Unit Cell and Space Group of Cesium Oxalate Monohydrate, $Cs_2C_2O_4 \cdot H_2O$

BERIT F. PEDERSEN and BJØRN PEDERSEN

Central Institute for Industrial Research, Oslo 3, Norway

As a part of an investigation of the hydrates of the alkalimetal oxalates with X-ray diffraction and proton magnetic resonance methods, we have determined the unit cell dimensions and space group of cesium oxalate monohydrate, $Cs_2C_2O_4 \cdot H_2O$. When this study was started we hoped that this compound was isomorphous with the corresponding potassium [1] and rubidium [2] salts, but this turned out not to be the case.

$Cs_2C_2O_4 \cdot H_2O$ crystallizes from a water solution at room temperature, either in the form of thin needles with the *a*-axis parallel to the needle axis, or as small diamond shaped plates with the *b*-axis perpendicular to the plate. Very often twinning occurs, which is most easily detected in higher level Weissenberg photographs. The crystals are relatively unstable, and had to be kept in sealed capillary tubes during the exposure. The larger crystals needed in the proton magnetic resonance study were easily grown by slow evaporation of a water solution at room temperature.

Cesium oxalate monohydrate crystallizes with monoclinic symmetry. From oscillation and Weissenberg diagrams taken rotating the crystal about the *a*- and *b*-axis, the unit cell dimensions are determined to:

$a = 6.17$ Å, $b = 11.04$ Å, $c = 6.19$ Å, $\beta = 114.0°$

With two formula units in the unit cell a density of 3.20 g/cm³ is derived, in agreement with the density determined by the floatation method: 3.23 g/cm³. Systematic absences are: in $0k0$ for $k = 2n + 1$. Only a few weak, low-order reflections are observed in $h0l$ when $l = 2n + 1$. From the systematic absences two space groups are possible: $P2_1$ and $P2_1/m$, but the quasi-symmetry indicates some relation to $P2_1/c$. We will now show how we can eliminate one of these possibilities from the information deduced from the proton magnetic resonance study.

The proton magnetic resonance spectra of a single crystal held in different orientations relative to an external magnetic field was recorded using a Varian As. DP-60 NMR spectrometer operating at 60 Mc/sec. The spectra contain in general four fine structure components, which are in several orientations clearly resolved. Each set of water molecules in the crystal with parallel intramolecular proton-proton line segments will give rise to *two* line components.[3] Hence, the obtained spectra with *four* components tell that we have two sets of water molecules in the crystal, where members of different sets are oriented differently in the crystal; a closer analysis of the data indicates that the two directions are approximately orthogonal. If the crystal symmetry is $P2_1/m$ *all* the molecules will have parallel proton-proton line segments for symmetry reasons. (There are only two water molecules in the unit cell. This requires in $P2_1/m$ that the water oxygens are on the mirror planes, and the hydrogen atoms are either on the plane or symmetry related on each side of the mirror plane). As the proton magnetic resonance spectra show that not all proton-proton line segments are parallel, the true space group for $Cs_2C_2O_4 \cdot H_2O$ is $P2_1$. In $P2_1$ the two water molecules in each unit cell are related to each other by a two-fold screw axis. Hence, with such a symmetry the water molecules will be divided in two sets, where members of different sets can make an arbitrary angle to each other in agreement with the proton magnetic resonance spectra.

The detected quasi-symmetry from the X-ray diffraction data, on the other hand, tells that very likely the cesium ions, and possibly also the oxalate ions, are arranged in the structure with the symmetry $P2_1/c$. It is not possible to place two water molecules in a unit cell with symmetry $P2_1/c$ without introducing some kind of disorder as none of the symmetry elements of the isolated water molecule, $2mm$ are present in $P2_1/c$. The four weak reflections observed in $h0l$ with $l = 2n + 1$ must therefore be due to the water molecules.

A complete structure determination of $Cs_2C_2O_4 \cdot H_2O$ will not be undertaken, as the heavy cesium ions are expected to dominate the intensity distribution,

making it difficult to locate the lighter atoms with any precision.

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The Crystal Structures of Mo_2As_3 and W_2As_3

PER JENSEN, ARNE KJEKSHUS and TERJE SKANSEN

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Oslo 3, Norway

In the course of the continued studies of the transition metal chalcogenides and pnictides at this Institute an investigation of molybdenum and tungsten arsenides and antimonides has been carried out. The present communication gives a brief description of the crystal structures of the previously unknown phases Mo_2As_3 and W_2As_3. (The phases Mo_4As_5 and W_4As_5 reported by Boller and Nowotny [1] are undoubtedly identical with the phases Mo_2As_3 and W_2As_3, respectively. However, these authors did neither succeed in assigning the correct compositions nor the true crystallographic unit cells to their samples.) The results of the phase analytical studies of these systems and the structural and magnetic properties of the phases Mo_5As_4, $MoAs_2$, Mo_3Sb_7, and WAs_2 are discussed elsewhere.[2-4]

No extended ranges of homogeneity of these phases exist, and the compositions were unequivocally determined to be Mo_2As_3 and W_2As_3. The unit cells are monoclinic with the following dimensions (on the basis of Guinier photograph data taken with strictly monochromatized Cu$K\alpha_1$-radiation):

Mo_2As_3:
$a = 16.061 \pm 0.002$ Å,
$b = 3.2349 \pm 0.0004$ Å,
$c = 9.643 \pm 0.001$ Å,
$\beta = 136.74 \pm 0.02°$

W_2As_3:
$a = 15.966 \pm 0.001$ Å,
$b = 3.2791 \pm 0.0004$ Å,
$c = 9.599 \pm 0.001$ Å,
$\beta = 136.648 \pm 0.006°$

On the basis of the observed densities, 8.07 g cm^{-3} (Mo_2As_3) and 11.32 g cm^{-3} (W_2As_3), the unit cells contain 4 T_2As_3-groups ($Z_c = 4.00$ for Mo_2As_3 and $Z_c = 3.97$ for W_2As_3).

Needle-shaped single crystals (with the diad axis along the needle axis) of Mo_2As_3 and W_2As_3 were obtained by means of transport reactions using traces of bromine as a transport agent. The crystal structures were solved on the basis of integrated Weissenberg photographs of the *h*0*l* and *hll* reflections using direct methods for sign determination. (Attempts to derive trial structures from examination of Patterson syntheses and difference Patterson synthesis were unsuccessful.) The atomic arrangement in the crystal structures of Mo_2As_3 and W_2As_3 in terms of the space groups $C2/m$ is as follows (all atoms in position $4(i)$):

Mo_2As_3:
Mo_I with $x = 0.248$, $z = 0.125$
Mo_{II} with $x = 0.351$, $z = 0.567$
As_I with $x = 0.127$, $z = 0.207$
As_{II} with $x = 0.415$, $z = 0.144$
As_{III} with $x = 0.104$, $z = 0.580$

W_2As_3:
W_I with $x = 0.248$, $z = 0.124$
W_{II} with $x = 0.348$, $z = 0.567$
As_I with $x = 0.125$, $z = 0.204$
As_{II} with $x = 0.417$, $z = 0.147$
As_{III} with $x = 0.105$, $z = 0.579$

Details of the structures and discussion of the chemical bonding will be published in a forthcoming paper.

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