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## Structure Determination from Small Crystals of Two Aluminophosphates, CrAPO-14 and SAPO-43

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### Abstract

Small single crystals,  $ca\ 10^5\ \mu\text{m}^3$ , of two aluminophosphates have been used to determine their structures. Both compounds were synthesized with the aim of incorporating chromium into the framework, and for CrAPO-14 the X-ray diffraction results show that this has been achieved. For CrAPO-14,  $\text{Al}_{3.96}\text{Cr}_{0.04}(\text{PO}_4)_4(\text{OH})\cdot\text{C}_3\text{H}_{10}\text{N}\cdot\text{H}_2\text{O}$ , data recorded on a Rigaku AFC-5R diffractometer ( $\text{Cu}\ K\alpha$ ) and, independently, on an Enraf-Nonius FAST diffractometer ( $\text{Mo}\ K\alpha$ ), showed the structure to be like that of GaPO-14 [Parise (1986). *Acta Cryst.* **C42**, 670–673]; aluminium atoms occupy four-, five- and six-coordinated sites, and 4–5% of the aluminium in the six-coordinate site is replaced by chromium. For SAPO-43,  $\text{Al}_2(\text{PO}_4)_2(\text{C}_3\text{H}_{10}\text{N})$ , data were recorded independently on the AFC-5R ( $\text{Cu}\ K\alpha$ ) and on a FAST diffractometer with synchrotron radiation of wavelength  $0.895\ \text{\AA}$ ; the structure is like that of gismondine [Alberti & Vezzalini (1979). *Acta Cryst.* **B35**, 2866–2869], but replacement of Al by Cr to a significant extent could not be established. Framework Al, P and O atoms are located with e.s.d.'s of 0.001–0.005  $\text{\AA}$ , template atoms with e.s.d.'s

of  $ca\ 0.01\ \text{\AA}$  in CrAPO-14, and larger e.s.d.'s in SAPO-43 where there is disorder in the template-molecule position. In all these respects the two independent determinations for each structure are in agreement. The effectiveness of the different methods of intensity-data collection is compared.

### Introduction

The synthesis and characterization of aluminophosphates and related materials with catalytic properties provide considerable challenges. In the synthetic program at Ljubljana University, materials prepared include aluminophosphates (ALPO's), with compositions  $\text{Al}_2\text{O}_3\cdot\text{P}_2\text{O}_5\cdot xR\cdot y\text{H}_2\text{O}$  where  $R$  is a template molecule (usually an amine), and further aluminophosphates in which some aluminium and sometimes also phosphorus is replaced by silicon, known as SAPO's; in other materials small amounts of metals, usually transition metals, replace aluminium or phosphorus. These chemical variations lead to a wide range of structure types; some can be related to zeolite structure types and others are new (Flanigen, Lok, Patton & Wilson, 1986; Bennett & Marcus, 1988; Rajić, Kaučič & Stojaković, 1990; Nardini,

Randaccio, Kaučič & Rajić, 1991; Cheetham, Harding, Rizkallah, Kaučič & Rajić, 1991).

Preliminary characterization of a new aluminophosphate should include chemical analysis and powder diffraction, and will sometimes allow the material to be assigned to an already known structure type, thus defining the connectivity of the framework atoms. Full structural characterization can be considered in three stages: (1) the detailed description of the framework geometry including interatomic distances and angles, (2) the definition of template-molecule position(s), and (3) the identification of sites at which transition-metal ions have replaced a small and unknown proportion of the aluminium or phosphorus atoms. To answer these questions from diffraction experiments is progressively more difficult for stages (1) to (3).

Very high resolution powder diffraction with synchrotron radiation (SR) has had great success recently with a number of zeolite and ALPO materials (e.g. McCusker, Baerlocher, Jahn & Bulow, 1991; Briscoe, Johnson, Shannon, Kokotailo & McCusker, 1988) but is unlikely to get far beyond stage (1) when moderately complicated unit cells are involved. Single-crystal methods are essential, but zeolite and ALPO materials are well known to yield only rather small single crystals; also common in these materials are small deviations of the framework geometry from higher symmetry arrangements, twinning or disorder, and disorder of template-molecule positions. In addition to these difficulties, it should be noted that the establishment of the substitution of chromium for, say, 10% of the Al atoms at one site is equivalent to looking for one electron, and also that it will be more difficult than locating an H atom since it is at a site where there is already an atom (or ion). Detecting the partial replacement of phosphorus by silicon would be even more difficult.

Here we report four data-collection experiments on two different ALPO's. The primary aim was the characterization of the ALPO's, but the experiments also allow some evaluation of the different methods and their potential in these crystallographically difficult problems. For CrAPO-14 one data collection was performed on the FAST area-detector diffractometer with Mo  $K\alpha$  radiation, at Queen Mary and Westfield College, London (by courtesy of Professor M. B. Hursthouse); this used 'default' conditions for small molecules. A second data collection was carried out on the Rigaku AFC-5R diffractometer at Manchester University; the conditions were optimized as far as possible for the problem. With both data sets there was no difficulty in establishing good framework parameters and the template-molecule positions agree; there is agreement on the presence of chromium at one of the four crystallographically distinct aluminium sites, but the extent of

this substitution is very close to the error level. For SAPO-43 the data collection was first carried out with SR and the FAST area-detector diffractometer at SERC Daresbury Laboratory in 1989; the options chosen for exposure time *etc.* were suitable for a typical 'small-molecule' crystal, and time has not been available to repeat this data collection with conditions optimized for the more difficult question of characterization, *i.e.* the identification of possible chromium substitution sites. For the same crystal, data were recorded on the Rigaku AFC-5R diffractometer; in this case the conditions were optimized as far as possible for the problem. There is no difficulty in producing good framework geometry, and both experiments indicate a poorly ordered template molecule in the same region of the pore; the extent of chromium substitution is very small, and probably not significant. Chemical analysis indicated the presence of some silicon, but we have not attempted to verify this.

### Experimental

Crystalline CrAPO-14 was prepared in a teflon-lined autoclave under static conditions at 468 K for 7 days. The reaction gel was made up from aluminium isopropoxide, phosphoric acid, isopropylamine and chromium trioxide, CrO<sub>3</sub>, which had been reduced with ethanol in aqueous solution in the presence of phosphoric acid (Vasovic & Stojakovic, 1988); components were in the proportions Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, 0.3Cr<sub>2</sub>O<sub>3</sub>, 10PrNH<sub>2</sub>, 50H<sub>2</sub>O.

Crystalline SAPO-43 was prepared in teflon-lined autoclaves, under static conditions at 433 K for 5 days. In addition to all the above components the reaction gel contained a colloidal solution of SiO<sub>2</sub> (40%, ludox-AS, Du Pont), and the components were in the proportions Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, 0.7SiO<sub>2</sub>, 0.35Cr<sub>2</sub>O<sub>3</sub>, 10PrNH<sub>2</sub>, 50H<sub>2</sub>O.

Crystal data and information on data collection is summarized in Table 1. Both structures were determined (from both data sets) by direct methods using *SHELXS* (Sheldrick, 1986); other details of data collection and refinement are given below.

#### CrAPO-14/AFC-5R

Diffraction data were recorded on the Rigaku AFC-5R diffractometer at Manchester University, with a 12 kW rotating-anode source:  $\omega, 2\theta$  scans, with scan width  $(1.10 + 0.30 \tan \theta)^\circ$  and scan speed  $8^\circ \text{ min}^{-1}$ , three standard reflections did not change significantly; empirical absorption correction applied, minimum and maximum transmission factors 0.76, 1.00. After structure solution and some refinement (*TEXSAN*; Molecular Structure Corporation, 1985) the vibration parameter of Al(4) was  $0.0103(2) \text{ \AA}^2$ , markedly lower than the other

Table 1. *Crystal data and data-collection parameters*

	CrAPO-14		SAPO-43	
Formula	Al <sub>1.96</sub> Cr <sub>0.04</sub> (PO <sub>4</sub> ) <sub>4</sub> (OH) <sub>2</sub> C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> ·H <sub>2</sub> O		Al <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (C <sub>3</sub> H <sub>10</sub> N)	
Formula weight	583.95		304.02	
<i>a</i> (Å)	9.668 (1)	9.6455 (13)	14.158 (2)	14.052 (5)
<i>b</i> (Å)	9.6572 (8)	9.6406 (17)	14.441 (1)	14.360 (5)
<i>c</i> (Å)	10.623 (1)	10.5987 (27)	10.062 (2)	10.012 (3)
$\alpha$ (°)	74.161 (8)	74.159 (6)	—	—
$\beta$ (°)	74.675 (8)	74.714 (10)	—	—
$\gamma$ (°)	88.974 (8)	88.955 (9)	—	—
<i>V</i> (Å <sup>3</sup> )	918.7	913.1	2057.3	2020.3
System, space group	Triclinic, <i>P</i> $\bar{1}$		Orthorhombic, <i>Fddd</i>	
<i>Z</i>	2		8	
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	2.1		1.96	
<i>F</i> (000)	588		1240	
Diffractometer	Rigaku	Enraf-Nonius	Rigaku	Enraf-Nonius
Radiation source	AFC-5R	FAST	AFC-5R	FAST
Wavelength (Å)	Cu <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$	SR
$\mu$ (cm <sup>-1</sup> )	1.54178	0.71069	1.54178	0.895 (5)
Crystal size (mm)	68.3	6.34	59.4	11.2
Reflections for unit cell	0.12 × 0.05 × 0.02	0.11 × 0.07 × 0.02	0.05 × 0.03 × 0.05	0.05 × 0.03 × 0.05
	22	50	25	223
		79 < 2 $\theta$ < 80°		21 < 2 $\theta$ < 80°
2 $\theta$ <sub>max</sub> (°)	160	45.5	160	59
<i>d</i> <sub>min</sub> (Å)	0.78	0.92	0.78	0.91
Collimator (mm)	0.5	0.3	0.5	0.2
Crystal-detector distance (mm)	400	45.5	400	40.0
Refinement				
Reflections measured	4027	4381	3963	3283
				[830 with <i>F</i> > 3.5 $\sigma$ ( <i>F</i> )]
Number of unique reflections	3793	2338	607	310
<i>R<sub>int</sub></i>	0.026	0.100	0.125	0.053
Number used in refinement	3032	1259	375	287
Criterion	<i>I</i> > 3 $\sigma$ ( <i>I</i> )	<i>F</i> > 3 $\sigma$ ( <i>F</i> )	<i>I</i> > 3 $\sigma$ ( <i>I</i> )	<i>F</i> > 6 $\sigma$ ( <i>F</i> )
Weights <i>w</i> <sup>-1</sup>	$\sigma^2(F) + 0.0009F^2$	$\sigma^2(F)$	$\sigma^2(F)^*$	$\sigma^2(F) + 0.00017F^2$
Number of parameters	280	233	53	33
Final <i>R</i>	0.043	0.043	0.047	0.052
<i>wR</i>	0.063	0.045	0.056	0.054
Max. shift/e.s.d.	0.04	0.18	0.32	0.36
Max. and min. electron density (e Å <sup>-3</sup> )	0.51, -0.59	0.62, -0.63	0.49, -0.47	0.58, -0.58
<i>S</i> (goodness of fit)	2.21	0.38	2.14	1.09

\* *p* = 0.03 in evaluating  $\sigma^2(F)$  [see *TEXSAN* (Molecular Structure Corporation, 1985)].

three Al atoms [0.0122 (2)–0.0142 (2) Å<sup>2</sup>], whereas all four phosphorus atoms had *U* values in the range 0.0123 (2)–0.0132 (2) Å<sup>2</sup>. Refinement was continued to convergence with all non-H atoms anisotropic except Al(4), H atoms on the isopropylamine template molecule at calculated positions, and H atoms on the water molecule at difference map positions. The Al(4) site was then treated as [xCr + (1 - x)Al] with its vibration parameter fixed at *U*<sub>iso</sub> = 0.0127 Å<sup>2</sup>, equal to that of the other Al's; refinement of *x* converged with *x* = 0.043 (4). Finally *x* was fixed at 0.043 and refinement of all other parameters continued, as above. A subsequent difference map showed a peak of 0.8 e Å<sup>-3</sup> at a reasonable distance from O(9) for an H atom, and this was included in the final refinement with an isotropic vibration parameter. Neutral-atom scattering factors with dispersion corrections (*International Tables for X-ray Crystallography*, 1974, Vol. IV, Tables 2.2A, 2.3.1) were used.

#### CrAPO-14/FAST

Diffraction data were recorded on the Enraf-Nonius FAST (television detector) diffractometer at

Queen Mary and Westfield College, London (by courtesy of Professor M. B. Hursthouse), with a rotating-anode Mo *K* $\alpha$  source; three batches of data with ranges of goniostat angles chosen to cover a hemisphere of reciprocal space, detector 2 $\theta$  = -18°, 0.15° frames each accumulated for 20 s. The images were processed, on line, by *MADNES* software (Messerschmidt & Pflugrath, 1987) to give *hkl F*<sub>obs</sub> data; the effective mosaic spread was 0.9°. No absorption corrections were applied. Refinement was with *SHELX* (Sheldrick, 1976): Al and P were treated as neutral atoms (scattering factors as in *SHELX*); water and isopropylamine molecules were located in the electron-density difference map; the H atoms of isopropylamine were placed in calculated positions with one thermal parameter for all, but those of water and the hydroxyl group were not located; O atoms were assigned anisotropic vibration parameters, all others were isotropic; for weights, *w*<sup>-1</sup> = [ $\sigma(F)^2 + gF^2$ ], *g* refined to zero suggesting that values of  $\sigma(F)$  from *MADNES* give good estimates of errors in *F*. When no Cr substitution was assumed, refinement gave the *U* value for Al(4) = 0.0046 (7) Å<sup>2</sup>, much lower than the other three, [0.0076 (7), 0.0089 (8) and 0.0107 (8) Å<sup>2</sup>] suggesting

that this is the most likely site of Cr substitution. Therefore in final refinement rounds  $U$  for this site was fixed at  $0.010 \text{ \AA}^2$ , and the occupancy by Cr,  $x$  as above, refined; this gave  $x = 0.05$  (1).

#### SAPO-43/AFC-5R

Data collection by  $\omega, 2\theta$  scans, with scan width  $(1.21 + 0.30 \tan \theta)^\circ$  and scan speed  $2$  or  $4^\circ \text{ min}^{-1}$ ; weak reflections [ $I < 10\sigma(I)$ ] rescanned once or twice. The intensities of three standard reflections, measured every 150 reflections, fell by 10% over the data-collection period, a linear correction was applied to all reflections to compensate for this. (The reason for the fall off is not known, but possibly it was radiation damage.) No absorption corrections were applied. Density in the channel region indicated a highly disordered isopropylamine template molecule.

In the model used, the central C atom, C(2), is disordered over two symmetry-equivalent sites, as are the other carbon atoms [C(1), C(1)'], while the N atom is disordered over four symmetry equivalent sites; this last site was assigned as nitrogen since it is at a distance  $2.9 \text{ \AA}$  from O(1), suitable for hydrogen bonding. Refinement (TEXSAN; Molecular Structure Corporation, 1985) with anisotropic vibration parameters for Al, P and O gave the  $U$  value for Al,  $0.012$  (1)  $\text{\AA}^2$ , slightly lower than that for P,  $0.014$  (1)  $\text{\AA}^2$ ; various refinements of site occupancy were explored, but no significant amount of Cr substitution could be shown. Neutral-atom scattering factors were as in (1).

#### SAPO-43/FAST

Diffraction data were recorded on the FAST diffractometer on workstation 9.6 at the SRS (SERC, Daresbury). The crystal was rotated through  $200^\circ$  in  $\varphi$  (spindle);  $1^\circ$  frames, 20 s exposure time each, SRS at 2 GeV, 219 mA, detector  $2\theta = 28^\circ$ . The incident beam intensity was monitored continuously and intensity data were corrected for its decrease with time. Subsequent (off line) processing of this recorded data was done by MADNES (Messerschmidt & Pflugrath, 1987), with modifications for synchrotron radiation work by Papiz (1989). No absorption corrections. After solution, Al and P could easily be distinguished on the basis of their distances from oxygen [1.73 (7) for Al and 1.53 (6)  $\text{\AA}$  for P, before refinement], and then by refinement of their site occupancies. Subsequently electron density in the channel region was interpreted as isopropylamine disordered over two positions related by a twofold axis, and with the  $-\text{NH}_2$  group further disordered over two sites (consistent with the AFC-5R data). Lastly the site occupancy of the Al atom was included in the refinement to see whether

Table 2. Atomic parameters for CrAPO-14, with standard deviations

The first line gives values derived from AFC-5R data and the second from FAST data.

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i \cdot a_j, \text{ when derived from AFC-5R data.}$$

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3 \text{ when derived from FAST data.}$$

	$x$	$y$	$z$	$U_{\text{eq}}$ or $U$
P(1)	0.5027 (1)	-0.0312 (1)	-0.2055 (1)	0.0130 (8)
	0.5029 (3)	-0.0311 (4)	-0.2057 (3)	0.0082 (7)
P(2)	0.7243 (1)	-0.4759 (1)	0.0972 (1)	0.0122 (8)
	0.7241 (3)	-0.4761 (4)	0.0972 (3)	0.0087 (7)
P(3)	0.9658 (1)	-0.7996 (1)	0.3503 (1)	0.0123 (8)
	0.9660 (3)	-0.7987 (4)	0.3504 (3)	0.0077 (7)
P(4)	1.1872 (1)	-0.2321 (1)	0.1401 (1)	0.0127 (8)
	1.1871 (3)	-0.2319 (4)	0.1399 (3)	0.0082 (7)
Al(1)	0.7686 (1)	-0.7865 (1)	0.1610 (1)	0.0122 (9)
	0.7684 (3)	-0.7866 (4)	0.1611 (3)	0.0086 (8)
Al(2)	0.5152 (1)	-0.2247 (1)	0.0777 (1)	0.0141 (10)
	0.5157 (3)	-0.2243 (4)	0.0771 (4)	0.0104 (8)
Al(3)	0.8218 (1)	-0.9514 (1)	0.6579 (1)	0.0124 (9)
	0.8215 (3)	-0.9512 (4)	0.6578 (3)	0.0072 (7)
Al(4)†	1.0228 (1)	-0.5005 (1)	0.1329 (1)	0.0127 (3)
	1.0228 (3)	-0.5004 (4)	0.1325 (3)	0.0072 (7)
Cr(1)†	1.0228 (1)	-0.5005 (1)	0.1329 (1)	0.0127 (3)
	1.0228 (3)	-0.5004 (4)	0.1325 (3)	0.0072 (7)
O(1)	0.8329 (3)	-0.4468 (3)	0.1695 (3)	0.0152 (30)
	0.8304 (7)	-0.4466 (8)	0.1696 (7)	0.0085 (43)
O(2)	0.5963 (3)	-0.3830 (3)	0.1229 (3)	0.0177 (30)
	0.5961 (7)	-0.3839 (9)	0.1228 (8)	0.0132 (47)
O(3)	1.1993 (3)	-0.1569 (3)	-0.0095 (3)	0.0165 (30)
	1.1995 (7)	-0.1568 (8)	-0.0102 (8)	0.0112 (45)
O(4)	0.4474 (4)	0.0932 (4)	-0.1474 (4)	0.0253 (30)
	0.4483 (7)	0.0924 (9)	-0.1488 (8)	0.0206 (51)
O(5)	0.3881 (3)	-0.0869 (3)	0.2544 (3)	0.0152 (30)
	0.3895 (7)	-0.0872 (8)	-0.2548 (7)	0.0071 (44)
O(6)	0.6627 (3)	-0.6341 (3)	0.1616 (3)	0.0165 (30)
	0.6623 (6)	-0.6332 (9)	0.1623 (8)	0.0103 (44)
O(7)	1.0074 (3)	-0.6407 (3)	0.2927 (3)	0.0139 (30)
	1.0076 (7)	-0.6409 (8)	0.2928 (7)	0.0086 (44)
O(8)	0.8945 (4)	-0.8309 (3)	0.5021 (3)	0.0215 (30)
	0.8948 (7)	-0.8325 (9)	0.5016 (8)	0.0156 (49)
O(9)	0.9516 (3)	-0.6398 (3)	0.0526 (3)	0.0127 (30)
	0.9531 (7)	-0.6403 (8)	0.0529 (7)	0.0061 (42)
O(10)	0.7892 (3)	-0.4501 (3)	-0.0555 (3)	0.0152 (30)
	0.7883 (7)	-0.4500 (9)	-0.0552 (7)	0.0125 (46)
O(11)	0.8645 (5)	-0.8519 (3)	0.2827 (3)	0.0203 (30)
	0.8649 (7)	-0.8516 (9)	0.2827 (8)	0.0168 (49)
O(12)	0.3351 (3)	-0.2830 (3)	0.1538 (3)	0.0190 (30)
	0.3360 (7)	-0.2844 (8)	0.1539 (8)	0.0137 (46)
O(13)	1.1457 (3)	-0.1178 (3)	0.2169 (3)	0.0177 (30)
	1.1471 (7)	-0.1191 (8)	0.2158 (8)	0.0141 (47)
O(14)	0.6385 (3)	0.0198 (3)	-0.3220 (3)	0.0190 (30)
	0.6368 (7)	0.0201 (8)	-0.3211 (8)	0.0124 (47)
O(15)	0.5460 (4)	-0.1518 (4)	-0.0963 (3)	0.0228 (30)
	0.5455 (7)	-0.1503 (10)	-0.0975 (8)	0.0208 (51)
O(16)	1.0798 (3)	-0.3591 (3)	0.1979 (3)	0.0152 (30)
	1.0807 (7)	-0.3582 (8)	0.1967 (7)	0.0112 (45)
O(17)	1.1031 (3)	-0.8824 (3)	0.3311 (3)	0.0215 (30)
	1.1044 (7)	-0.8830 (9)	0.3315 (8)	0.0171 (49)
O(w)	0.8582 (5)	-0.1528 (5)	0.0103 (5)	0.0557 (40)
	0.8561 (9)	-0.1521 (11)	0.0138 (11)	0.0427 (68)
N(1)	0.3427 (6)	-0.6228 (6)	0.2871 (5)	0.0355 (40)
	0.3425 (9)	-0.6245 (12)	0.2886 (11)	0.0266 (68)
C(1)	0.3390 (10)	-0.6170 (10)	0.4267 (7)	0.0671 (80)
	0.3408 (21)	-0.6160 (24)	0.4245 (17)	0.0772 (157)
C(2)	0.3830 (20)	-0.7470 (10)	0.5060 (10)	0.1393 (127)
	0.3905 (23)	-0.7440 (25)	0.5013 (18)	0.1214 (219)
C(3)	0.2140 (10)	-0.5530 (10)	0.4891 (9)	0.1013 (127)
	0.2238 (22)	-0.5589 (25)	0.4866 (18)	0.1108 (209)

† Site occupancy together = 1.00 (see text).

partial substitution of Al by Cr had occurred; neutral Al-, P- and O-atom scattering factors were used,  $U_{\text{iso}}$  for Al was fixed at  $0.0077 \text{ \AA}^2$  [*i.e.* equal to P(2)], but no significant Cr occupancy was found. Thus in the final rounds of refinement the two O atoms were assigned anisotropic vibration parameters; isotropic vibration parameters were used for all other atoms and H atoms were not included.

Table 3. Atomic parameters for SAPO-43, with standard deviations

The first line gives values derived from AFC-5R data and the second from FAST data.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_{ij}, \text{ when derived from AFC-5R data.}$$

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3 \text{ when derived from FAST data.}$$

	x	y	z	U or $U_{eq}$
P(1)	0.4670 (1) 0.4669 (1)	1/8	1/8	0.0142 (9) 0.0071 (8)
Al(1)	5/8	0.2765 (1) 0.2766 (2)	1/8	0.0119 (10) 0.0048 (8)
O(1)	0.5292 (3) 0.5292 (3)	0.2078 (3) 0.2076 (3)	0.0825 (4) 0.0819 (4)	0.024 (3) 0.018 (2)
O(2)	0.4024 (3) 0.4027 (3)	0.0976 (3) 0.0975 (3)	0.0076 (4) 0.0077 (4)	0.030 (3) 0.020 (2)
N(1)†	0.705 (4) 0.707 (2)	0.034 (2) 0.038 (2)	-0.341 (4) -0.336 (3)	0.10 (3) 0.07 (1)
C(1)†	0.593 (3) 0.595 (2)	0.151 (2) 0.147 (3)	-0.264 (3) -0.255 (3)	0.16 (4) 0.14 (1)
C(2)†	5/8	0.092 (5) 0.092 (3)	-3/8	0.15 (6) 0.13 (2)

† Site occupancy = 0.25 for N, 0.50 for C.

Table 4. Comparison of coordinates obtained by different methods

		x	y	z	
(a) CrAPO-14	Al and P	Mean difference	0.0002	0.0003	0.0003
		Max. difference	0.0005	0.0009	0.0006
		E.s.d. $\times 10^4$	3	4	3-4
Framework O	Mean difference	0.0007	0.0007	0.0006	
	Max. difference	0.0025	0.0016	0.0014	
	E.s.d. $\times 10^4$	7	8-10	7-8	
C, N and O (water)	Mean difference	0.0039	0.0025	0.0028	
	Max. difference	0.0098	0.0059	0.0043	
	E.s.d. $\times 10^4$	9-23	11-25	11-18	
(b) SAPO-43	Al, P and framework O	Mean difference	0.0002	0.0002	0.0003
		Max. difference	0.0002	0.0005	0.0004
		E.s.d. $\times 10^4$	3	3	4
3 Template atoms	Mean difference	0.002	0.002	0.005	
	Max. difference	0.002	0.003	0.006	
	E.s.d. $\times 10^4$	4	3	4	

## Results and discussion

Tables 2 and 3 give atom parameters for the two structures, which are illustrated in Figs. 1 and 2. The two structure determinations for each are in good agreement, as shown in Table 4. Selected distances and angles are given in Tables 5 and 6; these have been calculated from the AFC-5R parameters.\*

### The framework structures

In CrAPO-14 all four independent P atoms are tetrahedrally coordinated to oxygen, Al(2) and Al(3) are tetrahedral, while Al(1) and Al(4) are five- and six-coordinated respectively. The structure is a close analogue of GaPO-14 (Parise, 1986) with Al

\* Lists of interatomic distances and angles from all four determinations, together with anisotropic vibration parameters, and observed and calculated structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55788 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0541]

Table 5. Interatomic distances (Å) and angles (°) for CrAPO-14

(a) Selected distances involving non-H atoms			
O(5)—P(1)	1.505 (3)	O(14)—P(1)	1.526 (3)
O(4)—P(1)	1.523 (3)	O(15)—P(1)	1.543 (3)
O(6)—P(2)	1.550 (3)	O(1)—P(2)	1.525 (3)
O(2)—P(2)	1.525 (3)	O(10)—P(2)	1.528 (3)
O(8)—P(3)	1.523 (3)	O(7)—P(3)	1.506 (3)
O(17)—P(3)	1.534 (3)	O(11)—P(3)	1.522 (3)
O(16)—P(4)	1.503 (3)	O(13)—P(4)	1.533 (3)
O(3)—P(4)	1.530 (3)	O(12)—P(4)	1.534 (3)
O(5 <sup>m</sup> )—Al(1)	1.838 (3)	O(6)—Al(1)	1.778 (3)
O(9)—Al(1)	2.143 (3)	O(11)—Al(1)	1.760 (3)
O(3 <sup>m</sup> )—Al(1)	1.788 (3)	O(4 <sup>m</sup> )—Al(2)	1.722 (3)
O(12)—Al(2)	1.745 (3)	O(2)—Al(2)	1.714 (3)
O(15)—Al(2)	1.733 (3)	O(8)—Al(2)	1.718 (3)
O(13 <sup>m</sup> )—Al(3)	1.740 (3)	O(17 <sup>m</sup> )—Al(3)	1.736 (3)
O(14 <sup>m</sup> )—Al(3)	1.747 (3)	O(7)—Al(4)	1.832 (3)
O(16)—Al(4)	1.840 (3)	O(9)—Al(4)	1.996 (3)
O(1)—Al(4)	1.868 (3)	O(9 <sup>m</sup> )—Al(4)	2.020 (3)
O(10 <sup>m</sup> )—Al(4)	1.898 (3)	C(1)—N(1)	1.49 (1)
C(1)—C(3)	1.43 (1)	C(1)—C(2)	1.44 (1)
(b) Range of bond angles at tetrahedral atoms			
P(1)	106.5 (2)—110.8 (2)	P(4)	106.6 (2)—112.9 (2)
P(2)	105.6 (2)—112.8 (2)	Al(2)	100.4 (2)—114.8 (2)
P(3)	108.3 (2)—112.9 (2)	Al(3)	106.9 (2)—112.2 (2)
(c) Selected bond angles			
O(3 <sup>m</sup> )—Al(1)—O(5 <sup>m</sup> )	94.8 (1)	O(3 <sup>m</sup> )—Al(1)—O(6)	114.6 (2)
O(3 <sup>m</sup> )—Al(1)—O(11)	121.9 (2)	O(5 <sup>m</sup> )—Al(1)—O(6)	92.3 (1)
O(5 <sup>m</sup> )—Al(1)—O(9)	179.8 (1)	O(5 <sup>m</sup> )—Al(1)—O(11)	94.1 (1)
O(1)—Al(4)—O(7)	97.9 (1)	O(1)—Al(4)—O(9)	84.6 (1)
O(1)—Al(4)—O(9 <sup>m</sup> )	85.7 (1)	O(1)—Al(4)—O(16)	91.9 (1)
O(7)—Al(4)—O(9)	91.3 (1)	O(9)—Al(4)—O(9 <sup>m</sup> )	84.6 (1)
O(9)—Al(4)—O(10 <sup>m</sup> )	86.9 (1)	O(9)—Al(4)—O(16)	174.7 (1)
O(9 <sup>m</sup> )—Al(4)—O(10 <sup>m</sup> )	83.7 (1)		
P(2)—O(1)—Al(4)	124.4 (2)	Al(1 <sup>m</sup> )—O(9 <sup>m</sup> )—Al(4)	125.2 (2)
P(2)—O(2)—Al(2)	149.9 (2)	Al(4 <sup>m</sup> )—O(9 <sup>m</sup> )—Al(4)	95.4 (1)
P(4 <sup>m</sup> )—O(3 <sup>m</sup> )—Al(1)	135.1 (2)	P(2 <sup>m</sup> )—O(10 <sup>m</sup> )—Al(4)	123.5 (2)
P(1 <sup>m</sup> )—O(4 <sup>m</sup> )—Al(2)	146.9 (2)	Al(1)—O(11)—P(3)	140.9 (2)
P(1 <sup>m</sup> )—O(5 <sup>m</sup> )—Al(1)	130.7 (2)	Al(2 <sup>m</sup> )—O(12 <sup>m</sup> )—P(4)	137.9 (2)
P(2)—O(6)—Al(1)	123.8 (2)	Al(3)—O(13 <sup>m</sup> )—P(4)	144.7 (2)
P(3)—O(7)—Al(4)	137.9 (2)	Al(3)—O(14 <sup>m</sup> )—P(1 <sup>m</sup> )	137.8 (2)
P(3)—O(8)—Al(3)	150.3 (2)	Al(2)—O(15)—P(1)	143.3 (2)
Al(1)—O(9)—Al(4)	122.5 (1)	Al(4)—O(16)—P(4)	135.2 (2)
P(3 <sup>m</sup> )—O(17 <sup>m</sup> )—Al(3)	147.3 (2)	C(2)—C(1)—N(1)	112.8 (7)
C(3)—C(1)—N(1)	113.0 (2)	C(3)—C(1)—C(2)	118.3 (9)
(d) Interatomic distances less than 3 Å, presumed to be hydrogen bonds			
O( <sup>w</sup> )...O(9)	2.791 (5)	N(1 <sup>m</sup> )...O(10)	2.976 (6)
O( <sup>w</sup> )...O(1)	2.858 (5)		

Symmetry equivalent positions: (i)  $1+x, y, z$ ; (ii)  $2-x, -1-y, -z$ ; (iii)  $1-x, -1-y, -z$ ; (iv)  $1-x, -y, -z$ ; (v)  $2-x, -1-y, 1-z$ ; (vi)  $x, -1+y, 1+z$ ; (vii)  $2-x, -2-y, 1-z$ .

Table 6. Interatomic distances (Å) and angles (°) for SAPO-43

(a) Selected distances involving non-H atoms			
P(1)—O(1)	1.546 (4)	Al(1)—O(1)	1.733 (4)
P(1)—O(2)	1.546 (4)	Al(1)—O(2)	1.728 (4)
(b) Range of angles at tetrahedral atoms			
P	107.5 (3)—110.5 (3)	Al	107.0 (3)—110.8 (2)
(c) Angles at O atoms			
P(1)—O(1)—Al(1)	145.1 (3)	P(1)—O(2)—Al(1 <sup>m</sup> )	151.1 (3)
(d) Hydrogen bond			
O(1)...N(1 <sup>m</sup> )	2.87 (3)		

Symmetry equivalent positions: (i)  $\frac{1}{4}-x, \frac{1}{4}+y, -z$ ; (ii)  $1-x, -\frac{1}{4}+y, -z$ ; (iii)  $-\frac{1}{4}+x, \frac{1}{4}+y, -\frac{1}{2}-z$ .

replacing Ga. An H atom on O(9) was located with the AFC-5R data, but not with the FAST data, confirming that this is a hydroxyl group as in GaPO-14.

The framework of SAPO-43 (Fig. 2) corresponds to that of gismondine (see Meier & Olson, 1987). In the structure of tetramethylammonium gismondine (Alberti & Vezzalini, 1979) in space group  $I4_1amd$ ,  $T$  atoms (Si in this case) lie on twofold axes, one of the two independent O atoms has site symmetry 2, and the other  $m$ . In SAPO-43, the fourfold symmetry is lost, because the P—O and Al—O distances are unequal; P and Al remain on twofold axes [16(*e*) and 16(*f*) in  $Fddd$ ], but the O atoms are both in general positions.

#### Template molecules

In CrAPO-14 the template molecule,  $(\text{CH}_3)_2\text{CH-NH}_3^+$ , is well located, and, as in GaPO-14, the hydrogen bonds linking it and the water molecule to

framework O atoms can be identified. The template molecule in SAPO-43 is highly disordered, over at least four positions close to a site of symmetry 222. The position assigned as nitrogen can make a hydrogen bond to O(1).

#### Chromium substitution

The X-ray data are only just sufficient to allow conclusions on this. In CrAPO-14, the two independent data collections and refinements gave unexpectedly low  $U$  values at one Al site, the six-coordinate site, Al(4). This is attributed to Cr substitution and, from the refined site occupancy, indicates 4–5% Cr at this site; so *ca* 1% of total Al has been replaced by Cr. Chemical analysis of a bulk

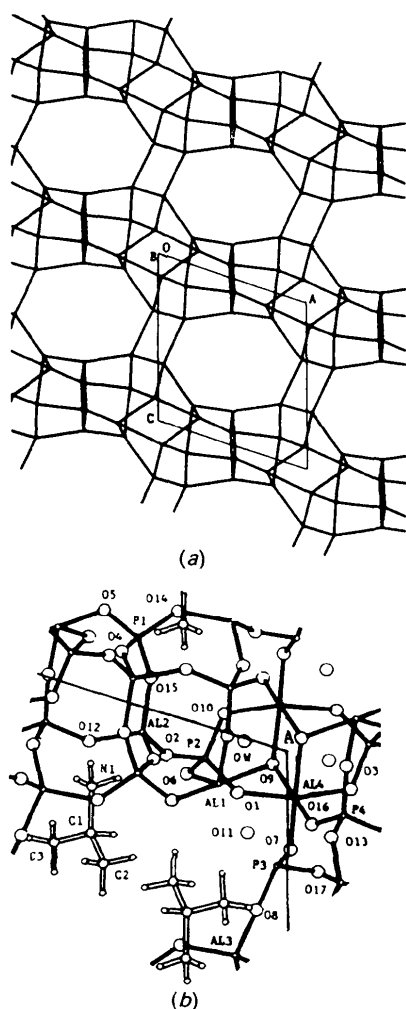


Fig. 1. (a) The framework of CrAPO-14, showing only Al and P atoms; the 'bonds' here represent Al—O—P linkages. (b) Expanded view of a portion of the structure, showing atom numbering and template molecule (PLUTO; Motherwell & Clegg, 1978).

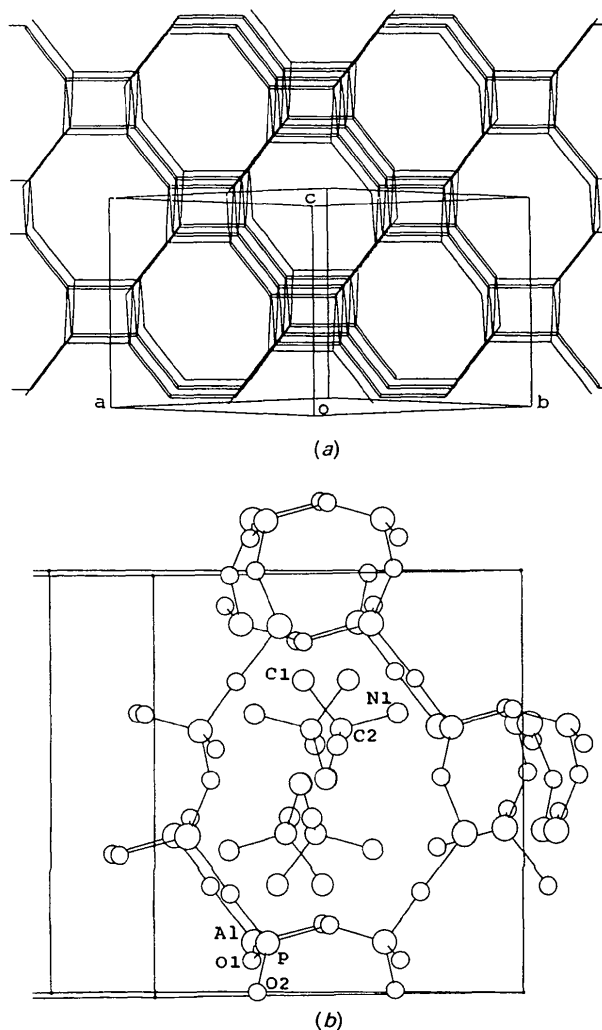


Fig. 2. (a) The framework of SAPO-43, showing only Al and P atoms, viewed along [110]; the 'bonds' here represent Al—O—P linkages. (b) Expanded view of a portion of the structure, showing atom numbering and template region (PLUTO; Motherwell & Clegg, 1978).

sample gave Cr 2.4%, compared with 0.4% calculated using the formula given in Table 1. Microprobe analysis of three individual crystals also indicated the presence of chromium in an amount consistent with this bulk analysis, but there were large variations from crystal to crystal, for example 25% in some atom ratios. Thus chemical and crystallographic evidence agree on the presence of chromium, but not on the amount. A possible explanation is the presence of additional  $\text{Cr}(\text{OH})_3$  [or  $\text{Cr}(\text{OH}_2)_6^3+$  ions] in the pores. This is believed to be the first chromium-containing zeolite or aluminophosphate.

In SAPO-43 refinement of the site occupancy of the one Al site, with its vibration parameter fixed equal to that of P, gave very small changes with both data sets, namely to 1.021 (7) and 1.020 (7). Chemical analysis of the bulk sample found 0.2% Cr, which would correspond to 0.01 Cr atoms in the molecular formula (Table 1); the sample was slightly green. Microprobe analysis of one crystal gave the ratio of atoms Al:Cr:Si:P:O as 1:0.002:0.36:0.71:4.00. In this case the analytical and X-ray results are consistent with the presence of a trace of chromium, but with this smaller crystal, the smaller amount of diffraction data, and the different symmetry (only one crystallographically independent Al site) it is not possible to draw useful conclusions about this.

#### *Comparison of experimental methods and prospects for similar small crystals*

The unit-cell parameters of CrAPO-14 measured on the two different instruments do not agree as well as we would wish, but their ratio ( $a_{\text{Cu}}:a_{\text{Mo}}$  etc.) is nearly constant, 1.0023, 1.0017 and 1.0023; there appears to be a systematic error in one or both experiments which we have not yet traced. For the SAPO-43 there is again a near constant ratio 1.0075, 1.0056 and 1.0050, between Cu  $K\alpha$  and SR measurements; here we conclude that the true wavelength of the monochromatized SR was 0.900 Å and take the AFC-5R unit cell as correct. On this SRS workstation, if knowledge of wavelength to better than 0.5% is required, it is necessary to calibrate it at the time of the experiment.

Table 4 summarizes the agreement of atom coordinates, which is extremely satisfactory. The vibration parameters from the AFC-5R data are systematically higher than those from the FAST data;  $U_{\text{FAST}}/U_{\text{AFC-5R}}$  is 0.67 (13) based on results for all framework atoms in both structures. We suspect that area-detector intensity measurement procedures give slightly high results for high-angle reflections.

When diffraction data are recorded for small crystals such as these, the total number of reflections adequately measured is often small in relation to the number of atoms in the asymmetric unit or the

theoretically accessible number (Andrews *et al.*, 1988; Papiz, Andrews, Damas, Harding & Highcock, 1990; Cheetham *et al.*, 1991; Rizkallah, Harding, Lindley, Aigner & Bauer, 1990). For good structure determination 50–100 reflections per atom is usually regarded as a good objective. A high source intensity is the primary requirement for small crystals or weak diffractometers, and high-resolution measurements are very desirable. This study shows that the Rigaku AFC-5R, with rotating-anode source, is capable of giving good data for crystals of this volume, *ca*  $10^5 \mu\text{m}^3$ , and composition. In terms of numbers of reflections to use for refinement, per framework atom, the AFC-5R was significantly better for CrAPO-14, 121 reflections per atom, than for the rather smaller crystal, SAPO-43, 94 reflections per atom. The total data-collection times in these two cases were 39 and 90 h. In the FAST experiments, the Mo  $K\alpha$  source achieved 50 reflections per atom, in a total data collection time of 15 h, while on the SRS wiggler 70 reflections per atom were achieved in a total time of 1.75 h. In the latter experiment the high intensity of SR is a big advantage, but we now consider that FAST data-collection times should have been increased by a factor of 2 or 3. Time has not been available to repeat either of these. For smaller crystals it still seems probable that the SR source will be even more advantageous, and a structure determination has just been completed where the aluminophosphate crystal had dimensions  $35 \times 20 \times 15 \mu\text{m}$ ; 315 reflection intensities were used for the refinement of the positions of 19 framework atoms, and six template atoms were well located (Harding, Kariuki, McCusker & Simmen, 1993).

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## A Two-Wavelength Crystallographic Study of a New Aluminophosphate Containing Nickel

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### Abstract

This paper describes the structure of a new aluminophosphate containing nickel. A single crystal of  $\text{NiAl}_3\text{P}_4\text{O}_{18}\text{C}_4\text{H}_{21}\text{N}_4$  was used to collect data at Cu  $K\alpha$  and Mo  $K\alpha$  wavelengths on rotating-anode (Rigaku AFC-5R) and sealed-tube (Rigaku AFC-6S) diffractometers, respectively. The monoclinic unit cell was (for Cu  $K\alpha$ )  $a = 10.0209$  (8),  $b = 15.661$  (1),  $c = 14.0914$  (8) Å,  $\beta = 101.216$  (5)°, space group  $P2_1/n$ . Determination of the structure showed that a novel arrangement had been formed, in which nickel occupied an octahedral site in the framework. The elemental analysis confirmed the presence of nickel. The Ni atom is coordinated to two framework O atoms and one water molecule. In addition, two template molecules of ethylenediamine are coordi-

nated to the Ni atom, one monodentate and the other bidentate. The framework also contains three Al atoms and four P atoms that are all tetrahedrally bound to oxygen. A free water molecule is contained in the pores and is hydrogen bonded to the framework. The overall structure consists of aluminophosphate layers linked through Ni atoms. The crystal used for data collection was small ( $0.02 \times 0.05 \times 0.25$  mm), but with the Cu  $K\alpha$  data it was possible to refine all non-H atoms anisotropically to a final  $R$  (on  $F$ ) of 0.057,  $wR = 0.081$ , with 3497 observed reflections having  $I > 3\sigma(I)$  and 309 variables. Using the weaker Mo  $K\alpha$  data, the final agreement factors were  $R = 0.050$  and  $wR = 0.055$ , with 1057 observed reflections and 177 parameters. Between Cu  $K\alpha$  and Mo  $K\alpha$  wavelengths, the difference in  $f'$  is  $-3.32$  e for nickel versus 0.15 e for aluminium (*i.e.* a ratio of 24). An  $f'$  difference Fourier electron-density map, based on phases calculated excluding the Ni atom,

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