

is the only structure in which the isolated anions  $B_2O_5^{4-}$ ,  $BO_3^{3-}$  and  $O^{2-}$  are found together. The formula of this compound which represents a new type of structure should therefore be written as  $Cu_{15}[(B_2O_5)_2|(BO_3)_6|O_2]$ , with  $Z = 2$ . Since other cations like  $Pd^{2+}$  or  $Cr^{2+}$  show similar behaviour, it can be expected that they will form isotypic or similar borate structures. The palladium metaborate  $PdB_2O_4$ , isotypic with  $CuB_2O_4$ , has just been synthesized by Depmeier (1981).

#### References

- BERGER, S. V. (1949). *Acta Chem. Scand.* **3**, 660–675.  
 COULSON, C. A. & DINGLE, T. W. (1968). *Acta Cryst.* **B24**, 153–155.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 DEPMEIER, W. (1981). *Z. Kristallogr.* **156**, 28–29.  
 DONNAY, G. & DONNAY, J. D. H. (1973). *Acta Cryst.* **B29**, 1417–1425.  
 ECKER, E. (1966). Dissertation. Technische Hochschule Karlsruhe.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 LECUIR, L. & GUILLERMET, J. (1971). *C. R. Acad. Sci.* **273**, 1091–1094.  
 MARTÍNEZ-RIPOLL, M. MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1971). *Acta Cryst.* **B27**, 677–681.  
 RICHTER, L. (1976). Dissertation. Rheinisch–Westfälische Technische Hochschule Aachen.  
 TAKÉUCHI, Y. (1952). *Acta Cryst.* **5**, 574–581.  
 TENNYSON, C. (1963). *Fortschr. Mineral.* **41**, 64–91.  
 UHLIG, D. (1976). Diplomarbeit. Rheinisch–Westfälische Technische Hochschule Aachen.  
 WATANABE, T. (1939). *Fortschr. Mineral.* **23**, 166–167.  
 WEIR, C. E. & SCHROEDER, R. A. (1964). *J. Res. Natl Bur. Stand.* **68**, 465–487.  
 WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed. Oxford Univ. Press.  
 XRAY system (1976). Editor J. M. STEWART. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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## Preparation and Structure of Technetium Triphosphide and Rhenium Triphosphide, Isotypic Polyphosphides with Metal Chains

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#### Abstract

$TcP_3$  and  $ReP_3$  (prepared by reaction of the elemental components in the presence of iodine, and also in a tin flux) crystallize in a new structure type with four formula units in space group  $Pnma$  and the following lattice constants.  $TcP_3$ :  $a = 15.359$  (5),  $b = 3.092$  (1),  $c = 5.142$  (2) Å,  $V = 244.2$  (2) Å<sup>3</sup>;  $ReP_3$ :  $a = 15.354$  (8),  $b = 3.122$  (2),  $c = 5.130$  (2) Å,  $V = 245.9$  (3) Å<sup>3</sup>. The structure was determined from X-ray diffractometer data from a  $TcP_3$  single crystal and refined to a residual value of 0.022 for 996  $F$  values and 15 variables. The metal atoms ( $T$ ) are approximately octahedrally surrounded by P atoms. The P atoms are tetrahedrally coordinated to  $T$  and P atoms with the oxidation numbers  $-2$ ,  $-1$ , and zero. The resulting oxidation number of the metal atoms is  $+3$  ( $d^4$  system). Each metal atom forms two metal–metal bonds across the common edges of adjacent octahedra. Thus all spins are compensated in agree-

ment with the diamagnetism observed for  $ReP_3$ . The structure can be described as a stacking of identical layers of puckered pentagons and hexagons. In this way it is closely related to the structures of many compounds with compositions  $TX_2$  and  $TX_4$  ( $X = P, As, Sb, S, Se$ ).

#### Introduction

During our investigation of the Re–P system we have prepared and characterized the compounds  $ReP_4$  (Jeitschko & Rühl, 1979),  $Re_2P_5$  (Rühl & Jeitschko, 1982), and  $Re_6P_{13}$  (Rühl & Jeitschko, 1980). We had also recognized the existence of another Re polyphosphide of which we did not find crystals large enough for a structure determination. Recently, however, single crystals of the corresponding isotypic phase in the Tc–P system, designated as ‘phase  $D$ ’ (Rühl,

Jeitschko & Schwochau, 1982), were obtained. The structure determination showed that the compositions of these compounds are  $\text{ReP}_3$  and  $\text{TcP}_3$ .

### Preparation and properties

Both compounds were prepared in evacuated, sealed silica tubes in two different ways using the tin-flux technique or in the presence of iodine added as a mineralizer. Starting materials were powders of Tc (Oak Ridge National Laboratory, nominal purity 99.8%), Re (Ventron, 99.997%), red P, Sn and iodine (all from Merck, 'rein'). The red P was purified by boiling in diluted NaOH solution (Brauer, 1975).

A general description of the preparation of Tc phosphides was given previously (Rühl, Jeitschko & Schwochau, 1982). Single-phase  $\text{TcP}_3$  was obtained by reaction of the elemental components in a tin flux with the composition  $\text{Tc}:\text{P}:\text{Sn} = 1:4.5:6$ . The sample was heated to 1220 K within two days and kept at this temperature for three weeks. After quenching by taking the sample tubes out of the hot furnace, the Sn-rich matrix was dissolved in hot hydrochloric acid. The product contained crystals of  $\text{TcP}_3$  which were used for the structure determination. In samples with higher or lower P content, prepared in the same way, we have found  $\text{TcP}_3$  in equilibrium with  $\text{TcP}_4$  and a phase of unknown structure with the approximate composition  $\text{TcP}_2$ . Using iodine as a mineralizer we have observed the same phase equilibria. In these samples about 1 mg of iodine (tube volume of  $0.5 \text{ cm}^3$ ) was added to the mixtures of Tc and red P. Annealing times and temperatures were similar to those described above.

The best procedure for the preparation of  $\text{ReP}_3$  is the annealing of the elemental components in the ratio 1:3 in the presence of iodine for two weeks at 1070 K and subsequent quenching. At this temperature  $\text{ReP}_3$  is in equilibrium with  $\text{Re}_3\text{P}_4$  (Rundqvist, 1966) and  $\text{ReP}_4$ . We have also observed  $\text{ReP}_3$  in X-ray powder patterns of samples prepared in a tin flux with the starting composition  $\text{Re}:\text{P}:\text{Sn} = 1:4.5:6$ . The annealing was for about two weeks at temperatures between 970 and 1070 K.

$\text{TcP}_3$  and  $\text{ReP}_3$  are black with metallic luster. Their chemical stability is demonstrated by their resistance to boiling hydrochloric acid. Magnetic-susceptibility measurements for a sample of  $\text{ReP}_3$  with a Faraday balance showed diamagnetism.

### Cell dimensions and space group

Single crystals of  $\text{TcP}_3$ , examined in a Buerger precession camera with  $\text{Mo K}\alpha$  radiation, showed *mmm* Laue symmetry and the conditions for possible reflections  $hk0$  only with  $h = 2n$  and  $0kl$  only with  $k + l$

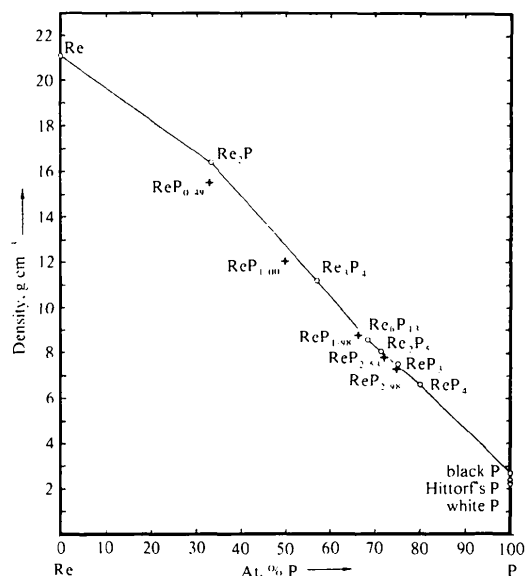


Fig. 1. Densities in the Re-P system. Experimental densities obtained by Haraldsen (1935) from more or less heterogeneous samples with the indicated overall compositions are marked with crosses. The densities calculated from the structure determinations are indicated by circles. For the sample with the composition  $\text{ReP}_{2.98}$  Haraldsen reported an X-ray powder pattern which resembles that of the compound  $\text{ReP}_4$  (Jeitschko & Rühl, 1979). We do not believe that Haraldsen's samples contained the compound reported here, because his samples were prepared by thermal decomposition of P-rich compositions whereas we obtain  $\text{ReP}_3$  only at relatively low temperatures.

$= 2n$ . This is characteristic for the orthorhombic space groups  $Pn2_1a$  and  $Pnma$  of which the centrosymmetric group  $Pnma (D_{2h}^{10})$  was found to be correct during the structure refinement.

Lattice constants (see *Abstract*) were refined from Guinier powder data using  $\alpha$ -quartz ( $a = 4.9130$ ,  $c = 5.4046 \text{ \AA}$ ) as standard. The values in parentheses are the deviations in the least significant digits obtained from samples prepared under a variety of conditions and differing starting compositions. Thus the homogeneity ranges of the compounds are certainly small. With  $Z = 4$  formula units per cell the calculated densities are  $5.22 \text{ g cm}^{-3}$  for  $\text{TcP}_3$  and  $7.54 \text{ g cm}^{-3}$  for  $\text{ReP}_3$ . The latter value fits well with the densities determined by Haraldsen (1935) for samples with similar overall compositions (Fig. 1).

### Structure determination

The shape of the  $\text{TcP}_3$  crystal was approximately globular (diameter:  $90 \mu\text{m}$ ). 2457 reflections were measured on an automated four-circle diffractometer within one quadrant up to  $(\sin \theta)/\lambda = 1 \text{ \AA}^{-1}$  with graphite-monochromated  $\text{Mo K}\alpha$  radiation, scintillation counter, pulse-height discriminator,  $\theta$ - $2\theta$  scans,

and background counts at both ends of each scan optimized by fast prescans. Absorption was corrected empirically ( $\mu_{\text{MoK}\alpha} = 68.2 \text{ cm}^{-1}$ ) from  $\psi$ -scan data. The ratio of the highest to lowest transmission was 1.03. After averaging of equivalent reflections and omitting those with  $F_o < 3\sigma$ , 996 independent  $F$  values remained. The internal  $R$  value was 0.020.

The structure was deduced from Patterson and difference Fourier syntheses, refined with a full-matrix least-squares program (Sheldrick, 1976), scattering factors for neutral atoms (Cromer & Mann, 1968) corrected for anomalous dispersion (Cromer & Liberman, 1970) and weights from counting statistics. An isotropic secondary-extinction parameter was refined and applied to the  $F_c$  values. The final conventional  $R$  value was 0.022 for a refinement with isotropic thermal-parameters, 996  $F$  values and 15 variable parameters. A final difference Fourier map showed only unextended ripples between  $-1.8$  and  $+1.5 \text{ e } \text{Å}^{-3}$ . Final atomic parameters are listed in Table 1. The

Table 1. Atomic parameters of  $\text{TcP}_3$

All atoms are in position 4(c) of space group  $Pnma$ . Numbers in parentheses are e.s.d.'s in the least significant digits.

	$x$	$y$	$z$	$B (\text{Å}^2)$
Tc	0.15034 (1)	$\frac{1}{4}$	0.14980 (3)	0.195 (2)
P(1)	0.01257 (4)	$\frac{1}{4}$	0.3529 (1)	0.328 (6)
P(2)	0.38157 (4)	$\frac{1}{4}$	0.3196 (1)	0.321 (6)
P(3)	0.29295 (4)	$\frac{1}{4}$	0.9780 (1)	0.331 (6)

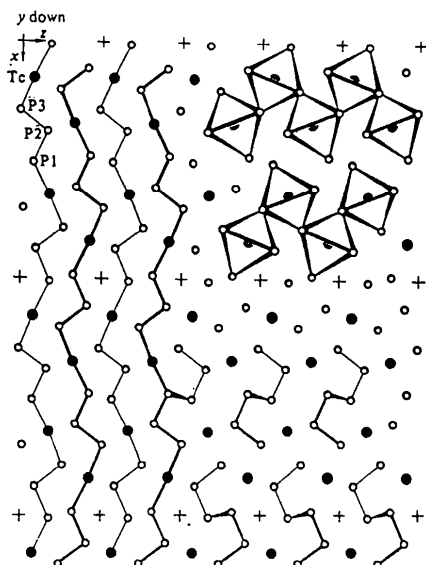


Fig. 2. The crystal structure of  $\text{TcP}_3$  projected along the short axis. In the left-hand part of the drawing atoms at  $y = \frac{1}{4}$  are connected by thin lines and atoms at  $y = \frac{3}{4}$  are connected by thick lines. In the right-hand part the two-dimensionally infinite sheets of linked  $\text{TcP}_6$  octahedra are shown. The superimposed octahedra share edges which are parallel to the  $xz$  plane. In the lower right-hand corner the branched infinite chains of the P polyanions are projected along the chain ( $y$ ) direction.

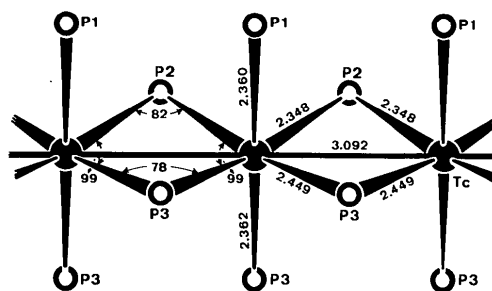


Fig. 3. Near-neighbor environment of the Tc atoms in  $\text{TcP}_3$ . All atoms lie on mirror planes which are perpendicular to the Tc–Tc bonds. Interatomic distances are given in Å. Standard deviations are all 0.002 Å or less. The shortest nonbonding Tc–P distance is 3.657 Å.

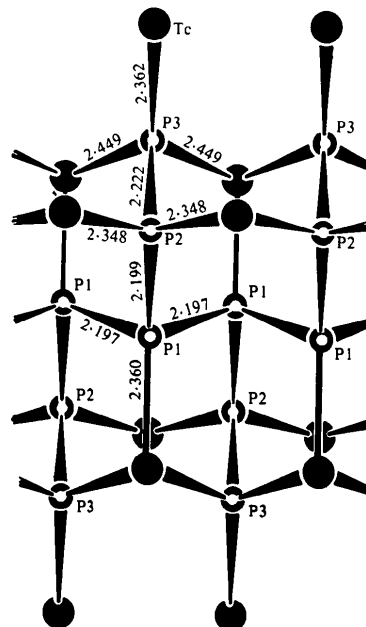


Fig. 4. Coordination of the P atoms in  $\text{TcP}_3$ . The infinite chain of P(1) atoms extending along the  $y$  direction is shown in the middle of the drawing. The P(2) and P(3) atoms form two-membered side chains. Interatomic distances (Å) have standard deviations of 0.002 Å or less, which result mainly from the variations of the lattice constants. The shortest nonbonding P–P distances correspond to the  $b$  translation period (3.092 Å).

introduction of anisotropic thermal parameters lowered the residual from 0.022 to 0.021. All positional parameters remained the same within the standard deviations. The deviations of the anisotropic thermal parameters from isotropic parameters were judged to be caused mainly by insufficient correction for absorption.\* The structure and near-neighbor environments are shown in Figs. 2, 3, and 4.

\* Lists of structure factors and the results of a refinement of the structure with anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36983 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

### Discussion

Although the structure of  $\text{TcP}_3$  is relatively simple it seems to be of a new type. The Tc atoms are approximately octahedrally surrounded by P atoms. The  $\text{TcP}_6$  octahedra are linked *via* corners and edges to form two-dimensionally infinite, puckered sheets perpendicular to the  $a$  axis. The three kinds of P atoms are tetrahedrally coordinated to either three Tc and one P, or two Tc and two P, or one Tc and three P atoms and thus (by counting two electrons for each of these near-neighbor interactions) attain the oxidation numbers  $-2$ ,  $-1$ , and zero. The resulting oxidation number of the Tc atoms is  $+3$  ( $d^4$  system). Each Tc atom forms two Tc–Tc bonds across the common edges of adjacent octahedra. These bonds can be clearly recognized by the distortions of the coordination polyhedra as has been discussed before, *e.g.* for  $\text{CrP}_4$  (Jeitschko & Donohue, 1972). The tetrahedral bond angles Tc–P(2)–Tc and Tc–P(3)–Tc (ideally  $109.5^\circ$ ) are reduced to  $83.3$  (1) and  $78.3$  (1) $^\circ$  and the octahedral angle P(2)–Tc–P(3) (ideally  $90^\circ$ ) is widened to  $99.0$  (1) $^\circ$  to permit a close approach of the Tc atoms to each other. In this way the chemical bonding in  $\text{TcP}_3$  can be completely rationalized on the basis of classical two-electron bonds. The two  $4d$  orbitals of each Tc atom, usually designated  $e_g$  for ideal octahedral coordination, are involved in the six nearly covalent Tc–P bonds ( $'d^2sp^3$  hybrid'). The four  $4d$  electrons of Tc not involved in Tc–P bonding are then assigned to the other three  $4d$  orbitals. Two of these electrons can be thought of as occupying one essentially nonbonding orbital which is situated perpendicular to the Tc–Tc bonding direction. The other two  $4d$  electrons use the two remaining orbitals to form one half- $\sigma$  and one half- $\pi$  bond to each of the two neighboring Tc atoms. The metal–metal bonding in  $\text{TcP}_3$  (and  $\text{ReP}_3$ ) corresponds to the bonding in the  $d^4$  marcasites where it has been discussed in more detail before (Jeitschko & Donohue, 1975). The Tc–Tc bond length of  $3.092$  (1) Å and the Re–Re bond length of  $3.122$  (2) Å (this distance is equivalent to the  $b$  axis) seem rather long at first sight, but one has to keep in mind that it is the result of a compromise involving considerable deviations from ideal octahedral and tetrahedral bond angles as has been discussed above. Rather long Tc–Tc and Re–Re bonds of  $3.036$  (6) and  $3.02$  (1) Å also occur in the molecules  $\text{Tc}_2(\text{CO})_{10}$  (Bailey & Dahl, 1965) and  $\text{Re}_2(\text{CO})_{10}$  (Dahl, Ishishi & Rundle, 1957) where the metal–metal bonding is undisputable. In  $\text{TcP}_4$  (Rühl, Jeitschko & Schwochau, 1982) and  $\text{ReP}_4$  (Jeitschko & Rühl, 1979) the Tc–Tc ( $3.002$  Å) and Re–Re bonds ( $3.012$  Å) are shorter because the  $\text{TcP}_6$  and  $\text{ReP}_6$  octahedra need to distort only towards one side to form the metal–metal pairs. The average Tc–P distance of  $2.386$  Å in  $\text{TcP}_3$  compares well with the corresponding distance of

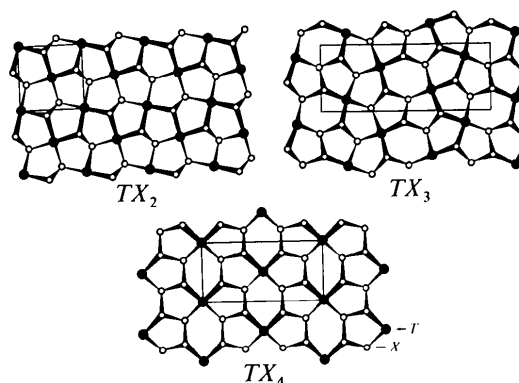


Fig. 5. The puckered nets of pentagons and hexagons which form the basic building elements in structures of compositions  $\text{TX}_2$ ,  $\text{TX}_3$ , and  $\text{TX}_4$ . The translation periods of the nets are indicated by thin lines.

$2.398$  Å in  $\text{TcP}_4$ , and the average P–P distances of  $2.206$  Å in  $\text{TcP}_3$  and  $2.203$  Å in  $\text{TcP}_4$  are also quite similar.

The structure of  $\text{TcP}_3$  can be visualized as a stacking of puckered nets consisting of pentagons and hexagons (Fig. 5), although bonding within and between the nets is of equal strength. The nets are (two-dimensionally) infinite, extend along the (011) plane, and are all parallel to each other. A similar net, consisting only of puckered pentagons, was recognized (Jeitschko, 1974) to be the basic building element of many  $\text{TX}_2$  ( $X =$  pnictogen or chalcogen) compounds including the structures of pyrite, marcasite, arsenopyrite,  $\text{PdP}_2$ ,  $\text{PdS}_2$ , and  $\text{PdPS}$ . Similarly, many polyphosphides of composition  $\text{TP}_4$  can be visualized as stacking variants of a related puckered net consisting of pentagons and hexagons (Jeitschko & Donohue, 1975; Rühl & Jeitschko, 1981). The ratios of pentagons to hexagons in the nets of the structures with the general compositions  $\text{TX}_2$ ,  $\text{TX}_3$ , and  $\text{TX}_4$  are 4:0, 3:1, and 2:2. The future will show whether the net observed here as a building element in  $\text{TcP}_3$  will be found in other structures with the general composition  $\text{TX}_3$ .

We are indebted to Dr U. Flörke and M. H. Möller for the magnetic measurements of  $\text{ReP}_3$  and for the single-crystal X-ray data collection of  $\text{TcP}_3$ . Professor K. Schwochau (KFZ Jülich) advised us in handling radioactive  $^{99}\text{Tc}$  compounds. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

### References

- BAILEY, M. F. & DAHL, L. F. (1965). *Inorg. Chem.* **4**, 1140–1145.  
 BRAUER, G. (1975). *Handbuch der Präparativen Anorganischen Chemie*. Stuttgart: Enke.

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DAHL, L. F., ISHISHI, E. & RUNDLE, R. E. (1957). *J. Chem. Phys.* **26**, 1750–1751.
- HARALDSEN, H. (1935). *Z. Anorg. Allg. Chem.* **221**, 397–417.
- JEITSCHKO, W. (1974). *Acta Cryst.* **B30**, 2565–2572.
- JEITSCHKO, W. & DONOHUE, P. C. (1972). *Acta Cryst.* **B28**, 1893–1898.
- JEITSCHKO, W. & DONOHUE, P. C. (1975). *Acta Cryst.* **B31**, 574–580.
- JEITSCHKO, W. & RÜHL, R. (1979). *Acta Cryst.* **B35**, 1953–1958.
- RÜHL, R. & JEITSCHKO, W. (1980). *Z. Anorg. Allg. Chem.* **466**, 171–178.
- RÜHL, R. & JEITSCHKO, W. (1981). *Acta Cryst.* **B37**, 39–44.
- RÜHL, R. & JEITSCHKO, W. (1982). *Inorg. Chem.* **21**, 1886–1891.
- RÜHL, R., JEITSCHKO, W. & SCHWOCHAU, K. (1982). *J. Solid State Chem.* In the press.
- RUNDQVIST, S. (1966). *Acta Chem. Scand.* **20**, 2075–2080.
- SHELDRIK, G. M. (1976). *SHELX 76*. A program for crystal structure determination. Univ. of Cambridge, England.

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## A New Form of Sodium Kurrol Salt studied by the Rietveld Method from X-ray Diffraction Data

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### Abstract

A new form of sodium Kurrol salt, sodium metaphosphate,  $(\text{NaPO}_3)_n$ , obtained by finely grinding samples of the *B* form, has been studied by the Rietveld method from powder X-ray diffraction data. Only by using constrained refinement does convergence occur. A comparison between two distinct models is made and the importance of reducing the number of variables is demonstrated. [Crystal data for the two models refined in  $I4_1/a$  are: (model I)  $a = b = 13.177$  (5),  $c = 5.940$  (3) Å; (model II)  $a = b = 13.176$  (6),  $c = 5.931$  (3) Å.]

### Introduction

In recent papers (Immirzi, 1978, 1980*a*) one of the authors discussed the advantages of combining the Rietveld procedure of refining a structure by means of powder diffraction patterns (Rietveld, 1967, 1969) with the use of constrained variables, for either neutron or X-ray diffraction. In addition a new general-purpose computer program using the generalized-coordinate approach was illustrated and it was shown how polymeric structures can profitably be handled (Immirzi, 1980*a, b*; Young, Lundberg & Immirzi, 1980).

Polymeric phosphates already studied by single-crystal techniques have been considered for testing

purposes. The different parameter sets obtained with various constrained models and powder patterns can be compared with the single-crystal parameter set, thus providing a check on both parameter reliability and refinement convergence. In particular, the polymeric phosphate  $\text{Na}_3\text{H}(\text{PO}_3)_4$ , studied by Jost (1968) by single-crystal techniques, was studied again by the Rietveld method using X-ray diffraction data (Immirzi, 1980*b*). The importance of using constrained-variable models was duly demonstrated.

The study of polymeric  $\text{NaPO}_3$ , Kurrol salt, of which two forms are known, *A* type (Jost, 1961) and *B* type (Jost, 1963), was undertaken as a further contribution in this direction. Unexpectedly, however, prolonged grinding of *B*-form samples gave rise to a new polymorph which we termed *C* type whose structure was elucidated using powder diffraction data and refined by the Rietveld method with X-ray radiation.

Although the lack of a single-crystal parameter set does not allow a comparison as for the  $\text{Na}_3\text{H}(\text{PO}_3)_4$  structure to be carried out, the critical role of constrained parameters was again demonstrated, using to this end two different constrained models.

### Experimental

A sample of Kurrol salt *B* type, kindly supplied by Dr K. H. Jost, was finely ground using a micro ball mill.