Unit cell and space group of the carbide Fe$_2$MoC. By D. J. Dyson and K. W. Andrews, *The United*

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The carbide described by Kuo (1953) as M_aC_b is probably identical with an iron–molybdenum carbide referred to by Lashko & Nesterova (1951) and by Habraken (1954). Kuo (1956) gave interplanar spacings but otherwise there are no previously published crystallographic data. It has now been established by the analysis of residues separated by electrolysis from suitably treated steels that the chemical composition is Fe$_2$MoC.

The carbide is obtainable only as a finely divided powder, and the unit-cell and lattice parameters have been determined from interplanar spacings using photographs from quadruple focusing and cylindrical powder cameras. An internal standard was used to correct the spacings and on the basis of these measurements it was established that an orthorhombic unit cell would account for all the spacings. The following lattice parameters were determined:

$$a_0 = 16{\cdot}27_6 \pm 0{\cdot}02, \quad b_0 = 10{\cdot}03_4 \pm 0{\cdot}01, \quad c_0 = 11{\cdot}32_3 \pm 0{\cdot}01 \text{ Å}.$$

The only systematic absences are odd values of l for $00l$ spacings. This indicates the space group $P222_1$ (D_2^2 — No. 17).

The process of indexing was materially assisted by recognition of certain similarities with the powder pattern of cementite. The b cell dimensions of the two structures appear to be related and this cell dimension in the new carbide is almost exactly double that of cementite. An explanation of the relationship between the cementite lattice and α iron has been proposed elsewhere (Andrews, 1963), and it may be that the new carbide is similarly related in a manner which involves close-packed straight or zigzag rows of atoms parallel to the cube diagonal or the carbide b axis respectively. Further work will aim to establish the mutual orientation of the two carbides completely and this should provide information which will assist the determination of atomic positions.

Confirmation of the unit cell of Fe$_2$MoC has been obtained from electron-diffraction patterns. Some of these patterns show systematic absences which might be taken to indicate a body-centred lattice. The effect has also been noted for cementite by Beattie (1961) who used the term 'spurious extinctions' since they do not occur in every orientation. Although two modifications of each structure are not entirely ruled out, it appears more likely that this is an electron-diffraction phenomenon.

A table of interplanar spacings is being submitted for inclusion in the X-ray Powder Data File and further details of the metallurgical aspects will be published elsewhere.

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Comment on three proposed hydrate structures. By Joan R. Clark, *School of Chemistry, University*

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In the course of preparing a review of hydrate structures (Clark, 1963), some anomalies in three proposed structures were discovered. The present note records these features, but no further study of the structures is planned by the present author. The three structures are those for potassium sodium DL-tartrate tetrahydrate, KNaC$_4$H$_4$O$_6$.4H$_2$O (Sadanaga, 1950), strontium formate dihydrate, Sr(HCOO)$_2$.2H$_2$O (Galigné & Falgueirettes, 1961), and lithium acetate dihydrate, LiCH$_3$COO.2H$_2$O (Amirthalingam & Padmanabhan, 1958).

The potassium sodium DL-tartrate tetrahydrate crystals are triclinic $P\bar{1}$, with two formula units per cell. In general the reported structural characteristics are reasonable. The tartrate molecules are joined in pairs

by two hydrogen bonds parallel to the **b** direction, one bond between adjacent carboxyl oxygen atoms (2·52 Å) and one between tartrate hydroxyl groups (2·73 Å).

There are two abnormally short distances involving tartrate oxygen atoms that are not noted by Sadanaga. The first is a separation of 2·11 Å between carboxyl oxygen atoms O(1) and O(2) of one tartrate molecule, and the second is a 1·93 Å distance between a carboxyl oxygen atom O(2) of one molecule and a hydroxyl group OH(6) of a paired molecule.

The sodium cation is described as six-coordinated by three water molecules, one carboxyl oxygen atom plus one hydroxyl group from a tartrate group, and one carboxyl oxygen atom from a second tartrate group. Two additional somewhat distant neighbors were not mentioned by Sadanaga. One of these is oxygen atom O(2)

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of a second tartrate group, and the other is a second $H_2O(7)$ water molecule (Table 1). The sodium coordination is in reasonable agreement with that found for other such compounds.

Table 1. Sodium coordination in potassium sodium DL-tartrate tetrahydrate

		Distance Na–X	
X^*		Sadanaga (1950)	Present study†
$H_2O(9)$		2·27 Å	2·27 Å
$H_2O(10)$		2·30	2·30
$H_2O(7)$		2·32	2·28
O(3) at $x, y, 1+z$		2·44	2·43
O(1) at $1-x, 2-y, 1-z$		2·50	2·60
OH(5)		2·75	2·75
O(2) at $1-x, 2-y, 2-z$		—	2·83
$H_2O(7)$ at $1-x, 1-y, 2-z$		—	3·13

* Na and other atoms at x, y, z (Table 1, Sadanaga, 1950) unless otherwise noted.

† Distances calculated from atomic coordinates and cell dimensions given by Sadanaga (1950).

On the other hand, the coordination about the potassium cation is abnormal. The potassium is said to be six-coordinated. A range of 2·72 to 2·91(± 8) Å is expected for distances from oxygen to sixfold coordinated potassium; for the more usual ninefold coordination, a distance range of 2·65 to 3·21(± 5) Å is found (*International Tables for X-ray Crystallography*, 1962). In the present compound, three water molecules are at distances approximately within these ranges, two at 2·62 Å and one at 2·90 Å. However, the other three oxygen atoms (one water, one hydroxyl and one carboxyl) are all at distances greater than 3·4 Å (given by Sadanaga as 3·48, 3·51 and 3·69 Å). No other close neighbors to potassium were found during the present calculations. This potassium coordination polyhedron cannot be considered satisfactory.

The structure has four crystallographically distinct water molecules, and details of their environments are given in Table 2. $H_2O(8)$ was said by Sadanaga to have a trigonal planar environment, but there is in fact a fourth contact at hydrogen bonding distance to a carboxyl oxygen atom. Another previously unrecorded contact is a 2·59 Å distance between $H_2O(7)$ and carboxyl O(3'). The environments of the three water molecules $H_2O(8)$, $H_2O(9)$ and $H_2O(10)$ appear reasonable, but the environment of $H_2O(7)$ is complicated by an unusually large number of neighbors (Table 2). Further refinement of the structure to clarify all these anomalies would be desirable.

In the note on strontium formate dihydrate (Galigné & Falgueirettes, 1961) neither structure factors, bond distances nor description of the structure are given.

Table 2. Water molecule environment in potassium sodium DL-tartrate tetrahydrate

Water molecule	Neighbor atom†	Distances water–neighbor		Angles neighbor–water–neighbor Present study‡	
		Sadanaga (1950)	Present study‡	Atoms	Angle
$H_2O(7)$	O(4) at $x, y, 1+z$	2·54 Å	2·50 Å	4–7–3'	120°
	O(3')	—	2·59	4–7–Na	109
	Na	2·32	2·28	4–7–Na''	71
	Na'' at $1-x, 1-y, 2-z$	—	3·13	3'–7–Na	109
	*$H_2O(10')$	2·90	2·90	3'–7–Na''	49
	*OH(5)	2·52	2·53	Na–7–Na''	124
	*O(3) at $x, y, 1+z$	—	2·62	4–7–10'	59
	*$H_2O(7'')$ at $1-x, 1-y, 2-z$	—	2·64	3'–7–10'	74
$H_2O(8)$	O(1) at $1-x, 2-y, 1-z$	—	2·62	1–8–6'	66
	OH(6')	2·95	2·95	1–8–K	90
	K at $x, 1+y, z$	2·62	2·62	1–8–K'	121
	K'	2·62	2·62	6'–8–K	146
				6'–8–K'	121
				K–8–K'	91
$H_2O(9)$	OH(5')	2·58	2·59	5'–9–4'	114
	O(4')	2·92	2·92	5'–9–Na	150
	Na	2·27	2·27	5'–9–K'	84
	K'	2·90	2·90	4'–9–Na	78
	*OH(5)	—	2·75	4'–9–K'	122
	*$H_2O(10)$ at $x, y, 1+z$	—	2·94	Na–9–K'	114
$H_2O(10)$	O(1)	2·56	2·56	1–10–7'	140
	*$H_2O(7')$	2·90	2·90	1–10–Na	147
	Na at $x, y, z-1$	2·30	2·30	1–10–K	74
	K at $x, 1+y, z$	3·48	3·47	7'–10–Na	73
	*$H_2O(9)$ at $x, y, z-1$	—	2·94	7'–10–K	97
	*O(1''') at $1-x, 2-y, \bar{z}$	—	3·18	Na–10–K	106

* This atom and the water molecule are members of the same cation polyhedron.

† All unprimed atoms are at x, y, z (Table 1, Sadanaga, 1950) unless otherwise noted; single primed atoms are at $1-x, 1-y, 1-z$.

‡ All calculations made from atomic coordinates and cell dimensions given by Sadanaga (1950).

The space group $P2_12_12_1$ and cell dimensions are said to be the same as those determined by Nitta (1928); no mention is made of conversion from kX units to Å. Locations of the atoms are shown on two projections, one along a and one along c, and atomic coordinates are listed as derived from the projections without transformation to a common origin.

Residual factors for the two projections are said to be 0·15 (0kl) and 0·19 (hk0). A routine check reveals that the y coordinate of carbon atom C(1) given in the text is not the one shown on the projections. Conversion of the atomic coordinates x, y, z given in the text to coordinates x', y', z', referred to an origin halfway between three pairs of non-intersecting screw axes (International Tables for X-ray Crystallography, 1952) can be made by the transformation $x' = x + \frac{1}{4}$, $y' = y - \frac{1}{4}$, $z' = z$. Calculation of bond distances with the transformed coordinates x', y', z' and the cell dimensions of Nitta (1928) yields the following results.

First, the distances involving carbon atom C(1) are impossible: C(1)–O(1) = 0·91 Å, C(1)–O(1') = 2·44 Å; Sr–C(1) (two contacts) 1·67 and 2·82 Å. Clearly the coordinates given in the text for C(1) are wrong. Second, in the second formate group C(2)–O(2) = 1·53 Å, C(2)–O(2') = 1·71 Å. For comparison, in cupric formate tetrahydrate (Kiriyama, Ibamoto & Matsuo, 1954) carbon-oxygen distances in the formate group were found to be 1·26 and 1·25 Å. Third, the oxygen neighbors of strontium do not produce a satisfactory coordination polyhedron. A Sr–O distance range of 2·60 to 2·64(±6) Å is given in International Tables for X-ray Crystallography (1962). In the present compound, the following Sr–O distances occur: O(1'), 2·40 and 2·92 Å; O(1), 2·44 and 2·46 Å; O(2), 3·13 and 3·38 Å; O(3) (water) 2·53 Å. Finally, there is a water–water O(3)–O(4) contact of 2·27 Å, and a water–oxygen O(4)–O(2') contact of 2·03 Å. These two atoms are the only neighbors at less than 3·0 Å to water O(4), and such an environment must be considered unlikely for a water molecule in this compound. In addition, no water–oxygen hydrogen-bond distances less than about 2·5 Å have been reported (Pimentel & McClellan, 1960).

Galigné & Falgueirettes (1961) indicate that the structure is approximate only, but these various features are not acceptable even for a trial structure. Quite apart from a possible error in recording the coordinates of carbon atom C(1), the 'structure' cannot be considered determined as reported.

For the lithium acetate dihydrate structure Amirthalingam & Padmanabhan (1958) give no structure factors, but packing considerations of the acetate ions are said to fix the space group as $Cmm2$. Bond-length calculations using the atomic coordinates and cell dimensions given cast the following doubts on the reported structure.

First, the lithium coordination, described as sixfold, includes two Li–H$_2$O contacts, confirmed as 2·57 Å,

two Li–O(2) contacts, listed as 2·27 Å and found to be 2·31 Å, and two Li–O(1) contacts of 3·01 Å for which no values were given initially. There are no other close Li–O contacts. A range of 2·00 to 2·41(±4) Å for Li–O distances around six-coordinated lithium is given in International Tables for X-ray Crystallography (1962). Four of the six distances in lithium acetate dihydrate are outside this range. In fact, adjacent lithium polyhedra share an O(2)–O(2') edge, and the neighbor lithium cations are only 2·22 Å apart, closer to one another than any of the oxygen atoms are to either. Certainly the lithium coordination cannot be considered plausible. Second, two hydrogen bonds of 3·08 and 3·14 Å to water are noted by the authors. The 3·14 Å H$_2$O–O(2) distance is verified, but the 3·08 Å distance does not occur. Instead a 2·84 Å distance between H$_2$O and its equivalent at $\frac{1}{2} - x, \frac{1}{2} - y, z$ is found. Unfortunately, a 2·14 Å distance between H$_2$O and its equivalent at $\bar{x}, y, z$ also occurs. Evidently this close contact was not taken into account in assigning atomic positions. For these reasons the structure needs further examination and should not be accepted as satisfactory at present.

The bond angles and bond distances were calculated by SILLIAC using programs V–19 and V–21 written by Dr F. M. Lovell, University of Sydney. The output for the bond distances lists all possible ones less than a pre-selected value (taken as 4·00 Å for the strontium compound and as 3·50 Å for the other two compounds). The program made possible the discovery of the anomalies described in the present note.

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