# Orientation of Pyridine in $NbS_2(C_5H_5N)_{0\cdot5}$. A Neutron Diffraction Study

By CHRISTIAN RIEKEL* and DIETMAR HOHLWEIN
(*Institut Laue-Langevin,* 156X *Centre de Tri,* 38042-*Grenoble Cédex, France*)
and ROBERT SCHÖLLHORN
(*Anorganisch-Chemisches Institut der Universität* 44 *Münster, Gievenbecker Weg* 9, *Germany*)

*Summary* Single-crystal studies on $NbS_2(C_5H_5N)_{0\cdot5}$ and $NbS_2(C_5D_5N)_{0\cdot5}$ by neutron diffraction established a position of the pyridine ring with the aromatic plane perpendicular to the metal sulphide layers and the nitrogen atom located midway between adjoining layered units.

A LARGE number of intercalation compounds of layered dichalcogenides with Lewis bases have been prepared in recent years. The anisotropic electronic properties of these materials are dependent upon the nature of the intercalated species. Opposing views as to the structural arrangement of the intercalated compounds have been published. Thus, in $TaS_2(C_5H_5N)_{0\cdot5}$ the pyridine ring is thought to be oriented either with its plane parallel to the chalcogenide sheets or with its C–N axis perpendicular to the host layers.[2] In both models the nitrogen atoms are situated close to the sulphur layers; charge transfer interactions between guest and host lattice have been discussed. In contrast, nitrogen was found to be located midway between the titanium disulphide slabs in $TiS_2.NH_3$.[3]

A recent kinetic study on the $ND_3$ intercalation into the 2H–$TaS_2$ lattice accentuated the superiority of neutron diffraction methods in structural investigations of this type of compounds.[4] In order to establish the orientation of the pyridine molecule, we decided to undertake a single-crystal neutron diffraction study on $NbS_2(C_5H_5N)_{0\cdot5}$.

Crystals of the 2H-$NbS_2$ modification, as verified by single crystal *X*-ray photographs, were prepared by standard vapour-phase transport techniques[5] and intercalated with pyridine (Py) or penta-deuteriopyridine (DPy) by refluxing. Two crystals of $NbS_2(Py)_{0\cdot5}$ and $NbS_2(DPy)_{0\cdot5}$ of hexagonal shape with 0·9 mm max. diameter and 0·4 mm thickness were selected. Neutron photographs at the D12 installation at the I.L.L.[6] (wavelength 1·63 and 1·87 Å) were taken by the rotating crystal and Weissenberg techniques at room temperature. The observed reflections can be divided into two types. Type I reflections, also visible on *X*-ray photographs, correspond to the reciprocal lattice of hexagonal $NbS_2$ with an increased *c*-spacing [$a = 3{\cdot}3_2$, $c = 23{\cdot}6_1$ Å for $NbS_2(Py)_{0\cdot5}$]. Further reflections (type II), corresponding to the pyridine lattice because they are only visible on neutron photographs, were found along the $a^*$ direction and could be indexed as $10l$ and $20l$ on an hexagonal lattice with $a = 3{\cdot}9_4$ and $c = 23{\cdot}6_1$ for $NbS_2(Py)_{0\cdot5}$. These reflections were perfect spots for $NbS_2(Py)_{0\cdot5}$ but disorder was present in $NbS_2(DPy)_{0\cdot5}$ as observed by streaking parallel to $c^*$. We infer from this that a perfect three-dimensional order of the pyridine lattice is possible at room temperature but that the conditions under which this is formed are not well understood.

Further weak reflections found along $a^*$ indicate that the true *a*-axis is a multiple of the value found which would be expected on grounds of the mismatch between the pyri-

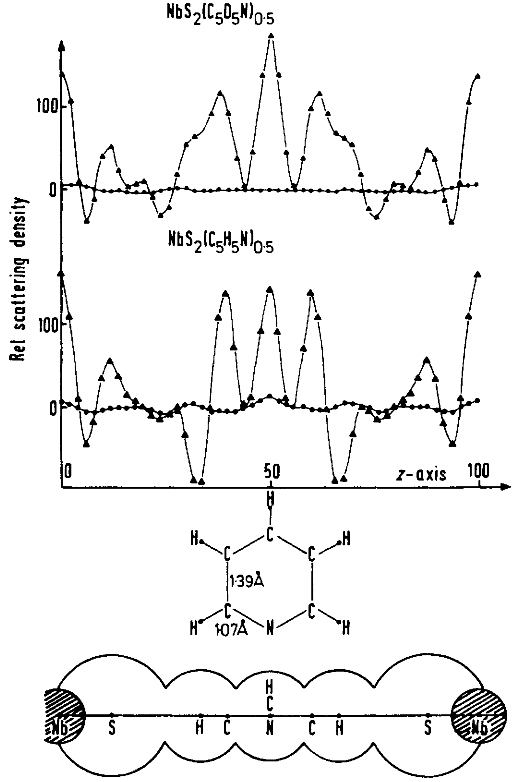

FIGURE. (Top) Fourier and difference synthesis of $NbS_2$-$(C_5D_5N)_{0\cdot5}$ and $NbS_2(C_5H_5N)_{0\cdot5}$. (Bottom) Packing of the pyridine ring using van der Waals radii for the hydrogen atoms.

dine lattice and the $NbS_2$ lattice. Furthermore, a $h + l = 2n$ extinction was found for the $h0l$ reflections of the pyridine lattice which indicates that every second sheet is shifted by $a/2 + c/2$ against the first sheet and that the true lattice of pyridine is not hexagonal.

The intensities of the $00l$ series were measured by computerized integration of the photometrically processed films.[6] A total of ten $00l$ reflections (not including the systematic extinctions) were obtained in each case. The structure was solved by phasing the structure amplitudes with the known $NbS_2$ parameters.[7] To simplify the calculation procedure the Nb atom was set at the origin and the repeat unit was taken as half the $c$-axis.

The scattering lengths, $b$, are quite different for C, N, D, and H-atoms, namely, 6·65, 9·37, 6·67, and −3·74 Fermi, respectively.[8] The hydrogen atoms could thus be located in the one-dimensional Fourier synthesis near the sulphur layer; holes were found for $NbS_2(Py)_{0\cdot5}$ and maxima for $NbS_2(DPy)_{0\cdot5}$. A further hydrogen and the nitrogen atom were found to reside midway between the sheets at $z = 0\cdot5$.

The only model which fits these data is a pyridine ring oriented perpendicular to the $NbS_2$ sheets but with the nitrogen atom symmetrically between the layers. A least-squares refinement of the scale parameter and the $z$ parameters of S, C, and H (D) established further the accuracy of the model. Using an overall thermal parameter $B$ of $1\cdot0$ Å$^2$ the final discrepancy factor $R_F$ was, in both cases, 0·08. The corresponding Fourier and difference Fourier projections in the direction of the $c$-axis are shown, along with a scheme of the molecular dimensions, in the Figure. We infer from a comparison of the interlayer spacings that a similar position of the heterocyclic ring is to be expected for the other known pyridine intercalation compounds of transition-metal dichalcogenides.

There are two principal conclusions which may be derived from our results: (i) the steric position of the aromatic ring in $NbS_2(Py)_{0\cdot5}$ would basically allow charge transfer between neighbouring ring systems but is obviously highly unfavourable for charge transfer from pyridine to the $NbS_2$ layers. (ii) The distance of 4·4 between the centre of the N-atoms and the sulphur atom centres is such that an interpretation of a potential interaction between the nitrogen atom and the metal sulphide layers in terms of a S–N–S three centre bond, which has been put forward in the case of $TaS_2NH_3$,[9] is rather unlikely. Thus, it is obvious that the nature of the bonding between guest species and the host lattice in the compounds under consideration remains a problem yet to be solved.

(*Received*, 22*nd March* 1976; *Com.* 295.)

---

[1] For a review see F. R. Gamble and T. H. Geballe, Treatise Solid State Chem., ed. N. B. Hannay, Plenum Press, New York, 1975, Vol. 3.

[2] G. S. Parry, C. B. Scruby, and P. M. Williams, *Phil. Mag.*, 1974, **29**, 602; F. R. Gamble and H. J. Osiecki, *J. Chem. Phys.*, 1971, **55**, 3525; R. Schöllhorn and A. Weiss, *Z. Naturforsch.*, 1972, **27b**, 1278.

[3] R. R. Chianelli, J. C. Scanton, M. S. Whittingham, and F. R. Gamble, *Inorg. Chem.*, 1975, **14**, 1963.

[4] C. Riekel and R. Schöllhorn, *Mat. Res. Bull.*, 1976, **11**, (4), 369.

[5] H. Schäfer, Chemical Transport Reactions, Academic Press, New York, 1964.

[6] D. Hohlwein, Proc. Neutron Diffraction Conf., Petten-NH, RCN-Rep. 1975, **234**, 410.

[7] F. Jellinek, G. Brauer, and H. Müller, *Nature*, 1960, **185**, 377.

[8] L. Koester and K. Knopf, unpublished results.

[9] F. R. Gamble and B. G. Silbernagel, *J. Chem. Phys.*, 1975, **63**, 2544.