

## Structure of the Intercalate $\text{NaWO}_2\text{Cl}_2$

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$\text{NaWO}_2\text{Cl}_2$ ,  $F_w = 309.74$ , is formed by the intercalation of sodium into  $\text{WO}_2\text{Cl}_2$ . The structure of the intercalate has been determined using a combination of constant wavelength and time-of flight powder neutron diffraction data.  $\text{NaWO}_2\text{Cl}_2$  adopts orthorhombic symmetry, space group  $Ammm$  (No. 65), with  $a = 3.7943(3)$ ,  $b = 3.8006(4)$ , and  $c = 15.739(1)$  Å;  $Z = 2$ ;  $V = 226.96$  Å<sup>3</sup>; and  $D_{\text{cal}} = 4.53$  g cm<sup>-3</sup>. The structure consists of blocks, each containing a layer of both W and O atoms sandwiched between two layers of Cl atoms. The trilayer blocks [Cl-WO<sub>2</sub>-Cl] are stacked in the direction perpendicular to the layers, i.e., parallel to the  $c$ -axis, and are separated by Na<sup>+</sup> ions located in two sets of sites between adjacent chlorine layers. The basic structure is related to that of the parent material  $\text{WO}_2\text{Cl}_2$  by a displacement of the [Cl-WO<sub>2</sub>-Cl] blocks in the basal plane. © 1991 Academic Press, Inc.

### Introduction

The intercalation of atoms into solids represents an important route to the preparation of novel compounds which are otherwise unobtainable using conventional methods of solid state synthesis. In these materials guest species may diffuse through the host structure; therefore such materials also have important technological applications, for example, as cathodes in recharge-

able batteries. Interest has focused on lithium intercalation, with far less work on the intercalation of the other alkali metals.

Recently we have successfully intercalated sodium into the host structure  $\text{WO}_2\text{Cl}_2$  (1, 2). This has been achieved by a chemical intercalation method in which two new intercalating agents, Na-O-2,6-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and  $n\text{-C}_4\text{H}_9\text{-Na}$  were employed as sources of sodium. Compositions may be prepared covering the range  $0 \leq x \leq 2$ ,  $\text{Na}_x\text{WO}_2\text{Cl}_2$ . Three new compounds have been identified with compositions  $x = 0.25, 1.0, \text{ and } 2.0$  (2).

The layered structure of  $\text{WO}_2\text{Cl}_2$  may be

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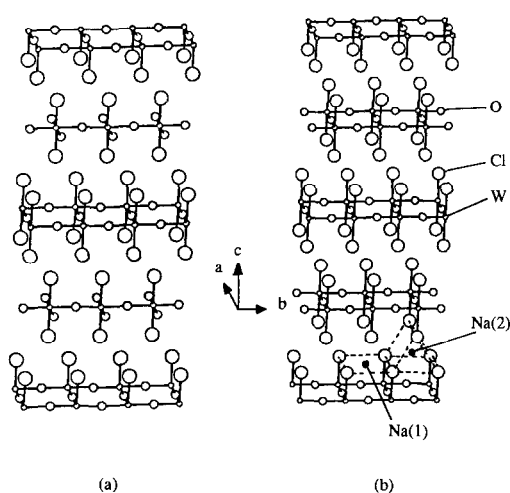


FIG. 1. (a) An idealized model for the structure of  $\text{WO}_2\text{Cl}_2$ , derived from that of  $\text{SnF}_4$ . (b) Structure of  $\text{NaWO}_2\text{Cl}_2$ , with sodium sites indicated by dashed lines.

derived from that of tetragonal  $\text{SnF}_4$ , which itself consists of  $\text{SnF}_2$  layers between which are located layers of F atoms (3). In  $\text{WO}_2\text{Cl}_2$ , Fig. 1a, the  $\text{SnF}_2$  layers are replaced by those of  $\text{WO}_2$ , and above and below these layers are located sheets of Cl atoms, thus forming a  $[\text{Cl}-\text{WO}_2-\text{Cl}]$  trilayer block. The blocks are stacked in the  $c$ -direction, forming the overall three-dimensional structure by van der Waals bonding between adjacent chlorine layers. The precise structure of  $\text{WO}_2\text{Cl}_2$  remains in doubt. Jarchow *et al.* (4), based on single crystal X-ray data from twinned crystals, suggested that the structure is distorted, with the W, O, and Cl atoms being displaced somewhat, from their ideal  $\text{SnF}_4$  positions, thus lowering the tetragonal symmetry to one that is monoclinic with space group  $Aa$ ,  $a = 7.68 \text{ \AA}$ ,  $b = 3.89 \text{ \AA}$ ,  $c = 14.42 \text{ \AA}$ , and  $\beta = 105.4^\circ$ . An alternative, smaller, body-centered orthorhombic unit cell has been reported to fit the  $d$ -spacings observed by powder X-ray diffraction (5). We have confirmed that the orthorhombic cell, with dimensions  $a = 3.847 \text{ \AA}$ ,  $b =$

$3.888 \text{ \AA}$ , and  $c = 13.885 \text{ \AA}$ , fits both powder X-ray and neutron data and is compatible with a less distorted structure than that proposed by Jarchow *et al.*

The structure of the host material suggests that the intercalated ions reside between adjacent van der Waals bonded Cl layers. This is supported by the fact that the intercalated materials show significant expansion in the direction perpendicular to the layers, with very little change in the basal plane dimensions. In a previous publication (1) we speculated that in  $\text{NaWO}_2\text{Cl}_2$ , the basic structure of  $\text{WO}_2\text{Cl}_2$  is retained, with the  $\text{Na}^+$  ions residing in square pyramidal sites but only in alternate layers; such ordering is termed a stage-two structure. This hypothesis appeared to be consistent with the preliminary X-ray diffraction data. As reported here, a detailed study involving powder neutron diffraction shows that a stage-two structure is not formed. In this paper we present the structure of  $\text{NaWO}_2\text{Cl}_2$  as determined by powder neutron diffraction.

## Experimental

The preparation of  $\text{NaWO}_2\text{Cl}_2$  was carried out by intercalation of  $\text{WO}_2\text{Cl}_2$  using  $\text{Na}-\text{O}-2,6\text{-Bu}_2\text{C}_6\text{H}_3$  as described previously (1). The host material was prepared by the solid state reaction of  $\text{WO}_3$  and  $\text{WCl}_6$  as follows. Crystalline  $\text{WCl}_6$  (99.9%, Aldrich) was ground and mixed with  $\text{WO}_3$  (grade Al, Johnson Matthey) in an argon-filled Miller-Howe high-integrity glove box, in which the  $\text{H}_2\text{O}$  and  $\text{O}_2$  contents were each maintained below 5 ppm. The mixture was placed in a sealed Pyrex tube, removed from the glove box, and heated for 3 days at  $290^\circ\text{C}$ .

Products were characterized by atomic absorption spectroscopy using a Pye-Unicam SP9 spectrometer and by X-ray powder diffraction using a Stoe-Guinier camera with  $\text{CuK}\alpha$  radiation. Powder neutron diffraction data were collected on two instru-

ments, HRPD at ISIS, Rutherford Appleton Laboratory, and D1A at the ILL, Grenoble. In both cases the sample was loaded into a 12-mm-diameter vanadium can in an argon-filled glove bag. On HRPD the sealed can was mounted on the diffractometer, 1 m in front of the backscattering detectors. On D1A, data were collected at a constant wavelength of 1.911 Å and in the  $2\theta$  range  $6^\circ$ – $160^\circ$ . Time-of-flight refinements were performed using a modified Rietveld code with peak shapes modeled by a convolution of Voigt and two exponential curves (6). In the case of the constant wavelength data the program MPROF, version X14.4 (7), was used for refinement with a simple Gaussian peak shape assumed throughout. The scattering lengths used were 0.477, 0.5805, 0.9579, and  $0.363 \times 10^{-12}$  cm for W, O, Cl, and Na, respectively (8).

### Structure Determination

In a previous, preliminary, investigation using X-ray powder diffraction the reflections of  $\text{NaWO}_2\text{Cl}_2$  could be satisfactorily indexed on a tetragonal unit cell (1). This cell was used as a starting point for the analysis of the high-resolution time-of-flight data. However, close examination of the HRPD data indicated that the  $h00$  and  $0k0$  reflections were split, characteristic of an orthorhombic distortion from tetragonal symmetry (Fig. 2). The high-resolution HRPD data permitted refinement of an orthorhombic cell, and general systematic absences suggested  $A$ -face centering. With no special systematic absences the centrosymmetric space group  $Ammm$  (No. 65) (9) was assumed. The similarity of the  $a$  and  $b$  unit cell dimensions to those of the orthorhombic cell for pure  $\text{WO}_2\text{Cl}_2$  suggested that a layered structure is maintained. The expansion in the  $c$ -direction is associated with the accommodation of the  $\text{Na}^+$  ions. The nature of the centering in  $\text{NaWO}_2\text{Cl}_2$  suggested that the layers were related by the  $A$ -face transla-

tion of 0,0.5,0.5. Additionally,  $a$  and  $b$  unit cell dimensions of approximately 3.8 Å strongly suggested W–O bonding along these axes. With the above in mind a model containing a planar tungsten oxide layer at  $z = 0$  and Cl layers above and below was suggested with W at 0,0,0 and oxygen atoms at 0,0.5,0 and 0.5,0,0. Using a W–Cl bond length of 2.311 Å from pure  $\text{WO}_2\text{Cl}_2$  the height of the Cl layer could be estimated at 0.15 in the  $c$ -direction above the tungsten oxide layer, giving a Cl position of 0,0,0.15.

The above model was used as a starting point for the profile refinement. Variation of background and scale parameters was carried out first, followed in subsequent iterations by the cell, zero point, and peak shape parameters. The chlorine  $z$  parameter was also refined. A difference Fourier map was then generated which revealed a strong peak at 0.5,0.5,0.18; this was subsequently refined as a sodium position. Despite a satisfactory visual fit, refinement of isotropic thermal parameters resulted in negative values for all the atoms.  $\text{NaWO}_2\text{Cl}_2$  exhibits significant absorption of neutrons. Such absorption is dependent on the wavelength of the neutrons, and as such its refinement in time-of-flight is more complex than that for data sets collected at a constant wavelength. Additional refinement of an absorption correction did yield improved values for isotropic  $B$ -factors on the W, O, and Cl atoms; however, it was still not possible to refine the sodium occupancy and  $B$ -factor simultaneously. The thermal parameters are heavily correlated with the absorption correction and this may, at least in part, account for the difficulties in the refinement. A second data set was collected on the same sample using the constant-wavelength D1A diffractometer at Grenoble. After refining scale and profile parameters convergence was quickly reached using the atomic and cell parameters from the time-of-flight refinements. Isotropic thermal parameters were refined on all atoms except Cl, for which

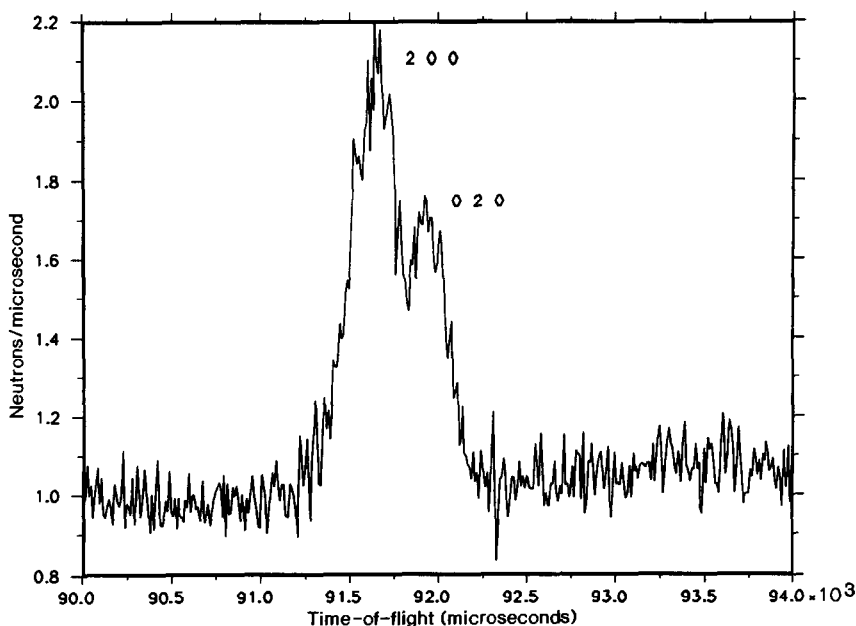


FIG. 2. Orthorhombic splitting of 200 and 020 peaks in  $\text{NaWO}_2\text{Cl}_2$  as seen on HRPD.

anisotropic thermal parameters were varied. Refinement of the sodium site occupation factor gave the calculated value of 0.5 within 1 e.s.d.; however, a rather high value, in excess of  $5 \text{ \AA}^2$ , was obtained for the simultaneously refined isotropic thermal parameter. Attempts to locate the sodium in a general position failed. Examination of the Fourier map indicated that the sodium scattering may not be centered on one site. The single Na site was therefore split into two closely spaced positions separated only in the  $c$ -axis. The site occupancies of these positions were allowed to vary, with the total occupancy being held at the value derived from the chemical formula. Refinement of the new Na positions proved successful. The final refined parameters are presented in Table I, with interatomic distances in Table II.

### Results and Discussion

The structure of  $\text{NaWO}_2\text{Cl}_2$  may be derived from the ideal structure of  $\text{WO}_2\text{Cl}_2$ ,

the major difference being the displacement of the  $[\text{Cl}-\text{WO}_2-\text{Cl}]$  blocks by half a unit cell along either of the basal plane unit cell axes. As a result of the displacement two trigonal prismatic sites per  $\text{NaWO}_2\text{Cl}_2$  formula unit are formed between adjacent Cl layers, and the two different sodium positions are located within these trigonal prisms. Na(2) is situated at the center of the trigonal prismatic sites with Na(1)-Cl distances of 2.85 and 2.81  $\text{\AA}$ , which are similar to the Na-Cl bond length of 2.82  $\text{\AA}$  for octahedrally coordinated  $\text{Na}^+$  in rock salt (10). Trigonal prismatic coordination of  $\text{Na}^+$  has been noted before, for example, in oxides such as  $\text{NaCuO}_2$  (11). Na(1) exists in a less common coordination; the sodium ions reside close to one face of the trigonal prism, resulting in a near square planar coordination for sodium, Fig. 1b. The resulting Na(1)-Cl distances of 2.69  $\text{\AA}$  are short compared with the bond length of octahedrally coordinated  $\text{Na}^+$  in rock salt. The short distance between Na(1) and Na(2)

TABLE I  
REFINED ATOMIC PARAMETERS FOR NaWO<sub>2</sub>Cl<sub>2</sub> FROM DIA DATA

Atom	Wyckoff notation	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )	Occupancy
W	2 <i>a</i>	0.0(–)	0.0(–)	0.0(–)	1.1(1)	1.0(–)
O(1)	2 <i>a</i>	0.0(–)	0.0(–)	0.5(–)	1.0(1)	1.0(–)
O(2)	2 <i>a</i>	0.5(–)	0.0(–)	0.0(–)	1.0(1)	1.0(–)
Cl	4 <i>c</i>	0.0(–)	0.0(–)	0.1540(2)	—	1.0(–)
Na(1)	4 <i>c</i>	0.5(–)	0.5(–)	0.154(2)	2.3(4)	0.63(2)
Na(2)	4 <i>c</i>	0.5(–)	0.5(–)	0.214(3)	2.3(4)	0.37(2)

## Anisotropic thermal parameters

Atom	<i>B</i> (11)	<i>B</i> (22)	<i>B</i> (33)	<i>B</i> (12)	<i>B</i> (13)	<i>B</i> (23)
Cl	2.5(2)	2.5(2)	0.34(1)	0.0(–)	0.0(–)	0.0(–)

Note. *R*<sub>wp</sub> = 6.29%, *R*<sub>ex</sub> = 3.89%, *a* = 3.7943(3) Å, *b* = 3.8006(4) Å, *c* = 15.739(1) Å.

sites precludes simultaneous occupation of these sites within one trigonal prism.

In NaWO<sub>2</sub>Cl<sub>2</sub> tungsten is in a distorted octahedral environment with four bonds to oxygen and two to chlorine. The W–O bonds of 1.900 and 1.897 Å lie within the range of 1.6–2.3 Å observed in pure WO<sub>2</sub>Cl<sub>2</sub> (4). But for a small rectangular distortion, these tungsten oxide layers approach square planar symmetry. The W–Cl distance of 2.424 Å is slightly larger than the value of 2.311 Å seen in the host material.

Displacement of layers upon intercalation into van der Waals bonded host compounds

is a well-established phenomenon; for example, in ZrS<sub>2</sub> the hexagonal close-packed layers of the host material are displaced upon intercalation of lithium to give a cubic close-packed intercalate.

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TABLE II  
BOND LENGTHS AND SIGNIFICANT CONTACT DISTANCES (Å) IN NaWO<sub>2</sub>Cl<sub>2</sub>

Atom	Distance	Multiplicity
W–Cl	2.424(3)	×2
W–O(1)	1.900(–)	×2
W–O(2)	1.897(–)	×2
Na(1)–Cl	2.69(3)	×4
Na(1)–Cl'	3.57(3)	×2
Na(2)–Cl	2.85(3)	×4
Na(2)–Cl'	2.81(3)	×2
Na(1)⋯Na(2)	0.94(6)	

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