

so dass dieser Mechanismus auch für das Hyoscyamin angenommen werden kann. Daneben besitzt der Rezeptor noch die Fähigkeit, nebervalente Bindungen einzugehen. So wurde von Prince (1967) die inhibitorische Wirkung einer Reihe von Isomeren des 1-Methylhydroxychinolins untersucht und gefunden, dass ein steiler Anstieg der inhibitorischen Wirkung beim 1-Methyl-7-hydroxychinolin erfolgt. Parallel damit geht eine Abnahme der Dissoziationskonstanten dieser Verbindung gegenüber dem 1-Methylchinolin mit dem Rezeptor. Der (N → OH)-Abstand beim 1-Methyl-7-hydroxychinolin beträgt etwa 5 Å, das entspricht beim 1-Hyoscyamin dem Abstand der Estergruppe vom Stickstoff. Bereits Pfeiffer (1948) hat aufgrund von Molekülmodellen vermutet, dass Nebervalenzbindungen im Abstand von 5 und 7 Å vom Stickstoff bei der Bindung von ACh, Pilocarpin und Atropin wirksam sind.

Cushny (1920) hat aufgrund von pharmakologischen Untersuchungen mit einer Reihe von Parasympathikolytika der Atropingruppe und an abgewandelten Verbindungen gezeigt, dass die hydrophile und die lipophile Gruppe am C(10)-Atom für die Wirkung erforderlich sind. Dabei kann der Phenylrest durch Pyridin und die CH₂OH-Gruppe wie im Homatropin durch -OH ersetzt werden.

Die Kenntnis der Kristallstruktur des 1-Hyoscyaminhydrobromids gibt einen weiteren Einblick in die Bindungsverhältnisse zwischen dieser Substanz und dem Rezeptorprotein. Die Beziehung zwischen Rezeptor und Inhibitormolekül sieht demnach etwa folgendermaßen aus: Das Molekül wird zunächst mit seinem

tertiären Stickstoff an die anionische Gruppe des Rezeptors gebunden. Durch Nebervalenzbindungen, an denen die Sauerstoffatome (Abstand zum N 3,7–5,3 Å) der Estergruppe beteiligt sind, erfolgt eine Bindung, die der des ACh an den Rezeptor analog ist. Auf derselben Seite des Moleküls im Abstand von 7–8 Å vom Stickstoff besteht eine weitere Nebervalenzbindung zwischen Rezeptor und Hydroxylgruppe des Hyoscyamins. In einem Abstand von etwa 5 Å von dieser Wasserstoffbrücke und ihr gegenüber tritt der Phenylrest des Hyoscyamins in Beziehung zu einem lipophilen Bereich des Rezeptorproteins. Möglicherweise handelt es sich dabei um ein Phenylalanin. Es ist anzunehmen, dass diese Bindungsverhältnisse beim atropin-sensiblen Rezeptor sowie entsprechende Verhältnisse an den anderen Rezeptoren dafür verantwortlich sind, dass die ACh-Antagonisten rezeptorspezifisch sind.

Literatur

- BARTELS, E. (1962). *Biochim. Biophys. Acta*, **63**, 365.
 CUSHNY, A. R. (1920). *J. Pharmacol.* **15**, 105.
 FODOR, G. & CSEPREGHY, G. (1961). *J. Chem. Soc.* p. 3222.
 HAASE, J. & KUSSÄTHER, E. (1972). *Z. Naturforsch.* **27B**, 212.
 NACHMANSOHN, D. (1971). In *Handbook of Sensory Physiology*. Vol. 1. Berlin, Heidelberg, New York: Springer-Verlag.
 PAULING, P. & PETCHER, T. I. (1969). *J. Chem. Soc.* p. 1001.
 PFEIFFER, C. C. (1948). *Science*, **107**, 94.
 PRINCE, A. K. (1967). *Proc. Natl. Acad. Sci. U. S.* **57**, 1117.
 VISSER, J. W., MANASSEN, J., & DE VRIES, J. L. (1954). *Acta Cryst.* **7**, 288.

Acta Cryst. (1972). **B28**, 2899

Accurate Cell Dimensions for ABO₄ Molybdates and Tungstates

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Accurate cell dimensions for ABO₄ molybdates and tungstates with either the wolframite or scheelite structure are presented. The cell volume of a molybdate is always found to be smaller than that of the corresponding tungstate. Other systematic differences between these molybdates and tungstates are discussed.

Introduction

The wolframite and scheelite structures are common structure types for ABO₄ compounds. The wolframite structure may be described as made up of hexagonally close-packed oxygens with certain octahedral sites filled by A and B cations in an ordered way. The oxy-

gens are not close packed in the scheelite structure and the coordination number of the A cation is eight while the B cation is in approximate tetrahedral coordination to oxygen. The scheelite structure may be regarded as a cubic close-packed array of A²⁺ and BO₄²⁻ units which are ordered. The oxygens are three-coordinated to cations in both the scheelite and the wolframite structure. However, all are coordinated to two A cations and one B cation in the scheelite structure, whereas in the wolframite structure half are co-

* Contribution No. 1881.

ordinated to two B cations and half are coordinated to two A cations.

All known AWO₄ tungstates normally have either the wolframite or scheelite structure with the exception of HgWO₄ (Sleight & Lics, 1971) and both forms of SnWO₄ (Jeitschko & Sleight, 1971). Many AMoO₄ molybdates normally have the scheelite structure, but pressure is required to form molybdates with the wolframite structure (Young & Schwartz, 1963; Sleight & Chamberland, 1968). Nevertheless, all known AMoO₄ molybdates can have either the wolframite or scheelite structure with the exception of HgMoO₄ (Sleight & Lics, 1971). The ideal wolframite structure is monoclinic, but FeMoO₄-II (Sleight, Chamberland & Weither, 1968) and CuWO₄ (Gebert & Kihlberg, 1967) are triclinic.

Experimental

The compounds were prepared by heating together appropriate quantities of oxides or carbonates. Sealed systems were necessary to prevent oxidation of certain transition metal cations, e.g. Fe²⁺, and high pressure was used to prepare molybdates with the wolframite structure (Sleight & Chamberland, 1968). The reactants were of the highest purity commercially available, and all had listed purities of better than 99.99%.

X-ray powder patterns were recorded at 25°C using a Hägg-Guinier camera with Cu K α radiation and an internal standard of high purity KCl ($a=6.2931$ Å at 25°C). The cell dimensions were refined by the least-

squares method using only uniquely indexed lines. The standard deviations calculated were always several times lower than the errors given in Table 1. The errors

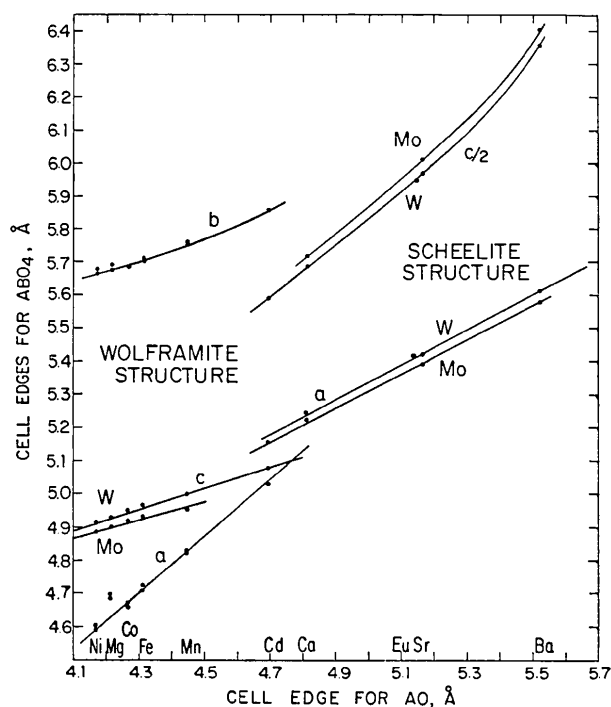


Fig. 1. Cell dimensions of ABO₄ wolframites and scheelites vs. cell dimensions of AO rock salt compounds.

Table 1. Cell dimensions of ABO₄ molybdates and tungstates with the scheelite or wolframite structure

Compound	V^* , Å ³	a , Å	b , Å	c , Å	β or c/a †
MgWO ₄	262.2	4.687 (4.69)‡	5.675 (5.68)	4.928 (4.92)	90.71° (89.67)
MgMoO ₄	261.7	4.694	5.689	4.900	90.35
MnWO ₄	280.0	4.829 (4.829)	5.758 (5.759)	4.996 (4.998)	91.15 (91.16)
MnNoO ₄	275.3	4.822	5.753	4.963	90.85
FeWO ₄	267.4	4.724	5.705	4.961	90.0
FeMoO ₄	264.2	4.708	5.701	4.944	90.27§
CoWO ₄	262.3	4.667 (4.669)	5.681 (5.683)	4.947 (4.948)	90.0 (90.0)
CoMoO ₄	260.2	4.657	5.682	4.917	90.45
NiWO ₄	255.9	4.599 (4.600)	5.665 (5.665)	4.910 (4.912)	90.0 (90.0)
NiMoO ₄	254.6	4.587	5.679	4.887	90.44
ZnWO ₄	264.2	4.690	5.718	4.926	90.64
ZnMoO ₄	263.2	4.695	5.729	4.894	90.32
CdWO ₄	298.7	5.027 (5.029)	5.858 (5.859)	5.073 (5.074)	91.49 (91.47)
CdMoO ₄	297.3	5.1539 (5.1554)		11.192 (11.194)	2.172
CaWO ₄	312.6	5.2419 (5.242)		11.376 (11.372)	2.170
CaMoO ₄	312.2	5.2256 (5.226)		11.434 (11.43)	2.188
SrWO ₄	350.0	5.4136 (5.4168)		11.942 (11.951)	2.206
SrMoO ₄	349.6	5.3936 (5.3944)		12.019 (12.020)	2.228
BaWO ₄	401.0	5.6148 (5.6134)		12.721 (12.720)	2.266
BaMoO ₄	399.1	5.5804 (5.5802)		12.818 (12.821)	2.297
PbWO ₄	359.4	5.4622 (5.4616)		12.048 (12.046)	2.206
PbMoO ₄	357.7	5.4355 (5.435)		12.108 (12.11)	2.228
EuWO ₄	350.2	5.4151		11.942	2.205

* Volume is doubled for compounds with the wolframite structure to allow direct comparison with scheelite volumes.

† β for the wolframite structure; c/a for the scheelite structure.

‡ Values in parentheses are taken from the *NBS Monograph* (1962).

§ FeMoO₄-II is really triclinic with $\alpha=90.67$ and $\gamma=87.68$; for the conventional cell $a=4.9443$, $b=5.7006$, $c=4.7078$, $\alpha=93.32$, $\beta=90.27$, and $\gamma=89.33$.

given are estimated by comparison of entirely separate experiments, *i.e.* comparison of the refined parameters from two or more preparations of a given compound.

Results

The cell dimensions of the ABO_4 molybdates and tungstates with either the wolframite or scheelite structure are given in Table 1. They are compared with values taken from the *U.S. National Bureau of Standards Monograph* (1962) when such values were given. The agreement for these cases is very good.

The β angle for compounds with the wolframite structure is always close to 90° , and no departure from 90° could be detected for $FeWO_4$, $CoWO_4$, or $NiWO_4$. The departure from 90° must be less than 0.3° for these compounds. However, the wolframite structure is not pseudo-orthorhombic, and thus the β angle cannot be constrained. For $FeWO_4$, Ülkü (1967) has estimated that β is about $90^\circ 5'$, and Keeling (1957) also estimated the β angle in $NiWO_4$ to be $90^\circ 5'$.

Although $Eu^{2+}W^{6+}O_4$ is readily prepared (Shafer, 1965), the existence of stoichiometric $Eu^{2+}Mo^{6+}O_4$ is questionable. McCarthy (1971) has reported $EuMoO_4$ and has given cell dimensions which would fit reasonably well on Figs. 1 and 2. However, all our attempts to prepare $EuMoO_4$ lead to multiphase products. A scheelite-type phase dominates the diffraction patterns of these products, but the line positions varied significantly from preparation to preparation. Also, the

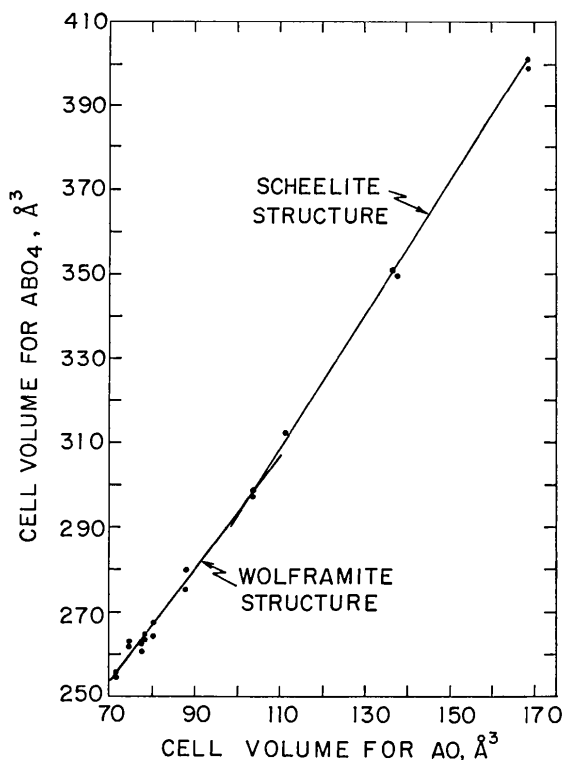


Fig. 2. Cell volumes of ABO_4 wolframites ($\times 2$) and scheelites vs. cell volumes of AO rock salt compounds.

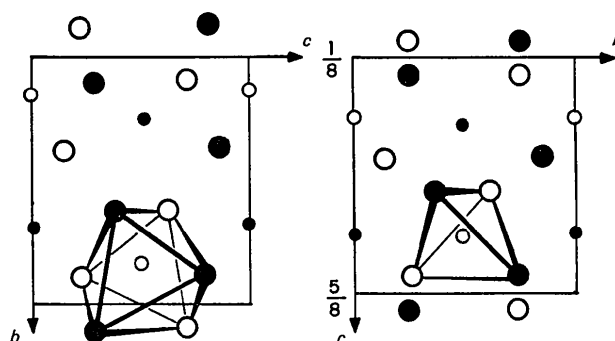


Fig. 3. The wolframite structure (left) is compared to a portion of the scheelite structure (right). Small closed circles are A cations at $\frac{1}{2}$. Small open circles are Mo or W at 0. Large open circles are oxygens at $+\frac{1}{4}$, and the large closed circles are oxygens at $-\frac{1}{4}$.

fact that $EuWO_4$ is orange, whereas $EuMoO_4$ attempts give black products, suggests that oxidation states other than Eu^{2+} and Mo^{6+} (such as Eu^{3+} or Mo^{5+}) are present in these black products. Nonetheless, it is clear that a scheelite-related phase exists in the $Eu/Mo/O$ system. This phase could be represented as $Eu_{1-3x}^{2+}Eu_{2x}^{3+}MoO_4$ since $\alpha-Eu_2Mo_3O_{12}$ ($x=0.33$) is known to have a scheelite-related structure (Brixner, Sleight, & Licit, 1971). However, it is very difficult, if not impossible, to obtain stoichiometric $Eu^{2+}Mo^{6+}O_4$.

Although $CuWO_4$ has a distorted wolframite-type structure, it is not included in Table 1 because it has been suggested that it may be oxygen deficient (Gebert & Kihlberg, 1967) and because there is no corresponding molybdate for comparison. The AMO_4 compounds where A is Pb, Cu, or Zn are not included in Figs. 1 and 2 because the corresponding AO compounds do not have the NaCl structure. The cell edges used for the other AO compounds were taken from Wyckoff (1965).

Discussion

A relationship exists between the scheelite and wolframite structures which has been described by Dem'yanets, Ilyukin, Chichagov & Belov (1967) and by Nicol & Durana (1971). Fig. 3 shows portions of the two structures to illustrate this relationship which justifies the plotting of a_w and c_w with a_s and the plotting of b_w with $c_s/2$ in Fig. 1. A feature not shown in Fig. 3 is that the consecutive wolframite cells are sheared by $a_w/2 + c_w/2$ when they are stacked up along b_w to form the scheelite structure.

Obviously a_w and c_w are destined to cross over in Fig. 1 as the size of the A cation increases. However, this cross-over never occurs because there is a switch to the scheelite structure. The cross-over would occur sooner for molybdates than tungstates which is perhaps related to the fact that $CdWO_4$ has the wolframite structure whereas $CdMoO_4$ has the scheelite structure.

Although c_w is consistently significantly larger in tungstates than in molybdates, there is no such general

trend for a_w and b_w . The chains of edge-shared octahedra run parallel to c_w ; thus the larger c_w in tungstates could be attributed to greater metal-metal repulsive interactions in the tungstates as opposed to the molybdates. This in turn could be due to the slightly more electropositive character of W relative to Mo. Although the MgMoO₄ and MgWO₄ cell dimensions are well behaved on the b_w and c_w plots, they fall well above the line on the a_w plot. This causes their cell volumes also to be larger than expected (Sleight & Chamberland, 1968).

The change from the wolframite to the scheelite structure is accompanied by an abrupt increase in a_w , c_w , or a_s , and an abrupt decrease in b_w or c_s . Such a change seems reasonable from Fig. 3.

The c/a ratio is always significantly larger for molybdate scheelites than for tungstate scheelites. Structure determinations (Zalkin & Templeton, 1964; Kay, Frazer & Almodovar, 1964; Leciejewicz, 1965; Gürmen, Daniels & King, 1971) have shown that the BO₄²⁻ tetrahedral unit is essentially the same in the molybdate and tungstate scheelites. The consistent difference in the c/a ratio is not therefore due to differences in the distances or angles of this unit.

Each cation in the scheelite structure is surrounded by four near-neighbor cations of the same kind and eight near-neighbor cations of the other kind. All these near-neighbor cation-cation distances would be exactly equal for a c/a ratio of two; consequently, electrostatic cation-cation repulsive interactions will tend to favor a c/a ratio of two while packing considerations favor a c/a ratio greater than two. The systematic difference between the c/a ratios of scheelite molybdates and tungstates is thus rationalized by assuming the MoO₄²⁻ group to be more covalent than the WO₄²⁻ group. This electrostatic argument also explains why the c/a ratio increases with the increasing size of the A cation since such an increase will cause a reduction of the cation-cation repulsive interactions.

The volumes of the ABO₄ molybdates are slightly smaller than the volumes of the analogous tungstates regardless of whether the structure is wolframite or scheelite. In the scheelite structure this is true despite the fact that for a given A cation the c axis is always larger for the molybdate. The cell volumes of A₂⁺BO₄ molybdates and tungstates were recently compared by Kools, Koster & Rieck (1970), and they also found that for the same A cation the molybdate volumes are consistently smaller than tungstate volumes. Furthermore, the cell volumes of A₂³⁺B₃O₁₂ molybdates are always smaller than those of corresponding tungstates (Brixner, Sleight & Licis, 1972). This is not always true, however, because the cell volume of HgWO₄ is definitely smaller than that of isostructural HgMoO₄ (Sleight & Licis, 1971), and the cell volumes of rare earth R₂MoO₆ molybdates are consistently larger than the analogous isostructural R₂WO₆ tungstates (Brixner, Sleight & Licis, 1972).

A comparison of the volumes of CdWO₄ (wolframite-

type) and CdMoO₄ (scheelite-type) does not indicate which structure should be favored by high pressure (Fig. 2). This is not surprising since the *average* coordination numbers in the two structures are the same. Nevertheless, the anion packing is nearer to close packing in the wolframite structure than in the scheelite structure. Consequently, CdMoO₄, CdWO₄, CaMoO₄, and CaWO₄ were all treated for two hours at 1000°C under 65 kbar pressure and rapidly quenched. All retained their original structure type. Still, it appears likely that some scheelites do transform to the wolframite structure at high pressures, but they apparently easily revert to the scheelite structure when the pressure is released. Nicol & Durana (1971) have recently studied the Raman spectra of CaMoO₄ and CaWO₄ at high pressure. They find evidence that CaWO₄ transform to the wolframite structure at about 12 kbars, and CaMoO₄ likewise transforms at about 27 kbars. The transformations were, of course, reversible.

The 65 kbar experiments were supervised by C. L. Hoover, and the X-ray data were obtained by M. S. Licis and J. F. Whitney.

References

- BRIXNER, L. H., SLEIGHT, A. W. & LICIS, M. S. (1972). *J. Solid State Chem.* In the press.
- DEM'YANETS, L. N., ILYUKHIN, V. V., CHICHAGOV, A. V. & BELOV, N. V. (1967). *Izv. Akad. Nauk SSSR, Neorg. Mat.* **3**, 2221.
- GEBERT, W. & KILBORG, L. (1967). *Acta Chem. Scand.* **21**, 2575.
- GÜRMEEN, E., DANIELS, E. & KING, J. S. (1971). *J. Chem. Phys.* **55**, 1093.
- JEITSCHKO, W. K. & SLEIGHT, A. W. (1971). Summer American Crystallographic Association Meeting, Abstract No. N12.
- KAY, M. I., FRAZER, B. C. & ALMODOVAR, I. (1964). *J. Chem. Phys.* **40**, 504.
- KEELING, R. C. JR (1957). *Acta Cryst.* **10**, 209.
- KOOLS, F. X. N. M., KOSTER, A. S. & RIECK, G. D. (1970). *Acta Cryst.* **B26**, 1974.
- LECIEJEWICZ, J. (1965). *Z. Kristallogr.* **121**, 158.
- MCCARTHY, G. J. (1971). *Mater. Res. Bull.* **6**, 31.
- Natl. Bur. Std. U.S. Monograph* (1962). 25.
- NICOL, M. & DURANA, J. F. (1971). *J. Chem. Phys.* **54**, 1436.
- SHAFFER, M. W. (1965). *J. Appl. Phys.* **36**, 1145.
- SLEIGHT, A. W. & CHAMBERLAND, B. L. (1968). *Inorg. Chem.* **7**, 1672.
- SLEIGHT, A. W., CHAMBERLAND, B. L. & WEIHER, J. F. (1968). *Inorg. Chem.* **7**, 1093.
- SLEIGHT, A. W. & LICIS, M. S. (1971). *Mater. Res. Bull.* **6**, 365.
- ÜLKÜ, D. (1967). *Z. Kristallogr.* **124**, 192.
- WYCKOFF, R. W. G. (1965). *Crystal Structures*, Vol. 1, pp. 86-91. New York: John Wiley.
- YOUNG, A. P. & SCHWARTZ, C. M. (1963). *Science*, **141**, 348.
- ZALKIN, A. & TEMPLETON, D. H. (1964). *J. Chem. Phys.* **40**, 501.