

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Potassium Molybdocyanide Dihydrate. The Configuration of the Molybdenum Octocyanide Group

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Potassium molybdocyanide dihydrate, $K_4Mo(CN)_8 \cdot 2H_2O$, is one of the more familiar examples of the class of compounds containing discrete coordination groups in which eight atoms or radicals are bound to a common central atom. The configuration of a molecule or complex ion of formula MX_8 has not been established with certainty in any single case heretofore, although the cube and the square Archimedean antiprism have been regarded as geometrically plausible possibilities. In the present paper we describe an X-ray study of potassium molybdocyanide dihydrate from which we have succeeded in deducing the complete atomic arrangement existing within the crystal. We shall show that the actual configuration of the molybdenum octocyanide ion, $Mo(CN)_8^{-4}$, is of a less obvious but apparently at least as satisfactory a type as either the cube or the antiprism.

The potassium molybdocyanide dihydrate used in this work was prepared and analyzed by Professor H. H. Willard and Dr. R. C. Thielke,¹ who very kindly supplied us with samples of two different preparations. The color of the crystals varied from a nearly pure yellow to an orange yellow depending, apparently, on their size and habit; the lighter colored preparation was made up of particularly thin leaflets. The crystals belong to the orthorhombic system,² being tabular on (100). When examined with a polarizing microscope they exhibit the required parallel extinction.

Using Cu-K α radiation complete sets of fifteen degree oscillation photographs were prepared with each of the three crystallographic axes in turn as the rotation axis. The reflections were recorded on film in a cylindrical camera of 5 cm. radius, the positions of the knife edges corresponding to $2 \sin \theta = 1.990$. For the photographs with b and c vertical, it was possible to cut and grind the crystals into cylindrical form; the specimens used in these two cases were very nearly 0.10 mm. in diameter and about 0.50 mm. long. For the case of a vertical it was not feasible to pre-

pare an entirely satisfactory specimen because of the habit and the cleavage properties of the crystals. Photographs taken with a specimen approximately $0.28 \times 0.60 \times 0.70$ mm. in size afforded diffraction data which proved to be very useful even though the estimated intensities were necessarily quite approximate.

As required by the orthorhombic system, the X-ray photographs exhibit the complete symmetry of the point group $D_2^h - mmm$. The lattice constants are $a = 16.55 \text{ \AA}$., $b = 11.70 \text{ \AA}$., $c = 8.68 \text{ \AA}$., $a:b:c = 0.7073:1:0.3709$. Goniometric measurements² give $a:b:c = 0.7028:1:0.3711$. Using these lattice constants to construct reciprocal lattice plots, it was possible to index all reflections appearing upon our photographs.³

Examination of the data demonstrates the regular and complete absence of $\{hk0\}$ reflections with h odd, and $\{0kl\}$ reflection with $k + l$ odd. These data render it almost certain that the space group⁴ is either $D_{2h}^{16} - pnma$ or $C_{2v}^9 - pna$. (The sequence of axes chosen on the basis of the crystallographic data happens to be the same as that used in the International Tables in describing these space groups.) The crystallographic data quoted by Rosenheim² assign the crystals to the point group D_2^h , and we assume accordingly the isomorphous space group D_{2h}^{16} . All later developments support this choice.

The space group requires that the unit cell contain 4, 8, 12, . . . $4n$ molecules of $K_4Mo(CN)_8 \cdot 2H_2O$. An approximate experimental determination of the density by the pycnometer method resulted in $d = 1.94 \text{ g./cc.}$; the calculated density with four stoichiometric molecules per unit cell is 1.964 g./cc. We are required then to place 4Mo, 16K, 32C, 32N, and 8H₂O within the unit cell.

During indexing the relative intensities of all $\{hk0\}$, $\{h0l\}$, and $\{0kl\}$ reflections (appearing on the equators of photographs taken with c , b , and a , respectively, as rotation axes) were carefully estimated by visual comparison with an intensity

(3) Cf. J. D. Bernal, *Proc. Roy. Soc. (London)*, **A113**, 117 (1926).(1) H. H. Willard and R. C. Thielke, *This Journal*, **57**, 2609 (1935).(2) A. Rosenheim, *Z. anorg. Chem.*, **64**, 97 (1907).

(4) "Internationale Tabellen zur Bestimmung von Kristallstrukturen." Gebrüder Borntraeger, Berlin, 1935, Erster Band, Gruppentheoretische Tafeln.

scale prepared for this purpose. To obtain the important $\{hk0\}$ and $\{h0l\}$ data each of the authors independently went through the entire experimental procedure of photographing (different specimens, indexing the reflections, and estimating the relative intensities. Using cylindrical specimens very nearly 0.10 mm. in diameter, the resulting photographs were exceptionally clear.

Comparison of the independently derived $\{hk0\}$ data disclosed that the intensities estimated by the senior author showed a larger spread in magnitudes by a factor of about two in going from reflections with small $\sin \theta$ to those with large $\sin \theta$. The two sets of data for $\{h0l\}$ reflections were in rather closer agreement. For each set of reflections mean intensities were computed, and these were divided by the Lorentz and polarization factor to obtain values of $|F_{(hkl)}|^2$. The $\{hk0\}$ and the $\{h0l\}$ reflections were not corrected for absorption of X-rays in the irradiated specimens. Approximate absorption corrections were required in the case of the $\{0kl\}$ data. Questions having to do with the self-consistency and probable accuracy of our data are considered in greater detail later in this paper.

Following methods which were employed to determine the structures of potassium heptafluorocolumbate and potassium heptafluotantalate,⁵ we use the $|F_{(hkl)}|^2$ data to make Patterson projections upon each of the three axial planes in order to place approximately molybdenum and potassium atoms within the unit cell. A knowledge of the positions of molybdenum and potassium suffices to determine the signs of the more important reflection amplitudes required in making approximate Fourier projections of relative electron density upon the axial planes. Refinement of these projections by a process of successive approximations leads ultimately to a complete structural determination.

The formula required for computing the Patterson projection on (010) is

$$P(X,Z) = \sum h \sum l |F_{(h0l)}|^2 \cos 2\pi(hX + lZ)$$

Similar expressions apply to the calculations of the projections on (100) and (001). The actual summations were carried out by the method of Lipson and Beavers⁶ using a set of the Lipson and Beavers strips. Collected data from the three projections are given in Table I.

Remembering that coordinates of maxima on

(5) J. L. Hoard, *This Journal*, **61**, 1252 (1939).

(6) Lipson and Beavers, *Phys. Soc. London*, **48**, 772 (1936).

the Patterson plot represent components of interatomic distances in the projections on (010) of the contents of the actual unit structure, four molybdenum atoms placed in the centers of symmetry⁴—either 4(a) or 4(b) of D_{2h}^{16} —would require very large maxima at $X = 1/2, Z = 1/2$. This is not observed. The remaining possibility for molybdenum is 4(c); $x, 1/4, z; \bar{x}, 3/4, \bar{z}; 1/2 - x, 3/4, 1/2 + z; 1/2 + x, 1/4, 1/2 - z$. These would lead to maxima on the Patterson plot at the following values of X, Z : $\pm 2x, \pm 2z; \pm(1/2 - 2x), 1/2; 1/2, \pm(1/2 - 2z); 0, 0$. Large peaks (Table I) are observed at 0.28, 0.20; 0.22, $1/2; 1/2, 0.30$, in addition to the identity maximum at 0,0. Upon solution we obtain $x = \pm 0.14, z = \pm 0.10$, of which the positive values may be chosen arbitrarily provided that a consistent selection of positions for other atoms be made thereafter.

The next most prominent set of peaks on the projection are in general to be associated with molybdenum-potassium separations. A large peak comparable in magnitude with those associated with molybdenum-molybdenum separations is observed at $X = 0, Z = 0.375$. This peak is most reasonably interpreted as involving potassium in the general positions 8(d): $xyz; 1/2 + x, 1/2 - y, 1/2 - z; \bar{x}, 1/2 + y, \bar{z}; 1/2 - x, \bar{y}, 1/2 + z; \bar{x}, \bar{y}, \bar{z}; 1/2 - x, 1/2 + y, 1/2 + z; x, 1/2 - y, z; 1/2 + x, y, 1/2 - z$, since these atoms superimpose in pairs on any (010) projection. Maxima are expected then at $X = 0.14 \pm x, Z = 0.10 \pm z$. Upon solution we find for K_1 the values $x = 0.14, z = 0.475$ or 0.725 of which the latter value is shown later to be roughly correct. This peak, in fact, involves also several other atomic separations and the z parameter of K_1 turns out to be about 0.690. On the basis of $x = 0.14, z = 0.725$ for K_1 three other molybdenum-potassium maxima are expected at 0.28, 0.18; 0.22, 0.075; 0.50, 0.29. These may be supposed to contribute to the observed peaks at 0.28, 0.20; 0.20, 0.14; 0.50, 0.30. These comparisons are improved on the average by using $z = 0.69$ for K_1 .

Indications of the positions of other potassium atoms on this projection are quite indefinite. It turns out later that another structurally different type of potassium atom has very nearly identical x and z coordinates as molybdenum and contributes to the set of peaks first discussed.

The Patterson projection on (001) possesses a plane of symmetry at $X = 1/4$ since only even

values of h are permitted for $(hk0)$ reflections. With molybdenum placed in 4(c) we expect maxima at $\pm 2x, \frac{1}{2}; \pm(2x - \frac{1}{2}), \frac{1}{2}; 0, 0; \frac{1}{2}, 0$. Large peaks (Table I) are observed at $0.28, \frac{1}{2}; 0.22, \frac{1}{2}; 0, 0; \frac{1}{2}, 0$, the symmetry of the plot causing two Mo-Mo separations to be included in the identity peak. These data lead to molybdenum parameters of $x = 0.14, y = \frac{1}{4}$.

With potassium in the general positions, Mo-K_I maxima are expected at $\pm(x - 0.14), \pm(y - \frac{1}{4}); \pm(x + 0.36), \pm(y - \frac{1}{4}); \pm(x + 0.14), \pm(y + \frac{1}{4}); \pm(x - 0.36), \pm(y + \frac{1}{4})$. Using the large peaks at $X = 0$ (or $\frac{1}{2}$), $Y = 0.20$ and $X = 0.22$ (or 0.28), $Y = 0.30$, we obtain $x = 0.14, y = 0.05$ (or 0.45) for K_I, the alternative values for y referring to a pair of equivalent atoms related one to the other through the symmetry plane of the unit cell at $y = \frac{1}{4}$.

It is possible to associate the peaks observed at $X = 0$ (or $\frac{1}{2}$), $Y = \frac{1}{2}$ and $X = 0.22$ (or 0.28), $Y = 0$ with Mo-K separations involving four potassium atoms in 4(c). Maxima are then expected at $\pm(0.14 - x), 0; \pm(0.14 + x), \frac{1}{2}; \pm(0.36 - x), \frac{1}{2}; \pm(0.36 + x), 0$. Approximate parameter values for K_{II} are then $x = 0.36$ (or 0.86), $y = \frac{1}{4}$, the alternative values for x referring to two equivalent atoms related through the screw axis lying in the plane $y = \frac{1}{4}$.

Since there is no indication that the centers of symmetry 4(a) or 4(b) are occupied, the remaining four potassium atoms must be placed in 4(c) also. Peaks observed at $X = 0.18$ (or 0.32), $Y = 0$ and $X = 0.10$ (or 0.40), $Y = \frac{1}{2}$ are interpreted in terms of Mo-K_{III} separations, the atomic coordinates of K_{III} being then $x = -0.04$ (or 0.46), $y = \frac{1}{4}$.

The projection on (100) possesses a center of symmetry at $Y = \frac{1}{4}, Z = \frac{1}{4}$ in addition to the usual one at the origin. Four molybdenum atoms placed in 4(c) should lead to large maxima at $0, \pm(\frac{1}{2} - 2z); \frac{1}{2}, \pm 2z; \frac{1}{2}, \frac{1}{2}; 0, 0$. These are observed (Table I) at $0, 0.30; \frac{1}{2}, 0.20; \frac{1}{2}, \frac{1}{2}; 0, 0$, all atoms contributing, of course, to the identity peak. As anticipated, these data lead to $y = \frac{1}{4}, z = 0.10$.

The peaks observed at $0.30, 0.21; 0.30, 0.09; 0.20, 0.41; 0.20, 0.29$ are interpreted as arising from Mo-K_I separations, such maxima being expected at $\pm(y + \frac{1}{4}), \pm(z + 0.10); \pm(y + \frac{1}{4}), \pm(z + 0.40); \pm(\frac{1}{4} - y), \pm(z - 0.10); \pm(\frac{1}{4} - y), \pm(z - 0.40)$. These data lead to $y = 0.05$ (or 0.45), $z = 0.69$ (or 0.81), the alternative

values for z referring to equivalent atoms related through the screw axis mentioned above.

With potassium in 4(c) Mo-K maxima are expected at $0, \pm(z - 0.10); \frac{1}{2}, \pm(z + 0.10); \frac{1}{2}, \pm(z + 0.40); 0, \pm(z - 0.40)$. The peaks observed at $0, \frac{1}{2}; \frac{1}{2}, 0.30; \frac{1}{2}, 0; 0, 0.20$ lead to $y = \frac{1}{4}, z = 0.60$ (or 0.90) as coordinates of K_{II}.

The peaks observed at $0, 0.40; \frac{1}{2}, 0.40; \frac{1}{2}, 0.10; 0, 0.10$ are associated with Mo-K_{III} separations, yielding $y = \frac{1}{4}, z = 0.50$ (or 0) for K_{III}.

By considering simultaneously the results derived from the three projections, we get for Mo, $x = 0.14, y = \frac{1}{4}, z = 0.10$; for K_I, $x = 0.14, y = 0.05$ (or 0.45), $z = 0.69$. Since we obtained no information about the positions of K_{II} and K_{III} from the (010) projection we have in each case two possible non-equivalent combinations of x and z coordinates for $y = \frac{1}{4}$. The correct combinations turn out to be for K_{II}, $x = 0.36, y = \frac{1}{4}, z = 0.60$ (or $x = 0.86, y = \frac{1}{4}, z = 0.90$); for K_{III}, $x = -0.04, y = \frac{1}{4}, z = 0.50$ (or $x = 0.46, y = \frac{1}{4}, z = 0$). Some information on this point was derived from Patterson-Harker⁷ summations, which will not be described here.

Table I lists the approximate values of the parameters of molybdenum and potassium together with the coordinates of the observed peaks on the projections from which the parameter data were derived. The brief account of the treatment accorded the Patterson data which we have presented is in some respects quite incomplete, and is probably somewhat misleading with regard to the apparent simplicity of the interpretations. We doubt, however, that we could have arrived at the approximate positions of potassium atoms in a reasonable period of time by any purely trial and error process.

In order to make a Fourier projection of relative electron density on any axial plane of potassium molybdocyanide dihydrate, for instance on (001), a double sum of the following type must be calculated.

$$\rho(x,y) = \Sigma h \Sigma k F_{(hk0)} \cos 2\pi(hx + ky)$$

The relative magnitudes of the $F_{(hk0)}$ are given by the square roots of the $|F_{(hk0)}|^2$ which were used in the computation of the Patterson projection. The signs to be attached to the more important reflection amplitudes can be computed on the basis of the approximate molybdenum and potassium positions of Table I. The pertinent

(7) D. Harker, *J. Chem. Phys.*, **4**, 381 (1936).

structure factors for the general position of D_{2h}^{16} are

$$\begin{aligned} S_{(hko)} &= 8 \sum_i f_i \cos 2\pi h x_i \cos 2\pi k y_i, \quad k \text{ even} \\ S_{(h\bar{k}o)} &= -8 \sum_i f_i \sin 2\pi h x_i \sin 2\pi k y_i, \quad k \text{ odd} \\ S_{(h0l)} &= 8 \sum_i f_i \cos 2\pi h x_i \cos 2\pi l z_i, \quad h + l \text{ even} \\ S_{(h\bar{o}l)} &= -8 \sum_i f_i \sin 2\pi h x_i \sin 2\pi l z_i, \quad h + l \text{ odd} \end{aligned}$$

TABLE I
APPROXIMATE PARAMETERS DEDUCED FROM PATTERSON
DATA

Atom	Approximate parameters			Peak from which parameters are derived		
	x	y	z	X	Y	Z
Mo	0.14		0.10	0.28		0.20
				.22		.50
				.50		.30
Mo	.14	1/4		.28	0.50	
				.22	.50	
Mo		1/4	.10		0	.30
					.50	.20
K _I	.14		.725	0		.375
				.28		.20
				.20		.14
K _I	.14		.70	.50		.30
K _I	.14	0.05		0	.20	
				.50	.20	
				.22	.30	
				.28	.30	
K _I		0.05	.69		.30	.21
					.30	.09
					.20	.41
					.20	.29
					.50	
K _{II}	.36	1/4		0	.50	
				.50	.50	
				.22	0	
				.28	0	
K _{II}		1/4	.60	0	.50	
				.50	.30	
				.50	0	
				0	.20	
K _{III}	.96	1/4		.18	0	
				.32	0	
				.10	.50	
				.40	.50	
K _{III}		1/4	.50	0	.40	
					.50	.40
					.50	.10
				0	.10	

The atomic f -values of Pauling and Sherman⁸ are used throughout this paper.

Table II gives the relative reflection amplitudes for $(h\bar{k}0)$ and $(h0l)$ reflections. It was possible to assign correctly about 85% of the phases for the first projections, those for which the sign seemed seriously in doubt being omitted.

The actual projections were calculated by the method of Lipson and Beevers.⁶ For the (001) projection $\rho(x, y) = A(x, 0) + \sum_k A(x, k) \cos 2\pi$

$ky - \sum_k B(x, k) \sin 2\pi ky$, in which $A(x, 0) = F_{(000)} + 2 \sum_h F_{(h00)} \cos 2\pi hx$, $A(x, k) = 2F_{(0k0)} + 4 \sum_h F_{(hk0)} \cos 2\pi hx$, and $B(x, k) = 4 \sum_h F_{(h\bar{k}0)} \sin 2\pi hx$.

Since $F_{(\bar{h}k0)} = F_{(hk0)}$ for k even, and $F_{(\bar{h}k0)} = -F_{(hk0)}$ for k odd, the A-series includes only reflections with k even, the B-series only those with k odd. Expressions of a similar kind apply to the (010) projection.

From the first incomplete Fourier projections it was possible not only to conclude that an essentially correct assignment of positions to molybdenum and potassium had been derived from the Patterson data but also to secure more accurate values of their atomic coordinates for use in subsequent calculations. In addition, certain minor peaks which appeared were indicative of the positions of carbon, nitrogen, and oxygen atoms.

Some of these minor peaks were immediately interpretable as cyanide groups linearly attached to molybdenum atoms with approximately the interatomic separations calculated from the "Tables of Covalent Radii"⁹ (using the "trigonal prism" radius of molybdenum). These separations are 2.14 Å. for Mo-C, 1.15 Å. for C-N (triple bond), and therefore 3.29 Å. for Mo-N. On the basis both of theory and of many experimental data the bond angle Mo-C≡N is expected to be 180°.

During the course of attempts to use the molybdenum and potassium positions as a framework into which to fit various geometrically plausible configurations for the Mo(CN)₈ complex which would be compatible with the indications of carbon and nitrogen positions given by the projections, the following possibilities for placing eight cyanide groups about a central molybdenum atom were excluded quite definitely: (a) the configuration outlined (exactly or approximately) by the vertices of a cube; (b) the configuration outlined by the corners of an (approximately) square Archimedean antiprism; and (c) the configuration outlined by the vertices of a figure derived from a trigonal prism by adding two extra cyanide groups along normals to two of the rectangular faces. All of these possibilities, moreover, could be excluded also by arguments based on considerations of interatomic distances, since in every case one or more improbably small N-N separations between adjacent anions were encountered.

(8) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(9) L. Pauling and M. J. Huggins, *ibid.*, **87**, 295 (1934).

TABLE II

COMPARISON OF CALCULATED WITH OBSERVED RELATIVE REFLECTION AMPLITUDES FOR (hkl) AND $(h0l)$ REFLECTIONS^a

(hkl)	$F^{(hkl)}$		(hkl)	$F^{(hkl)}$		(hkl)	$F^{(hkl)}$		(hkl)	$F^{(hkl)}$		(hkl)	$F^{(hkl)}$	
	Obsd.	Calcd.		Obsd.	Calcd.		Obsd.	Calcd.		Obsd.	Calcd.		Obsd.	Calcd.
200	5	7	14·2·0	6	-12	16·9·0	10	25	306	0	12	17·0·1	0	7
210	28	44	2·10·0	0	6	20·3·0	0	-6	904	0	12	808	0	3
020	44	-72	14·3·0	8	29	18·7·0	6	-20	705	11	-48	209	0	0
220	8	-13	12·6·0	10	37	6·14·0	2	-11	406	8	28	11·0·7	0	-1
400	46	-107	4·10·0	20	80	12·12·0	8	-16	12·0·1	0	9	13·0·6	0	-1
410	12	-21	890	6	30	14·11·0	4	8	805	0	-3	309	5	-10
230	6	-21	14·4·0	16	42	20·5·0	0	-4	11·0·3	0	-5	17·0·2	7	42
420	4	-3	10·8·0	10	-44	18·8·0	12	-14	506	3	-25	409	1	-10
040	76	167	6·10·0	10	-35				10·0·4	0	-5	908	3	-6
430	6	-17	12·7·0	0	-18	101	9	25	12·0·2	12	-20	15·0·5	7	-31
600	48	85	14·5·0	0	-7	201	4	15	606	0	-1	16·0·4	1	-13
240	16	-32	2·11·0	14	-24	301	29	-50	905	8	30	509	3	-10
610	24	-55	16·0·0	0	-1	002	10	30	13·0·1	0	5	12·0·7	7	20
620	0	7	16·1·0	16	41	102	28	93	12·0·3	7	-29	17·0·3	0	-1
440	36	-78	4·11·0	6	17	202	1	-5	107	7	-25	14·0·6	4	-1
250	24	40	10·9·0	6	25	401	3	15	706	5	18	609	0	1
630	16	29	8·10·0	12	-50	302	9	25	11·0·4	6	14	18·0·1	1	5
800	28	79	16·2·0	4	-24	501	7	7	207	10	-52	10·0·8	0	5
810	10	17	14·6·0	8	-39	402	24	-51	13·0·2	13	-48	18·0·2	2	-4
450	22	-28	12·8·0	12	-45	103	5	-20	307	0	4	709	7	27
640	16	41	16·3·0	10	-29	203	39	122	10·0·5	0	-3	16·0·5	0	9
060	64	-137	6·11·0	6	20	502	26	-58	407	5	-7	13·0·7	0	1
820	20	-42	0·12·0	16	51	601	9	-27	806	4	-12	17·0·4	11	20
260	0	-15	16·4·0	0	13	303	39	-98	14·0·1	12	-29	11·0·8	4	15
830	10	26	2·12·0	0	12	403	18	-52	507	0	-22	15·0·6	0	1
650	32	-75	14·7·0	8	26	602	3	-4	13·0·3	11	31	809	0	7
460	24	44	10·10·0	14	45	701	10	29	12·0·4	3	32	18·0·3	3	12
840	20	61	4·12·0	0	-3	503	4	-35	906	0	7	0·0·10	15	47
10·0·0	40	-83	8·11·0	0	-3	004	1	-15	11·0·5	19	75	1·0·10	3	-16
10·1·0	6	17	12·9·0	8	-33	104	1	4	14·0·2	0	-14	2·0·10	0	-3
270	6	-15	16·5·0	16	44	204	5	14	607	9	42	19·0·1	9	-20
660	14	-36	6·12·0	0	7	702	9	24	707	0	-6	3·0·10	0	9
10·2·0	24	48	18·0·0	16	-37	304	0	-7	13·0·4	0	8	909	1	14
850	14	32	14·8·0	6	20	801	8	-19	14·0·3	0	-12	14·0·7	0	3
470	0	0	18·1·0	0	6	603	31	-80	15·0·1	14	47	12·0·8	0	-6
10·3·0	14	-30	16·6·0	0	-10	404	20	43	10·0·6	3	-18	4·0·10	8	-30
080	24	72	18·2·0	16	37	802	4	-21	008	2	-18	19·0·2	9	-12
10·4·0	26	-62	2·13·0	0	10	703	11	27	108	3	-12	17·0·5	5	25
280	0	1	18·3·0	6	-32	504	0	0	208	2	8	18·0·4	3	-3
670	8	20	10·11·0	6	-9	901	0	-5	12·0·5	4	-14	5·0·10	0	12
860	28	-65	12·10·0	8	34	105	16	-29	308	5	-5	16·0·6	6	-17
12·0·0	16	-45	8·12·0	6	23	205	9	29	15·0·2	3	16	10·0·9	0	-3
480	6	-19	4·13·0	0	0	604	4	13	807	18	-30	6·0·10	8	-17
12·1·0	16	-41	16·7·0	0	-5	902	21	64	408	0	7	19·0·3	0	-5
10·5·0	0	10	18·4·0	14	-40	803	16	44	11·0·6	0	-10	13·0·8	7	18
12·2·0	20	59	14·9·0	6	-15	305	25	47	14·0·4	7	-13	20·0·1	5	-10
12·3·0	4	-14	18·5·0	0	0	10·0·1	9	9	508	14	50	11·0·9	5	-14
870	6	28	6·13·0	8	-24	405	11	-34	907	0	6	20·0·2	1	-9
680	2	8	16·8·0	0	-14	704	0	-2	15·0·3	1	15	17·0·6	5	-7
290	14	52	10·12·0	4	-15	903	0	-3	13·0·5	6	-20	19·0·4	0	5
10·6·0	20	47	12·11·0	0	8	505	0	15	16·0·1	5	-10	8·0·10	7	22
12·4·0	14	-42	0·14·0	12	-54	10·0·2	0	-1	608	4	-14	14·0·8	0	-2
490	0	-15	2·14·0	0	5	804	10	-13	16·0·2	0	5	16·0·7	3	-11
880	8	47	14·10·0	10	-52	11·0·1	6	-15	12·0·6	0	8	20·0·3	6	-12
12·5·0	20	-70	20·0·0	0	2	605	9	-33	10·0·7	5	-35	12·0·9	0	-4
14·0·0	16	36	18·6·0	10	25	006	3	-15	708	2	9	1·0·11	2	3
14·1·0	4	-24	20·1·0	8	-16	106	6	35	15·0·4	1	-6	19·0·5	2	8
690	12	-49	8·13·0	0	-8	10·0·3	12	40	14·0·5	0	-6	15·0·8	0	-4
10·7·0	0	-12	4·14·0	10	28	206	1	13	16·0·3	13	34	21·0·2	3	-9
0·10·0	44	-130	20·2·0	4	13	11·0·2	6	-18	109	5	8	3·0·11	3	-7

^a Exclusive of reflections incompatible with the symmetry of the space group.

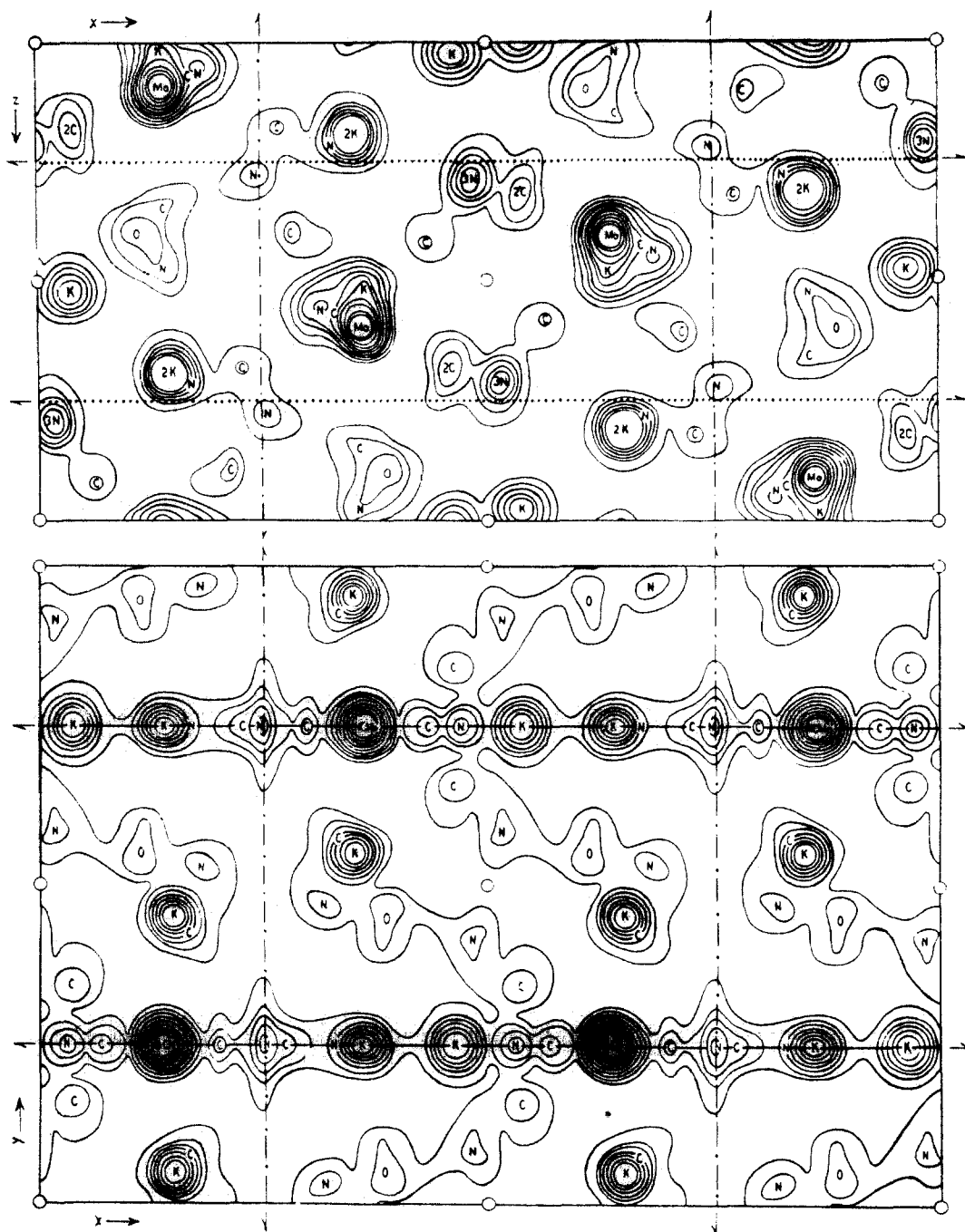


Fig. 1.—Fourier projections of relative electron density on (010) and (001).

The complete structure of potassium molybdo-cyanide dihydrate (Fig. 2) was gotten as a direct interpretation of the final Fourier projections (Fig. 1) of relative electron density on (001) and (010), without the use of any preconceived notions as to the geometric form of the complex. To obtain the projections in the final form of Fig. 1 it was necessary to recalculate each set of data sev-

eral times, taking advantage in each calculation of the more nearly complete phase data resulting from the previous approximation.

The peaks on the contour maps of Fig. 1 are marked with the symbols of the atoms whose projections they represent. The atomic positions given by the Fourier analyses are shown still more clearly and completely in Fig. 2, in which diagram-

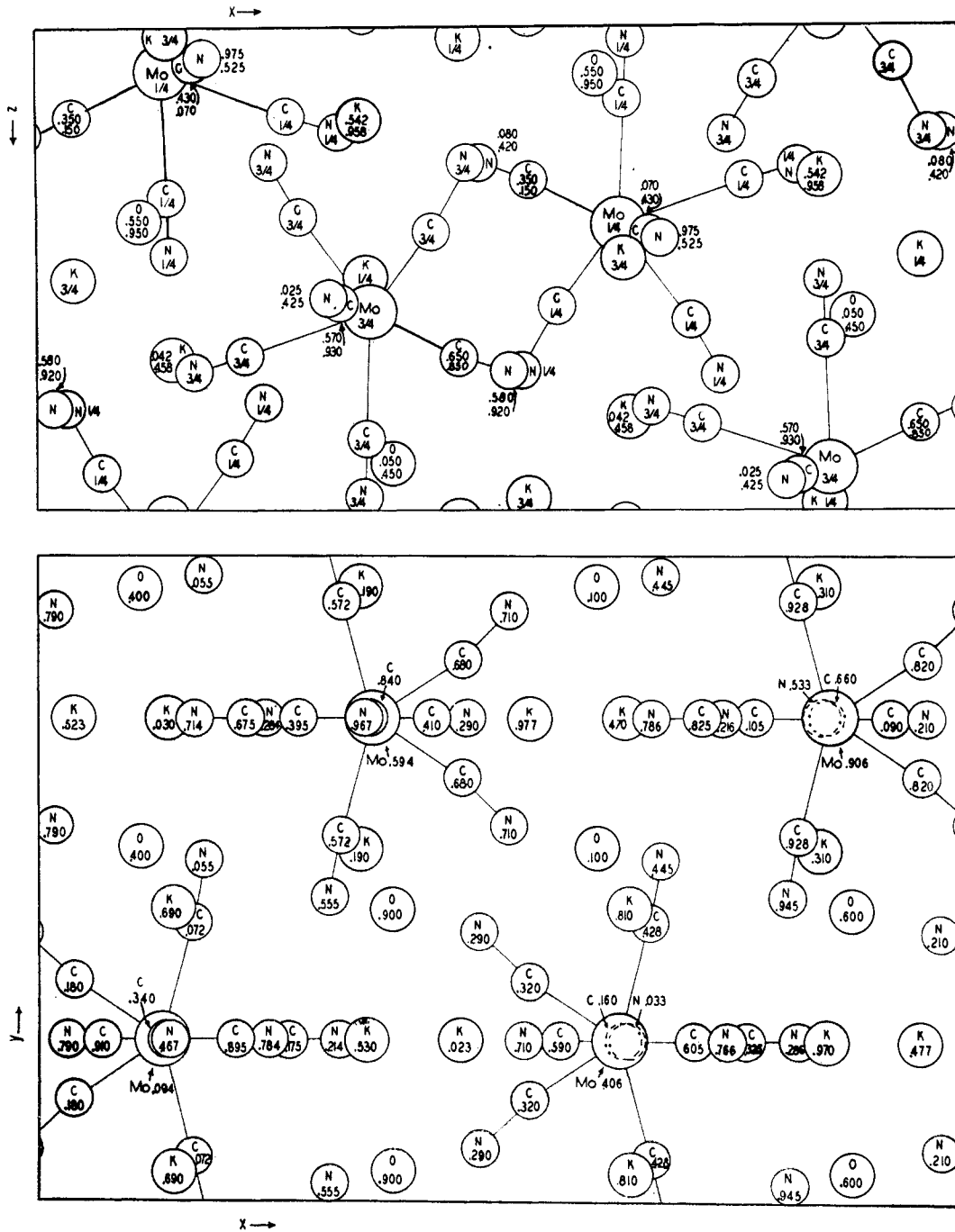


Fig. 2.—Diagrammatic projections of the unit of structure on (010) and (001). The distance of each atom above the plane of projection is indicated.

matic projections of the unit of structure on (010) and (001) are reproduced. Parameter data for all atoms (except hydrogen) as derived from these projections are listed in Table III. The positions of molybdenum and potassium given by the Fourier projections are appreciably different from the approximate values derived from the Patterson data.

A brief critical discussion of the Fourier plots and of the data used in their calculation is appropriate. For those peaks which are completely resolved on the projections the contour lines are nearly circular for the most part, the principal exceptions being oxygen and one type of nitrogen (N_1) on the (001) map. The especial

TABLE III

PARAMETER DATA FOR POTASSIUM MOLYBDOCYANIDE DIHYDRATE

Atom	Atomic coordinates		
	x	y	z
Mo	0.135	$\frac{1}{4}$	0.094
K _I	.147	0.042	.690
K _{II}	.363	$\frac{1}{4}$.530
K _{III}	— .037	$\frac{1}{4}$.477
C _I	.036	0.150	.180
C _{II}	.168	0.070	.072
C _{III}	.059	$\frac{1}{4}$	— .090
C _{IV}	.214	$\frac{1}{4}$	— .105
C _V	.264	$\frac{1}{4}$.175
C _{VI}	.140	$\frac{1}{4}$.340
N _I	— .009	0.080	.210
N _{II}	.181	—0.025	.055
N _{III}	.015	$\frac{1}{4}$	— .210
N _{IV}	.256	$\frac{1}{4}$	— .216
N _V	.325	$\frac{1}{4}$.214
N _{VI}	.140	$\frac{1}{4}$.467
O	.110	—0.050	.400

prominence of the molybdenum peaks is not fully indicated in Fig. 1, since it was not practicable to maintain the density interval characteristic of the rest of the plot in drawing in the contour lines of high density on these peaks.

The maximum relative electron density observed for carbon or nitrogen on the (001) projection is appreciably greater for an atom situated in one of the densely populated symmetry planes than for a chemically similar atom in the general position. When similarly situated, however, the densities of peaks due to structurally non-equivalent, but chemically identical, atoms are seen to be nearly equal.

Nitrogen peaks, for the most part, are observed to be larger than those of similarly situated carbon atoms. Otherwise stated, we may conclude from the relative values of the peak densities that carbon rather than nitrogen of the cyanide group is bonded to molybdenum.

There are on each plot several cases of partial superposition of two or more peaks. By considering the two projections simultaneously and taking into account the observed asymmetry of the peaks, there prove to be no difficulties of interpretation, and a reasonable estimate can be gotten for every parameter value.

A comparison of corresponding values of the x -parameters as read from the two plots furnishes a partial test of the internal consistency of the Fourier data. We find virtually identical values for molybdenum and potassium and, at most, slight variations for less prominent atoms. In

general, however, we should expect both projections to furnish more accurate values of the x -parameters than of the variable parameters along the other axes.

A comparison of calculated with observed relative reflection amplitudes for ($hk0$) and ($h0l$) reflections is given in Table II. The observed amplitudes are those used in the calculation of the Fourier projections. The calculated amplitudes contain no temperature factor and are, therefore, just the corresponding structure factors. The agreement is quite satisfactory on the whole, but seems to be slightly better for ($hk0$) than for ($h0l$) reflections.

Considering that the effects of thermal agitation are included in the experimental amplitudes, their values seem to be *relatively* somewhat large for the larger values of the scattering angle. Correction of these amplitudes for absorption in the crystal would result in some improvement in this respect, since for the specimens used the relative correction factor varies from 1.0 for the amplitude of smallest $\sin \theta$ to about 0.9 for that of largest $\sin \theta$. The experimental amplitudes do fall off so rapidly with increasing angle of scattering that it is probable that slightly large values for them at large $\sin \theta$ are of less significance in limiting the precision of the Fourier projections than are the errors in estimating intensities of the strong reflections appearing at small $\sin \theta$.

On the average, the amplitude data seem to be satisfactory. Each Fourier series, moreover, contains an unusually large number of terms. The satisfactory character of the results is to be understood in terms of these factors.

We have made also an approximate Fourier projection of relative electron density on (100), using the ($0kl$) amplitudes for which the phases could be assigned readily on the basis of the parameter values resulting from the first Fourier projections on (010) and (001). This incomplete contour map proved to be quite useful during the early stages of refining the (010) and (001) projections. Since the irregular shape and comparatively large size of the specimen used made the absorption corrections on the ($0kl$) data subject to considerable uncertainty, and since, moreover, but few of the minor peaks in which we are mainly interested at this stage are completely resolved on the (100) projection, we have not attempted to put these Fourier data into final

form. While not giving accurate values for the parameters of carbon, nitrogen, and oxygen, the (100) projection constitutes a satisfactory check upon our general conclusions about the structure.

Diagrammatic projections of the structure on (010) and (001) are shown in Fig. 2 and a drawing of the complex $\text{Mo}(\text{CN})_8$ group is shown in Fig. 3. Table IV contains interatomic distances as calculated from the parameter data of Table II.

TABLE IV
INTERATOMIC DISTANCES IN POTASSIUM MOLYBDOCYANIDE DIHYDRATE

Atom pair	Separation, Å.	Atom pair	Separation, Å.
Inside the anion			
$\text{Mo}-\text{C}_I(2)$	2.14	$\text{C}_I-\text{N}_I(2)$	1.13
$\text{Mo}-\text{C}_{II}(2)$	2.17	$\text{C}_{II}-\text{N}_{II}(2)$	1.14
$\text{Mo}-\text{C}_{III}$	2.04	$\text{C}_{III}-\text{N}_{III}$	1.27
$\text{Mo}-\text{C}_{IV}$	2.16	$\text{C}_{IV}-\text{N}_{IV}$	1.18
$\text{Mo}-\text{C}_V$	2.24	C_V-N_V	1.07
$\text{Mo}-\text{C}_{VI}$	2.14	$\text{C}_{VI}-\text{N}_{VI}$	1.11
C_I-C_I	2.34	N_I-N_I	3.98
$\text{C}_I-\text{C}_{II}(2)$	2.55	$\text{N}_I-\text{N}_{II}(2)$	3.64
$\text{C}_I-\text{C}_{III}(2)$	2.56	$\text{N}_I-\text{N}_{III}(2)$	4.17
$\text{C}_I-\text{C}_{VI}(2)$	2.51	$\text{N}_I-\text{N}_{VI}(2)$	3.88
$\text{C}_{II}-\text{C}_{III}(2)$	3.10	$\text{N}_{II}-\text{N}_{III}(2)$	4.68
$\text{C}_{II}-\text{C}_{IV}(2)$	2.74	$\text{N}_{II}-\text{N}_{IV}(2)$	4.06
$\text{C}_{II}-\text{C}_V(2)$	2.79	$\text{N}_{II}-\text{N}_V(2)$	4.24
$\text{C}_{II}-\text{C}_{VI}(2)$	3.18	$\text{N}_{II}-\text{N}_{VI}(2)$	4.82
$\text{C}_{III}-\text{C}_{IV}$	2.57	$\text{N}_{III}-\text{N}_{IV}$	3.99
$\text{C}_{IV}-\text{C}_V$	2.56	$\text{N}_{IV}-\text{N}_V$	3.91
C_V-C_{VI}	2.50	N_V-N_{VI}	3.78
Outside the anion			
K_I-N_I	2.83	$\text{K}_{II}-\text{N}_I(2)$	3.58
$(\text{K}_I-\text{N}_{II})_1$	3.33	$\text{K}_{II}-\text{N}_{II}(2)$	2.74
$(\text{K}_I-\text{N}_{II})_2$	3.06	$\text{K}_{II}-\text{N}_{III}$	2.96
$\text{K}_I-\text{N}_{III}$	3.36	$\text{K}_{II}-\text{N}_{IV}$	2.83
K_I-N_{IV}	3.14	$\text{K}_{II}-\text{N}_V$	2.82
K_I-N_V	3.43	$\text{K}_{III}-\text{N}_I(2)$	3.09
K_I-N_{VI}	3.12	$\text{K}_{III}-\text{N}_{III}$	2.85
K_I-O	2.82	$\text{K}_{III}-\text{N}_V$	2.82
$\text{K}_I-\text{C}_{III}$	3.42	$\text{K}_{III}-\text{N}_{VI}$	2.90
K_I-C_{IV}	3.21	$\text{K}_{III}-\text{O}$	2.83
$\text{O}-\text{N}_I$	2.99	$\text{K}_{III}-\text{C}_I(2)$	3.08
$\text{O}-\text{N}_{II}$	3.30	$\text{O}-\text{N}_V$	3.74
$\text{O}-\text{N}_{IV}$	3.25	$\text{O}-\text{N}_{VI}$	3.54

Molybdenum-carbon separations lie between 2.04 and 2.24 Å., the average being 2.15 Å. The sum of the covalent radii,⁹ using the "trigonal prism" radius for molybdenum, is 2.14 Å. The carbon-nitrogen separations are between 1.07 and 1.27 Å., the average being 1.15 Å., just the "triple bond" value. The average molybdenum-nitrogen separation is 3.29 Å., and the individual $\text{Mo}-\text{C}\equiv\text{N}$ chains are practically linear throughout. The carbon-carbon separations of adjacent pairs of

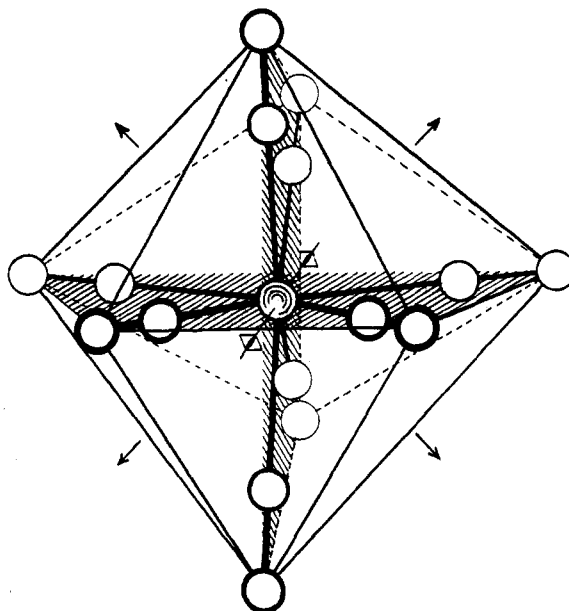


Fig. 3.—The configuration of the idealized molybdenum octocyanide group of symmetry D_2^d .

atoms within the complex vary between 2.34 and 3.18 Å. The separations may be divided empirically into two types: four longer distances, averaging 3.14 Å., and fourteen shorter distances, averaging 2.59 Å. The corresponding nitrogen-nitrogen separations lie between 3.64 and 4.82 Å., the average of the four longer distances being 4.75 Å., and of the fourteen shorter distances 3.98 Å.

The potassium ion in the general position K_I is surrounded by a rather irregular coordination figure consisting of seven nitrogen, one oxygen, and two carbon atoms, at distances ranging from 2.82 Å. (K_I-O) to 3.43 Å. Each potassium ion of the second kind, K_{II} , has five close neighbors at positions approximating to the vertices of a trigonal bipyramid, the average K-N separation being 2.82 Å. There are two additional nitrogen atoms about 3.58 Å. from each potassium of this kind. The coordination group of the third type of potassium ion consists of an oxygen atom at a distance of 2.83 Å., two carbon atoms at 3.08 Å., and five nitrogen atoms at an average distance of 2.95 Å.

There is no evidence for the existence of a definite hydrogen bridge between nitrogen of a cyanide group and oxygen of the water molecule, since the smallest O-N separation is about 2.99 Å.

The closest distance of approach between two nitrogen atoms of adjacent complexes is in no case less than 3.25 Å.

The complex anion, $\text{Mo}(\text{CN})_8^{-4}$, which is shown to exist within crystals of potassium molybdocyanide dihydrate, is required by the space group to possess only a plane of symmetry. A study of the structure shows, however, that the configuration departs but little from the symmetry of the point group $D_2^d - \bar{4}2m$, that is, a four-fold axis of rotary inversion with two mutually perpendicular two-fold axes and two diagonal planes of symmetry. The $\text{Mo}(\text{CN})_8$ polyhedron is a duodecahedron with eight vertices and triangular faces. It can be described as the figure outlined by the vertices of two interpenetrating bisphenoids oriented in the same way as the positive and negative tetrahedra of a cube; as compared with these regular tetrahedra one bisphenoid is considerably elongated, and the other is much flattened along the unique axis.

The symmetry of D_2^d divides the eighteen nitrogen-nitrogen (or carbon-carbon) separations of the complex into four structurally distinct types. Corresponding to the empirical distinction already noted it is convenient to divide these distances into but two classes. Assuming linear $\text{Mo}-\text{C}\equiv\text{N}$ chains with $\text{Mo}-\text{C} = 2.15 \text{ \AA}$., $\text{C}\equiv\text{N} = 1.15 \text{ \AA}$., we calculate the separations listed in Table V for the idealized $\text{Mo}(\text{CN})_8$ group of symmetry D_2^d . We see at once that there are no significant differences between these calculated distances and the corresponding experimentally determined average values.

TABLE V
DIMENSIONAL COMPARISON OF VARIOUS ANION CONFIGURATIONS

Configuration	Separation, \AA	
	C-C	N-N
(Mo-N = 3.30 \AA .)		
Experimental $\text{Mo}(\text{CN})_8$		
Four longer distances (av.)	3.14	4.75
Fourteen shorter distances (av.)	2.59	3.98
Idealized $\text{Mo}(\text{CN})_8$		
Four longer distances	3.09	4.75
Fourteen shorter distances	2.58	3.96
Cube—twelve distances	2.48	3.81
Antiprism—sixteen distances	2.62	4.01

Table V contains also nitrogen-nitrogen and carbon-carbon separations for the cube and the square Archimedean antiprism as calculated for linear $\text{Mo}-\text{C}\equiv\text{N}$ chains with $\text{Mo}-\text{N} = 3.30 \text{ \AA}$.. No quantum mechanical treatment of the directional characteristics of quadrivalent molybdenum forming eight bonds has been reported, but the configuration established for the $\text{Mo}(\text{CN})_8$

group in this paper seems to compare very favorably with either the cube or the antiprism from a stereochemical point of view. The repulsive potential energy arising from the interpenetration of the closed valence shells of adjacent coordinated atoms in the $\text{Mo}(\text{CN})_8$ type of complex is certainly smaller than in the cube, and is not much different from that in the antiprism.

Crystals of potassium tungstocyanide dihydrate, $\text{K}_4\text{W}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$, and potassium molybdocyanide dihydrate are almost surely isomorphous, and the $\text{W}(\text{CN})_8^{-4}$ ion probably has the configuration established for the $\text{Mo}(\text{CN})_8$ group. This configuration is also a reasonable one for the TaF_8^{-3} ion in crystals of sodium fluotantalate, Na_3TaF_8 , and for the osmium octofluoride molecule, for which the osmium-fluorine distance is known from electron diffraction studies.¹⁰

It has been pointed out to us by Professor Linus Pauling that the arrangement of eight oxygen atoms around zirconium in zircon,¹¹ ZrSiO_4 , is similar to that of the eight cyanide radicals around molybdenum in potassium molybdocyanide dihydrate. In zircon each oxygen atom is at once a part of two such ZrO_3 groups and one tetrahedral SiO_4 group. Other crystals having the zircon type of structure include yttrium phosphate, yttrium vanadate, and calcium chromate.

Subtracting the carbon "single bond" radius,⁹ 0.77 \AA ., from the experimental molybdenum-carbon separation, 2.15 \AA ., we get 1.38 \AA . for the radius of quadrivalent molybdenum form-eight bonds.

Summary

It is shown from X-ray data that the orthorhombic unit cell in crystals of potassium molybdocyanide dihydrate contains four molecules with $a_0 = 16.55 \text{ \AA}$., $b_0 = 11.70 \text{ \AA}$., $c_0 = 8.68 \text{ \AA}$., space-group $D_{2h}^{16} - Pnma$. Patterson projections on the three axial planes together with Patterson-Harker summations calculated from visually estimated intensity data were used to obtain approximate coordinates for molybdenum and potassium (Table I). These data were sufficient to determine the phases of the more important (hkl) and ($h0l$) reflection amplitudes (Table II) so that incomplete Fourier projections on (001) and (010) could be calculated. Recalculation and refinement

(10) J. Braune and S. Knoke, *Naturwissenschaften*, **21**, 349 (1933).

(11) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 2d ed., 1931, pp. 286-287, 326.

ment of these projections by familiar methods of successive approximations lead to the complete determination of the structure (Figs. 1 and 2). The parameter data of Table III account satisfactorily for the intensities of X-ray reflections (Table II) and lead to generally reasonable interatomic distances (Table IV).

The structure (Fig. 2) is an aggregate of K^+ ions, $Mo(CN)_8^{-4}$ ions, and water molecules.

The configuration of the $Mo(CN)_8$ group (Fig. 3) seems to be stereochemically very reasonable. The $Mo(CN)_8$ polyhedron is a duodecahedron with eight vertices and triangular faces. Although required by the space group to possess only a plane of symmetry, the complex ion in the crystal approximates to the symmetry of the point group D_2^d-42m .

ITHACA, N. Y.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Phase Equilibrium Relations in the System, Na_2SiO_3 - Li_2SiO_3 - SiO_2 *

BY F. C. KRACEK

The work described in this paper concerns itself with the general equilibrium relations at one atmosphere pressure in the system Na_2SiO_3 - Li_2SiO_3 - SiO_2 , and comprises the experimental determination of the temperatures at which the various crystalline phases are in equilibrium with one another, and with melts of the appropriate composition. The crystallization relations are comparatively simple, being only slightly complicated by the occurrence of solid solutions arising from a partial mutual replacement of sodium and lithium in the silicate compounds. Only one ternary compound is present in the system. This is $NaLiSiO_3$, formed by replacement of Li for Na in Na_2SiO_3 ; it is the Li-rich limit of the solid solution series $(Na_x, Li_{1-x})SiO_3$. The other silicates in the system, Li_2SiO_3 , $Na_2Si_2O_5$, and $Li_2Si_2O_5$, all form solid solutions of only limited extent.

Experimental Methods

The methods of study were in all respects similar to those already made familiar through the publications of this Laboratory on phase equilibrium relations. The liquidus and other significant temperatures were determined by quenching combined with microscopic examination,¹ except in compositions high in lithium metasilicate which crystallize too rapidly for the quenching technique to be effective. In such cases the temperatures were established by heating curve thermal analysis for the liquidus, and

by both heating and cooling curve methods in studying transition phenomena.²

Homogeneous glasses of the various compositions in the system were prepared from purified silica, used in the form of cristobalite derived from powdered quartz heated at 1500° , and from reagent grade lithium carbonate and sodium carbonate. Analyses proved the reagents all to be of high purity.³ The preparations were made up quantitatively from the thoroughly dried reagents, special care being taken to avoid losses, either mechanical, or by volatilization. Losses by volatilization were negligible except in the lithium metasilicate region of the system, where they approached 0.1% of the weight of the preparation. They were almost entirely of lithium, and could be compensated for by small additions of lithium carbonate to the original mixture. The fusions were made in platinum crucibles. To avoid attack on the crucibles by the corrosive melts of the easily fusible carbonate mixtures, it is necessary to exclude oxygen during the initial stages of the heating, until the reaction of the melt with the silica has absorbed most of the free alkali present. This was done by heating the mixtures in covered crucibles over carefully controlled Méker burners (the more convenient initial sintering of the mixtures by heating in electric furnaces always resulted in bad attack on the crucibles), the temperature being kept at the point of incipient fusion until most of the carbon dioxide was driven off. The final heatings were

* Presented before the Division of Physical and Inorganic Chemistry at the 98th meeting of the American Chemical Society, Boston, Mass., September, 1939.

(1) E. S. Shepherd, G. A. Rankin, and F. E. Wright, *Am. J. Sci.*, **28**, 293 (1909).

(2) F. C. Kracek, N. L. Bowen and G. W. Morey, *J. Phys. Chem.*, **41**, 1183 (1937).

(3) See F. C. Kracek, *THIS JOURNAL*, **61**, 2157 (1939), for analyses of reagents and further experimental details.