5000	3·4 (1)
O(1)	m	1192 (21)	2500	2383 (25)	5·0 (6)
O(2)	m	9841 (25)	2500	4873 (28)	4·8 (6)
C(1)	m	3940 (23)	7500	4673 (25)	1·9 (6)
C(2)	m	6048 (27)	7500	1605 (26)	2·6 (6)
N(1)	m	4005 (20)	7500	6066 (23)	2·7 (5)
N(2)	m	7212 (24)	7500	1315 (25)	3·0 (6)
Cs(2)	1	3241 (1)	4143 (0)	1533 (1)	2·8 (1)
C(3)	1	5431 (17)	8665 (10)	3567 (18)	1·5 (4)
C(4)	1	3181 (17)	8458 (10)	−131 (17)	1·8 (4)
C(5)	1	1738 (18)	8457 (9)	1918 (18)	1·9 (4)
N(3)	1	6247 (16)	9307 (10)	4309 (17)	3·1 (4)
N(4)	1	2879 (17)	8992 (9)	−1231 (17)	3·3 (4)
N(5)	1	740 (15)	8983 (9)	1863 (18)	3·0 (4)

reflections and anisotropic temperature factors for all the atoms) was 0·039. The final atomic and thermal parameters are given in Table 2.*

Description of the structure and discussion

The Cs$^+$ ions in special positions (Table 2) are approximately cubically surrounded by two O and six N atoms. The Cs–O and Cs–N distances are given in Table 3. The mean distance between the Cs$^+$ ion and the eight surrounding atoms is 3·35 (1) Å. The

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35239 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances (Å) involving Cs$^+$ ions*

Cube

Cs(1)–O(2)(I)	3·55 (0)	Cs(1)–N(3)(II)	3·18 (1)
Cs(1)–N(5)(III)	3·34 (2)	Cs(1)–N(4)(IV)	3·32 (1)

4,4,4-Tricapped trigonal prism

Cs(2)–N(2)(V)	3·25 (2)	Cs(2)–N(5)(III)	3·53 (1)
Cs(2)–N(1)(I)	3·28 (1)	Cs(2)–N(5)(VI)	3·31 (1)
Cs(2)–O(1)	3·21 (2)	Cs(2)–N(4)(VII)	3·50 (2)
Cs(2)–N(4)(III)	3·45 (1)	Cs(2)–N(3)(II)	3·35 (1)
Cs(2)–N(3)(III)	3·38 (1)		

Symmetry code (space group $P2_1/m$)

(I)	$1-x, 1-y, 1-z$	(V)	$1-x, 1-y, -z$
(II)	$1-x, y-\frac{1}{2}, 1-z$	(VI)	$-x, y-\frac{1}{2}, -z$
(III)	$x, \frac{3}{2}-y, z$	(VII)	$1-x, y-\frac{1}{2}, -z$
(IV)	$x, \frac{3}{2}-y, 1+z$		

calculation of the best planes through the six faces of the cube shows that the mean distance from the Cs^+ ion to these planes is 1·93 (2) Å, and that the planes on opposite sides are almost parallel to one another.

The Cs^+ ion in the general position is surrounded by one O and eight N atoms. The polyhedron can best be described as a 4,4,4-tricapped trigonal prism. The mean distance between these nine atoms and the Cs^+ ion is 3·36 (1) Å. The deviation of individual values from the mean value (Table 3) and also the calculation of the best planes through the surfaces of the polyhedron show that the deviation from an ideal 4,4,4-tricapped trigonal prism is not very great.

The main feature of this crystal structure is the coordination polyhedron of the $[Mo(CN)_8]$ group, which can be described as a C_{2v} (mm) 4,4-bicapped trigonal prism — a geometrical form which was not previously established for octacyanometallate complexes. Previous methods employed for establishing the type of polyhedron for discrete eight-coordinated moieties were either based on visual inspection of a good model or calculation of the angle between the interpenetrating trapezoidal planes for the dodecahedron or square antiprism. These angles ought to be 90 and 77·4° for the ideal D_{2d} and D_{4d} models respectively (Lippard & Russ, 1968). The experimental value of 85·3° for $Cs_3[Mo(CN)_8].2H_2O$ is about halfway, but nearer to the dodecahedron's value with the result that a description of a distorted dodecahedron could fit the $[Mo(CN)_8]$ group. However, any distortion of the ideal dodecahedron leading to either the bicapped trigonal prism or square antiprism involves a twisting of the above-mentioned trapezoidal planes leading to nonplanarity. The method of Muetterties & Guggenberger (1974) utilized this distortion in the form of a shape parameter (φ) to describe the ideal angle φ for different eight-coordinate geometries. This coupled with another shape parameter, δ, as the dihedral angle between certain shape-determining faces, gives an almost unique method of describing the specific type of polyhedron at hand. Calculations performed on published structures of cyano complexes by the above-mentioned authors together with those of bis(triethylammonium) dihydronium octacyanomolybdate(IV) (Leipoldt, Basson & Bok, 1979) and the present structure are given in Table 4. The ML_8 polyhedron in the aforementioned structure can thus be regarded as halfway between a dodecahedron and a bicapped trigonal prism, compared with $Na_3[W(CN)_8].4H_2O$ (Bok, Leipoldt & Basson, 1970) which is between a square antiprism and a bicapped trigonal prism.

The bonding angle (α) between the capping ligands and the central atom as well as the angle θ between the six prism ligands (D_{3h} structure) and the threefold axis of the prism were found to vary between $\alpha = 120°$, $\theta = 45°$ for a d^0 to $\alpha = 140°$, $\theta = 49°$ for a d^2 metal ion in
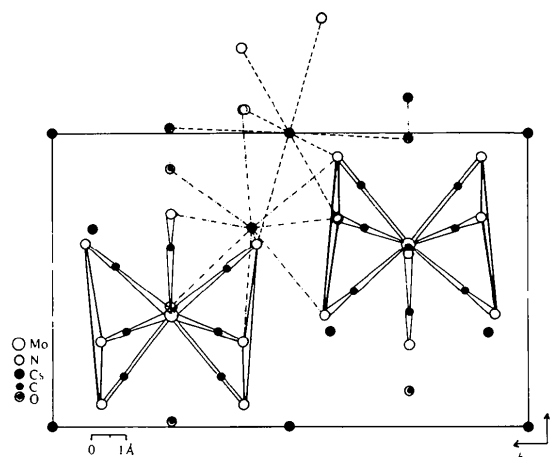

Fig. 1. Projection of the structure along [001]. Triangles of cyano N atoms indicate base planes of a trigonal prism. Dotted lines: O···O hydrogen bonding; dashed lines: cubic arrangement for Cs(1); dash–dotted lines: 4,4,4-tricapped trigonal prism for Cs(2).

Table 4. *Ideal and observed shape parameters for* $[M(CN)_8]^{n-}$ *ions*

Complex	δ (°)	φ (°)
Dodecahedron	29·5, 29·5, 29·5, 29·5	0·0
4,4-Bicapped trigonal prism	0·0, 21·8, 48·2, 48·2	14·1
Square antiprism	0·0, 0·0, 52·4, 52·4	24·5
$H_4[W(CN)_8].6H_2O$	0·0, 2·9, 48·7, 48·7	22·7
$Na_3[W(CN)_8].4H_2O$	2·7, 9·6, 45·7, 48·2	18·5, 19·3
$H_4[W(CN)_8].4HCl.12H_2O$	5·2, 5·2, 46·3, 52·5	22·0
$[NBu_4^n][Mo(CN)_8]$	29·4, 29·4, 33·1, 33·1	1·0
$[NH(C_2H_5)_3]_2[H_3O]_2$ $[Mo(CN)_8]$	17·3, 22·6, 38·9, 38·9	9·2
$Cs_3[Mo(CN)_8].2H_2O$	0·0, 22·7, 47·4, 48·5	17·5

an ideal bicapped trigonal-prismatic environment (Burdett, Hoffmann & Fay, 1978). The only constraint for these limits was that the six prism ligands maintained their D_{3h} structure. We calculated an average $\theta = 46·4°$ and $\alpha = 124·7 (7)°$ for $Cs_3[Mo(CN)_8].2H_2O$ with its d^1 metal ion. These compare well with the above-mentioned enlargement in angles in going from d^0 to d^2 ions. The most striking distortion of the $Mo(CN)_8$ polyhedron is the angle of 13·4° between the two symmetry-equivalent (mirror reflection) C(3)–C(4)–C(5) triangular planes (Fig. 1). It is also evidenced by the longer interatomic distance of 3·31 (2) Å for C(3)–C(3)(III) compared to 2·72 (2) Å for both the C(4) and C(5) sets respectively. The same phenomenon is also reflected in the C(3)–Mo–C(3)(III) angle of 100·3 (5)°, compared to 77·4 (5) and 76·3 (5)° for C(4) and C(5) respectively. This distortion indicates a shearing away of the two cyano

ligands situated between the capping ligands which could eventually lead to a square-antiprismatic environment. The opening up of these ligands is checked by strong Coulombic interactions with Cs(2)$^+$ ions of 3·38 (1) and 3·35 (1) Å respectively (Table 3).

The average Mo—C and C≡N bond distances and Mo—C≡N angles (Table 5) compare well with those of other octacyano complexes. There is also no observed lengthening in the metal—capping-ligand bond distances, as suggested by Burdett, Hoffmann & Fay (1978). Equal M—CN bond distances were also found in $K_4[Mo(CN)_8].2H_2O$ (Hoard, Hamor & Glick, 1968) in spite of permissible distinction between M—A and M—B bond classes in an ideal D_{2d} model. There is also a parallelism between the latter structure and the present one concerning the immediate environment of the N atoms. In both compounds water molecules are used to fill the coordination spheres of the two symmetry classes of cations whilst H_2O—N separations range upwards from 3·04 Å. This is in contrast to the remaining known crystal structures of octacyano complexes where H_2O molecules are strongly hydrogen bonded to cyano ligands.

Although the water molecules are not bound by strong hydrogen bonds [the shortest distance which can be considered as a hydrogen bond is between O(1) and O(2), i.e. 2·86 (4) Å], the compactness of the structure and the ion—dipole interaction between the Cs$^+$ ion and the water molecule [the mean Cs—O distance is 3·38 (2) Å] cause the water molecules to be held very firmly. This is confirmed by the relatively small temperature factors (see Table 2) of the O atoms.

The Cs(2)$^+$ and $[Mo(CN)_8]^{3-}$ ions with their tricapped and bicapped trigonal prisms respectively are stacked upon one another along [010]. These polyhedra each share the common triangular plane of the D_{3h} prism with one another. The stacking is such that each $[Mo(CN)_8]^{3-}$ ion is followed by two successive Cs polyhedra along [010]. The cubic arrangement of

Cs(1)$^+$ ions serves as a link-up between the mentioned polyhedra along [100].

This crystal structure determination confirms that the compounds crystallize in a very compact structure. This was to be expected as a result of the high density of the compounds and the fact that they are very stable against loss of water of crystallization.

The question as to the preferred type of coordination polyhedron for a specific octacyano complex appears to depend on the immediate physical environment of the ion rather than on electronic- or ligand-repulsion effects. It seems that the resultant packing of the counter cation in relation to its size and coordination number determine the closest approach to a somewhat flexible stereochemical $M(CN)_8$ arrangement.

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Table 5. *Bond distances (Å) and angles (°) within the* $[Mo(CN)_8]^{3-}$ *ions*

A—B—C	A—B	B—C	$\angle A$—B—C
Mo—C(1)—N(1)	2·14 (2)	1·16 (3)	179·7 (16)
Mo—C(2)—N(2)	2·17 (3)	1·15 (4)	178·7 (16)
Mo—C(3)—N(3)	2·16 (1)	1·15 (2)	177·4 (11)
Mo—C(4)—N(4)	2·17 (1)	1·13 (2)	176·7 (13)
Mo—C(5)—N(5)	2·20 (2)	1·13 (2)	176·5 (12)
Mean	2·17 (2)	1·14 (2)	177·8 (14)