parameters U_{eq} extrapolated to 322 K from the structure of the low-temperature phase on the basis of the harmonic model for thermal vibrations. The estimated values are $U_{eq}(P) = 1\cdot53$, $U_{eq}|O(1)| = 2\cdot8$, $U_{eq}|O(2)| = 3\cdot3$, $U_{eq}|O(3)| = 2\cdot9$ and $U_{eq}|O(4)| = 3\cdot1 \times 10^{-2}$ Å^2. It turns out that the observed values of U_{eq} at 322 K listed in Table 2 are still greater than the calculated ones by several tens of per cent or more. This fact suggests that the PO$_4$ tetrahedra in the intermediate phase are disordered while they are ordered in the low-temperature phase, indicating an order–disorder-type phase transition at 317 K.

Suzuki *et al.* (1983) reported that the high-temperature phase has the space group $P2_1/m$ with the basis lattice parameters a_o, b_o, c_o. Therefore, it follows that the sequence of successive phase transitions is as follows: $P2_1/m$ $(a_o,b_o,c_o) \to P2_1/c$ $(a_o,b_o,2c_o) \to P2_1$ $(2a_o,b_o,2c_o)$ with decreasing temperature. The high-temperature phase transition can be interpreted by b-directed average atomic displacements alternately along c to destroy the reflection symmetry and to double the parameter c. The low-temperature phase transition is interpreted by b-directed average atomic displacements to form the sublattice structure and to double the parameter a. In fact, considerable atomic displacements along b are found by comparing the structure of the intermediate phase to that of the reported low-temperature phase. The observed ferrielectric activity along b can be understood by sublattice formation.

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Structure of Ammonium Dihydrogenphosphite, NH$_4$H$_2$PO$_3$

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Abstract. $M_r = 99\cdot026$, monoclinic, $P2_1/c$, $a = 6\cdot273$ (1), $b = 8\cdot232$ (2), $c = 8\cdot902$ (2) Å, $\beta = 120\cdot11$ (2)°, $V = 397\cdot7$ (2) Å^3, $Z = 4$, $D_m = 1\cdot672$ (3), $D_x = 1\cdot654$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot54$ mm^{-1}, $F(000) = 208$, $T = 298$ K. Final $R = 0\cdot055$ for 1155 unique reflections. HPO$_3$ tetrahedra are connected through O–H$\cdots$O hydrogen bonds so that infinite chains of composition $(H_2PO_3)_n^{n-}$ are formed in the structure parallel to the z axis. The chains are further interwoven together by means of N–H$\cdots$O hydrogen bonds originating from the NH$_4^+$ ions, forming a three-dimensional network.

Introduction. The preparation of NH$_4$H$_2$PO$_3$ has been described by Amat (1891), and Ebert & Grospietsch (1968) found exact conditions for its formation from the solubility diagram of the (NH$_4$)$_2$HPO$_3$–H$_3$PO$_3$–H$_2$O system at 298 K. Preliminary crystal data (cell dimensions, space group, density) were determined by Norbert, Brun, Maurin & Barnoyer (1971). A crystal-structure study of NH$_4$H$_2$PO$_3$ was undertaken as part of an investigation of hydrogenphosphites.

Experimental. Spherical crystal, $r = 0\cdot8$ mm, $\mu r = 0\cdot43$, absorption ignored, Hilger & Watts diffractometer, lattice parameters refined from the setting of 29 centered high-angle reflections, 1233 reflections

measured by the learnt profile method (Clegg, 1981), $0 < 2\theta < 60°$, $h \in \langle -8, 7 \rangle$, $k \in \langle 0, 11 \rangle$, $l \in \langle 0, 12 \rangle$, no significant intensity variation ·in three standard reflections, 1155 unique reflections, 50 unobserved reflections $[I < 1.96\sigma_1(I)]$, heavy-atom method, H-atom positions from ΔF synthesis, the quantity $\sum w(F_o - |F_c|)^2$ minimized by full-matrix least squares, 71 parameters refined: scale factor, positions and aniso-tropic temperature factors of non-H atoms, positions and isotropic temperature factors of H atoms, isotropic extinction value $[g = 1.12$ (6) $\times 10^{-5}]$, $R = 0.055$, $wR = 0.076$, $w = 1/[\sigma^2(F_o) + 0.019461 F_o^2]$ derived from $\sigma(F_o)/|F_o| = \frac{1}{2}|\sigma_2(I)/I|$ and $\sigma_2(I) = [\sigma_1^2(I) + (0.06I)^2]^{1/2}$, $(\Delta/\sigma)_{max} = 0.09$, max. height in final ΔF map $0.5\,\mathrm{e\,\mathring{A}^{-3}}$, programs SHELX76 (Sheldrick, 1976)– source of scattering factors for neutral atoms, TLS (Sklenář & Petříček, 1981), ORTEP (Johnson, 1965), ICL 4–72 computer.

Discussion. The atomic parameters are given in Table 1 and the interatomic distances and angles in Table 2.* Every P atom is surrounded by three O atoms and one H atom in a tetrahedral configuration (Fig. 1). All values of the interatomic distances and angles are in accordance with the literature data, except for the O(1)–H(O1) distance, which is slightly shorter. During refinement the H(O1) atom always moved close to the O(1) atom regardless of the extinction-correction set.

The structure is related to those of LiH_2PO_3 [Philippot & Lindqvist, 1970 (X-ray data); Johansson & Lindqvist, 1976 (neutron data)] and KH_2PO_3 (Kratochvíl, Podlahová & Hašek, 1983). The phosphite tetrahedra are connected through the hydrogen bonds to form infinite chains of the $(H_2PO_3)_n^{n-}$ composition. The chains are held together by means of the electrostatic forces between the chains and the Li^+ or K^+ ions. In the $NH_4H_2PO_3$ structure the chains are parallel to the z axis and are formed through the O(1)–H(O1)···O(2) interaction.

The NH_4^+ tetrahedron is slightly distorted, the N–H distances varying in the range of usual values. The ammonium ion is firmly fixed in the structure by means of four N–H···O hydrogen bonds, which prevent free ammonium-ion rotation at 298 K. Only the O(2) and O(3) atoms act as proton acceptors; the O(1) atom does not take part in the N···O hydrogen bonding.

All hydrogen bonds (O–H···O and N–H···O types) give rise to a three-dimensional network in the structure. A similar structural motif with fixed NH_4^+ positions was found in $(NH_4)_2HPO_3.H_2O$ (Rafiq, Durand & Cot, 1982) and $(NH_4)_2Sn(HPO_3)_2$ (Yamaguchi & Lindqvist, 1982).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39156 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic thermal parameters* $(\times 10^4$, *for* H $\times 10^3)$ *with e.s.d.'s in parentheses*

U_{eq} corresponds to non-H atoms, U_{iso} to H atoms. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{eq},U_{iso}(\mathring{A}^2)$
P	−645 (1)	1090·1 (4)	1806·1 (5)	254 (4)
O(1)	−2197 (3)	2390 (2)	374 (2)	546 (9)
O(2)	−1425 (4)	1226 (2)	3133 (2)	436 (8)
O(3)	2046 (3)	1213 (2)	2443 (2)	400 (7)
N	4065 (3)	3723 (2)	1285 (2)	332 (8)
H(P)	−107 (8)	−41 (5)	131 (6)	56 (9)
H(O1)	−180 (7)	278 (4)	−24 (5)	45 (7)
H(1N)	340 (11)	280 (6)	164 (8)	83 (13)
H(2N)	342 (8)	339 (4)	5 (5)	55 (9)
H(3N)	315 (7)	452 (4)	146 (5)	46 (8)
H(4N)	568 (12)	415 (8)	197 (10)	108 (20)

Table 2. *Bond distances* $(\mathring{A})$ *and angles* $(°)$

Symmetry code: (i) $1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (ii) $1 - x$, $-y$, $1 - z$; (iii) $1 + x, y, z$.

P–O(1)	1·573 (1)	N–H(1N)	0·99 (6)
–O(2)	1·492 (1)	–H(2N)	1·00 (4)
–O(3)	1·491 (1)	–H(3N)	0·93 (4)
–H(P)	1·29 (4)	–H(4N)	0·95 (7)
O(1)–H(O1)	0·78 (4)		

O(1)–P–O(2)	106·0 (1)	H(1N)–N–H(2N)	98 (4)
O(1)–P–O(3)	112·6 (1)	H(1N)–N–H(3N)	95 (4)
O(1)–P–H(P)	116 (2)	H(1N)–N–H(4N)	124 (5)
O(2)–P–O(3)	116·9 (1)	H(2N)–N–H(3N)	116 (3)
O(2)–P–H(P)	105 (2)	H(2N)–N–H(4N)	121 (5)
O(3)–P–H(P)	101 (2)	H(3N)–N–H(4N)	101 (4)

O···O and N···O distances in the hydrogen bonds

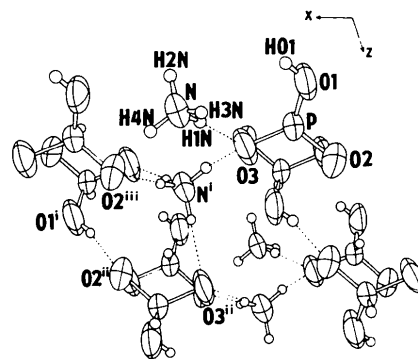| O(1^i)···O(2^{ii})	2·546 (3)	N^i···O(3^{ii})	2·993 (2)
N···O(3)	2·872 (3)	N^i···O(2^{iii})	2·849 (3)
N^i···O(3)	2·943 (3)		

Fig. 1. Perspective view of the unit-cell contents along the Y axis. The broken lines represent hydrogen bonding.

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Structure of a Second Form of 1,2;2,3-Di-μ-hydrido-μ₃-tetracarbonylferrio-*cyclo*-tris(tricarbonylruthenium)(3Ru–Ru), H₂FeRu₃(CO)₁₃

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Abstract. $M_r = 725 \cdot 21$, monoclinic, $C2/c$, $a = 31 \cdot 418$ (6), $b = 9 \cdot 724$ (3), $c = 13 \cdot 816$ (1) Å, $\beta = 110 \cdot 83$ (1)°, $V = 3945 \cdot 0$ Å^3, $Z = 8$, $D_x = 2 \cdot 442$ g cm^{-3}, $F(000) = 2736$, Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å, $\mu = 29 \cdot 970$ cm^{-1}, room temperature, $R = 0 \cdot 043$ for 3546 reflections. Crystals were grown from a tetrahydrofuran (THF) solution at room temperature to which Et$_2$O was added. The molecule contains a distorted tetrahedral FeRu$_3$ cluster. The molecules are aligned parallel to the plane (1 1 1).

Introduction. From the attempted synthesis of H$_2$Fe$_3$Ru$_3$(CO)$_{18}$ by protonating with HCl an equimolar mixture of K$_2$[Ru$_3$(CO)$_{11}$] and Fe$_3$(CO)$_{12}$ in THF a product was obtained which upon crystallization by adding Et$_2$O proved to be a previously unreported crystalline form of the known compound H$_2$FeRu$_3$(CO)$_{13}$ (Gilmore & Woodward, 1971). The previous description of this compound, form (I) (space group $P2_1/a$, two independent molecules in the asymmetric unit), differs markedly in shape and color from form (II) (space group $C2/c$, one independent molecule in the asymmetric unit) reported here. The more accurate and more extensive data obtained in the present study enable us to determine with greater accuracy and precision the molecular parameters of H$_2$FeRu$_3$(CO)$_{13}$ and to elucidate molecular features which were tentatively suggested in the earlier report. Furthermore, it is of interest to examine and compare the packing of molecules in each crystalline form.

Experimental. Crystal $0 \cdot 12 \times 0 \cdot 30 \times 0 \cdot 35$ mm, dark brown, plate-like. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions: least-squares fitting from 24 reflections well distributed in reciprocal space, 2θ range 15–30°. Data collected by $2\theta{:}\theta$ scan mode, 2θ range 4–55°. Intensities in hkl and $h\bar{k}l$ octants measured. Total of 4885 reflections collected, 4512 unique; 3546 with $I > 3 \cdot 0\sigma(I)$ used in structure refinement. Six standard intensities: max. variation 0·03. Intensities corrected for Lorentz and polarization effects and also for absorption by using the method of Gaussian quadrature with grid $18 \times 14 \times 4$ points; max. and min. transmission coefficients 0·7352 and 0·3424. Analytical form of scattering factors for neutral atoms used, f' and f'' terms included for all atoms (Cromer & Waber, 1974). All crystallographic computations carried out on a PDP 11/44 computer using the Enraf–Nonius *Structure Determination Package*. Intensity statistics indicated the space group likely to be the centrosymmetric $C2/c$, rather than Cc. Structure solved by *MULTAN*11/82 (Frenz, 1982; Hull & Irwin, 1978; Yao, 1981). Full-matrix least-squares refinement (anisotropic thermal parameters) minimizing $\sum w(|F_o| - |F_c|)^2$; $w = [\sigma(I)^2 + (pI)^2]^{-1/2}$, with $p = 0 \cdot 06$ chosen to make $\sum w\Delta F^2$ uniformly distributed in $|F_o|$. A difference Fourier synthesis gave the coordinates of two bridging H atoms. These were included with isotropic $B = 4 \cdot 5$ Å^2. No H parameters were refined. Final $R = 0 \cdot 043$ and $R_w = 0 \cdot 064$. Final difference Fourier map showed no significant features, with a max. peak height of 0·66 e Å^{-3} in the vicinity of the Ru atom. $(\Delta/\sigma)_{max} = -0 \cdot 15$.

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