respectively. Atomic scattering factors from *SHELXTL*.

The main cause of the relatively high R index was probably the poor quality of the crystal. This is indicated by the unusually high value of $R_{\text{sigma}} = \sum\sigma(F)/\sum F = 0{\cdot}061$.

Atomic parameters are given in Table 1, bond distances and angles in Table 2.* Fig. 1 shows the atom numbering.

Related literature. For the preparation of the compound see Schul (1984). For a recent structure of an indole derivative see Sawyer, Shariff & McLean (1985).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43054 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

SHORT COMMUNICATION

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Neutron powder time-of-flight Rietveld refinement and H-atom location in $NaNi_2(OH)(H_2O)(MoO_4)_2$. By

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Abstract

A new nickel sodium molybdate, $NaNi_2(OH)(H_2O)(MoO_4)_2$, has been synthesized by the reaction of $NiCl_2.6H_2O$ and $Na_2MoO_4.2H_2O$. $M_r = 495{\cdot}31$, $C2/m$, $a = 9{\cdot}3896$ (4), $b = 6{\cdot}2928$ (3), $c = 7{\cdot}5727$ (3) Å, $\beta = 116{\cdot}080$ (4)°, $V = 401{\cdot}89$ (2) Å^3, $Z = 2$, $D_x = 4{\cdot}092$, $T = 15$ K, microcrystalline powder, time-of-flight neutron data, Rietveld refinement 0·64–2·61 Å (150° data banks), 848 contributing reflections, $R_{wp} = 0{\cdot}0193$, $R_p = 0{\cdot}1275$, $R_e = 0{\cdot}0101$. The H atoms were located by difference Fourier techniques and closely agree with those found on an isomorphous compound by X-ray single-crystal methods.

Introduction

Reactions involving alkali-metal molybdates and salts of transition metals in aqueous solutions result in the formation of simple and mixed metal molybdate phases which are of interest because of their catalytic and magnetic properties in addition to their interesting structural characteristics (Van Uitert, Sherwood, Williams, Rubin & Ronner, 1964; Rajaram, Viswanathan, Sastri & Srinivasan, 1974). These molybdates tend to form in basic solutions and are usually micorcrystalline. Two single-crystal studies have been completed. One such phase, $NaZn_2(OH)(H_2O)(MoO_4)_2$ (Clearfield, Sims & Ramanathan, 1976), is also found to form when the transition metal is Co or Mn. We recently completed the X-ray single-crystal structure determination of $NaMn_2(OH)(H_2O)(MoO_4)_2$ which was found to be isostructural with the zinc phase (Clearfield, Moini & Rudolf, 1985). In this latter study we were able to locate peaks in the difference Fourier map that were assigned to H atoms and concluded that there are only two crystallographically unique H atoms in the structure with one of them occupying half of the available sites. This results in the presence of water and hydroxyl groups on alternating sites. The crystals used in the X-ray studies were exceedingly small and the absorption coefficient was large (*ca* 60 cm^{-1}). So it was of interest to verify the X-ray determination of H-atom placements. Our investigation of this matter led to the preparation of

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$NaNi_2(OH)(H_2O)(MoO_4)_2$, which was shown by X-ray powder diffraction to be isostructural with $NaMn_2(OH)(H_2O)(MoO_4)_2$. Although no large single crystals could be grown, excellent powder peak sharpness and lack of any additional phase led us to use it for neutron Rietveld analysis.

Experimental

$NiCl_2.6H_2O$ (0·5 *M*, 100 ml) was added dropwise to a well stirred boiling solution of $Na_2MoO_4.2H_2O$ (2 *M*, 100 ml) in a round-bottomed flask. A green-yellow precipitate formed immediately. This solution was refluxed for 15 h, yielding the final light-green product which was washed with distilled deionized water. Drying took place first in a desiccator followed by annealing in an open container at 363 K. The X-ray powder pattern demonstrated that the product was pure and isostructural with the original zinc phase.

Neutron time-of-flight (TOF) data were collected on an approximately 5·25 cm³ sample loaded into a sealed vanadium can under inert dry conditions. Data were taken on the Special Environments Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory (Jorgensen & Faber, 1982). 12 h data collection, data reduction on data collected by the 150° (back reflection) data banks. TOF Rietveld refinement using non-H atom positions of $NaMn_2(OH)(H_2O)(MoO_4)_2$ as starting model. Refinement on weighted profile using IPNS program set (Von Dreele, Jorgensen & Windsor, 1982). Weights as $1/\sigma(Y_i)^2$, extinction and absorption parameters applied, five-term refinable background function capable of fitting thermal diffuse scattering. Full-matrix least-squares refinement on positional and isotropic thermal parameters, H

Table 1. *Neutron TOF refinement parameters for* $NaNi_2(OH)(H_2O)(MoO_4)_2$

Data range μs/$Å^{-1}$	5000–20000/0·64–2·61
Number of contributing reflections	848
Number of degrees of freedom	2772
Temperature (K)	15
$R_{wp} = \{\sum_i w_i[Y_i(\mathrm{obs}) - Y_i(\mathrm{calc})]^2/\sum_i w_i[Y_i(\mathrm{obs})]^2\}^{1/2}$	0·0193
$R_p = \sum_i[Y_i(\mathrm{obs}) - Y_i(\mathrm{calc})]/\sum_i[Y_i(\mathrm{obs}) - \mathrm{bkg}_i]$	0·1275
$R_e = (df)^{1/2}/\sum_i w_i[Y_i(\mathrm{obs})]^2$	0·0101
Max. Δ/σ in last cycle (*B* of H2)	0·19
Extinction as 1-EX*F**2*M*D**4†	$8·18e^{-7}$
Absorption as exp(−AB*D)†	$8·81e^{-2}$

† Defined in the IPNS program package; Von Dreele, Jorgensen & Windsor (1982).

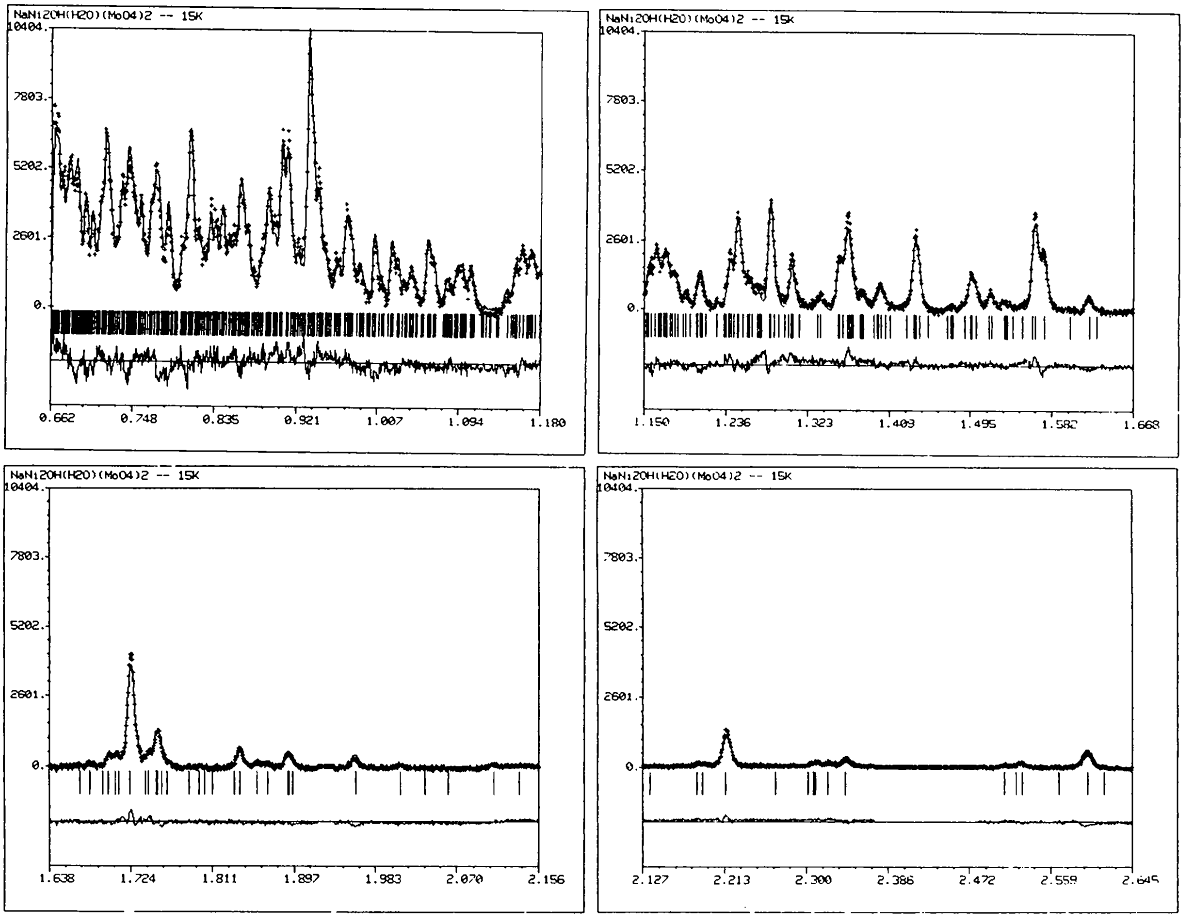

Fig. 1. Plots of neutron intensity (counts) *versus d* spacing (Å) for $NaNi_2(OH)(H_2O)(MoO_4)_2$. Observed data are represented by dots, calculated by the solid line. The lower plot is the difference. Vertical strokes indicate calculated Bragg-peak positions.

atoms by difference Fourier techniques, H-atom positions refined, 3000 data points, 0·64–2·61 Å *d* space range, 848 contributing reflections, $R_{wp} = 0{\cdot}0193$, neutron scattering lengths (Koester & Steyert, 1977), other refinement information in Table 1.*

Results and discussion

The final difference plot for the neutron TOF Rietveld refinement is shown in Fig. 1. The atom positions (both H and non-H) closely agree with those of $NaMn_2(OH)(H_2O)(MoO_4)_2$ (Clearfield, Moini & Rudolf, 1985). The Ni–O bond distances are very similar to each other [2·066 (3)–2·078 (5) Å], and the bond angles indicate the formation of a slightly distorted octahedron [81·1 (2)–98·9 (2)°]. On the other hand, the MoO_4 unit forms a regular tetrahedron consisting of three Mo–O bonds with very close distances [1·751 (7)–1·779 (5) Å] and one which is relatively longer [1·833 (10) Å]. The arrangement of the hydroxyl and water groups found for the $NaMn_2(OH)(H_2O)(MoO_4)_2$ structure is therefore confirmed. The O4–H1 distance of 1·009 (11) Å is about 0·14 Å longer than in the X-ray Mn phase. This lengthening is due to the neutron technique (Ceccarelli, Jeffrey & Taylor, 1981). The fully occupied H1 position is found to be hydrogen bonded, in the **c** direction, to O1 at a distance of 1·724 (11) Å. On the other hand, the half-occupied H2 does not enter into any hydrogen bonding with framework O atoms. The O4–H2 bonding vector is primarily in the **a** direction and is symmetry constrained. The lack of hydrogen bonding by this H atom results in the rather long O4–H2 distance of 1·294 (26) Å, and compared with the other H atom (*cf.* e.s.d.'s) is much more free to move. The coordination of O atoms around the Na atom represents a distorted octahedral arrangement with two of the angles approximately 12° from the ideal arrangement. Final atom positions show the title compound to be isostructural with $NaMn_2(OH)(H_2O)(MoO_4)_2$.

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* Positional and thermal parameters and all important bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43149 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Currently acceptable formats for the machine-readable media are: magnetic tape with fixed line length and fixed block size in 9 track, ASCII or EBCDIC, 800, 1600 or 6250 CPI; or punched cards with IBM 026 or IBM 029 codes.

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