smaller were it not for the long P—P bond. The S—P—S angle of 95·1 (1)° in α-P_4S_4 is much smaller than the corresponding angles in β-P_4S_5 [104·6 (1)°] and P_4S_7 [103·9 (3)°]; this is likely to direct the hybridized atomic orbitals away from the line joining the two P atoms, reducing the overlap and weakening the P—P bond. Kinetic factors arising from the high molecular symmetry presumably account for the stability of α-P_4S_4 at room temperature; NMR studies show that it is a very minor component of fused P/S mixtures, suggesting that it is thermodynamically unstable with respect to other phosphorus sulphides. Fig. 2 is an *ORTEP* plot of the molecule.

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Potassium Tetrachloroaluminate

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Abstract. $KAlCl_4$, monoclinic, $P2_1$ (non-standard setting with unique axis *a*), a = 10·481 (9), b = 7·183 (5), c = 9·273 (5) Å, α = 93·10 (3)°, Z = 4, D_c = 1·98 g cm^{-3}. The structure was refined to an R of 0·035 for 1501 counter reflections with $I > 3\sigma(I)$. The salt contains discrete $AlCl_4^-$ anions and K^+ cations. The $AlCl_4^-$ tetrahedra are distorted (average Al—Cl = 2·129 Å). The structure is a slight deformation of that of $NOAlCl_4$ ($BaSO_4$ type).

Introduction. In the alkaline and pseudo-alkaline tetrachloroaluminates the Rb^+, Cs^+ (Gearhart, Beck & Wood, 1975), NO^+ (Barbier, Mairesse, Wignacourt & Baert, 1976) and NH_4^+ (Mairesse, Barbier, Wignacourt, Rubbens & Wallart, 1977) salts crystallize in the space group *Pnma*. For the Na^+ salt, symmetry decreases to $P2_12_12_1$ (Baenziger, 1951) and for Li^+ to $P2_1/c$ (Mairesse, Barbier, Wignacourt & Baert, 1977). In most tetrahedral compounds such as tetrafluoroborates (Clark & Lynton, 1969) or perchlorates (Johansson & Lindqvist, 1977), the K^+ is always isostructural with the Rb^+ and NH_4^+ salts, whereas in the tetrachloroaluminates, a preliminary study showed that $KAlCl_4$ crystallized in a monoclinic system. The crystal structure of $KAlCl_4$ was determined to gain an understanding of the structural evolution of this family.

Single crystals were prepared and isolated by a method previously described (Barbier & Mairesse, 1971). The highly hygroscopic crystals were mounted in quartz capillaries.

We used a pear-shaped crystal with numerous faces and maximum dimensions 0·25 × 0·25 × 0·30 mm. The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections centered on a Philips PW 1100 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·7107 Å). Owing to the similarity of the cell parameters with those of $NOAlCl_4$ [a = 10·411 (8), b = 7·055 (3), c = 9·461 (5) Å], we ascribed a non-standard setting to the unit cell, with the twofold screw axis coincident with **a**. In this setting, systematic absences were $h00$: h odd, possible space groups $P2_1$ or $P2_1/m$. Data were collected on the diffractometer with an ω–2θ scan technique, a scan width of 1·60°, a scan speed of 0·03° s^{-1}, and background counts at each extremity for half the scan time. 2247 independent reflections were obtained. No absorption correction was applied (μ = 22·6 cm^{-1}).

Table 1. *Final positional parameters* ($\times 10^4$) *with their e.s.d.'s*

	x	y	z
Al(1)	6648*	68 (5)	9336 (4)
Cl(1)	8263 (5)	263 (6)	7977 (5)
Cl(2)	4914 (4)	−553 (4)	8200 (3)
Cl(3)	6914 (4)	−2121 (4)	10782 (4)
Cl(4)	6520 (5)	2656 (4)	10584 (5)
Al(2)	5565 (2)	4918 (5)	5641 (4)
Cl(5)	3928 (5)	4697 (5)	6996 (5)
Cl(6)	7230 (4)	5409 (5)	6892 (4)
Cl(7)	5321 (4)	7149 (4)	4255 (4)
Cl(8)	5718 (5)	2341 (4)	4423 (4)
$K^+(1)$	9178 (5)	4441 (4)	9452 (5)
$K^+(2)$	3049 (5)	528 (5)	5566 (5)

* Arbitrary origin-fixing coordinate.

The structure was solved in space group $P2_1$ with *MULTAN* (Germain, Main & Woolfson, 1971). The E map obtained from the most probable set contained the whole structure. Atomic coordinates and thermal parameters (isotropic then anisotropic) were refined by the full-matrix least-squares method, using the 1501 reflections with $I > 3\sigma(I)$, and the refinement converged to $R = 0{\cdot}035$ and $R_w = 0{\cdot}046$. The weighting scheme was $w = 1/\sigma^2(F)$ as derived from counting statistics. Scattering factors of K^+, Al and Cl were from Cromer & Waber (1965). The refined coordinates are shown in Table 1.*

Discussion. The ionic packing with the atomic numbering scheme is shown in Fig. 1. Intraionic bond lengths and angles are given in Table 2, interionic distances in Table 3. There are two independent formula units in the asymmetric unit. They are arranged in such a manner that the sum of the coordinates of two corresponding atoms [$K^+(1)$, $K^+(2)$; Al(1), Al(2); Cl(1), Cl(5); . . .] is nearly constant, with $\langle x_1 + x_2 \rangle = 1{\cdot}22079$ (0·00640), $\langle y_1 + y_2 \rangle = 0{\cdot}49661$ (0·01097), $\langle z_1 + z_2 \rangle = 1{\cdot}50173$ (0·00749) ($\langle\rangle$ means average value and the numbers in parentheses are the maximum shifts from average values). Therefore, this structure is close to a centrosymmetric one in $P2_1/m$, in which the x',y',z' coordinates of the single $KAlCl_4$ atoms would be derived from the x,y,z of the first formula unit [$K^+(1)$, Al(1) . . .] by the transformation: $x' = x - 0{\cdot}11040$, $y' = y + 0{\cdot}25169$, $z' = z - 0{\cdot}25086$. Nevertheless, applying this transformation and assigning each atom the isotropic B_{eq} value computed from the previous β_{ij} in $P2_1$, we obtained 0·33 for R and refinement was not possible.

Each $AlCl_4^-$ ion is slightly distorted both in bond lengths and angles, and it is not easy to define the K^+ coordination number. Each K^+ cation is surrounded by six Cl atoms at 3·20 to 3·40 Å, but we also found another at about 3·60 Å and two more at less than 3·90 Å.

The structure of $KAlCl_4$ can be described as a slight deformation of that of $NOAlCl_4$, probably due to steric effects. Moreover, a single-crystal Raman study showed that $KAlCl_4$ behaves very like an apparent

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33256 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with their e.s.d.'s in the* $AlCl_4^-$ *anions*

Al(1)—Cl(1)	2·119 (5)	Al(2)—Cl(5)	2·137 (6)
Al(1)—Cl(2)	2·136 (4)	Al(2)—Cl(6)	2·115 (5)
Al(1)—Cl(3)	2·139 (5)	Al(2)—Cl(7)	2·123 (5)
Al(1)—Cl(4)	2·140 (5)	Al(2)—Cl(8)	2·122 (5)
Cl(1)—Al(1)—Cl(2)	113·9 (2)	Cl(5)—Al(2)—Cl(6)	110·8 (2)
Cl(1)—Al(1)—Cl(3)	110·0 (2)	Cl(5)—Al(2)—Cl(7)	110·0 (2)
Cl(1)—Al(1)—Cl(4)	106·7 (2)	Cl(5)—Al(2)—Cl(8)	106·5 (2)
Cl(2)—Al(1)—Cl(3)	106·2 (2)	Cl(6)—Al(2)—Cl(7)	108·8 (2)
Cl(2)—Al(1)—Cl(4)	111·4 (2)	Cl(6)—Al(2)—Cl(8)	110·1 (2)
Cl(3)—Al(1)—Cl(4)	108·4 (2)	Cl(7)—Al(2)—Cl(8)	110·6 (2)

Table 3. *Interionic distances* (Å) *with their e.s.d.'s about the* K^+ *cations*

Coding of equivalent positions: (1) x,y,z; (2) $\frac{1}{2} + x, \bar{y}, \bar{z}$. K^+ cations are in position 1. Cl(4)2/012 means that Cl(4) is in position 2, translated by **0a**, **1b**, **2c**.

$K^+(1)\cdots$	Cl(4)2/012	3·222 (6)	$K^+(2)\cdots$	Cl(8)2/$\bar{1}$01	3·197 (6)
	Cl(6)1/000	3·235 (6)		Cl(2)1/000	3·255 (6)
	Cl(4)1/000	3·264 (6)		Cl(8)1/000	3·285 (6)
	Cl(3)2/002	3·319 (6)		Cl(1)2/$\bar{1}$01	3·311 (6)
	Cl(5)2/012	3·329 (6)		Cl(7)2/$\bar{1}$11	3·311 (6)
	Cl(1)1/000	3·370 (6)		Cl(5)1/000	3·338 (6)
	Cl(3)1/010	3·594 (6)		Cl(7)1/0$\bar{1}$0	3·566 (6)
	Cl(2)2/002	3·714 (5)		Cl(3)2/$\bar{1}$02	3·712 (6)
	Cl(7)2/011	3·760 (6)		Cl(6)2/$\bar{1}$11	3·894 (5)

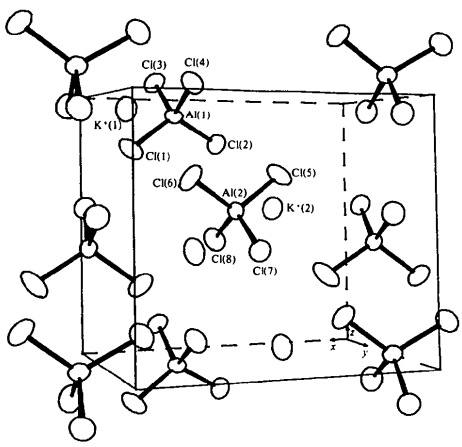

Fig. 1. Atom-numbering system and ionic packing with 50% probability thermal ellipsoids (Nowogrocki, 1977).

orthorhombic crystal with $P2_12_12_1$ symmetry, which is the space group of $NaAlCl_4$ (Rubbens, Barbier, Mairesse, Wallart & Wignacourt, 1977). All these results show the important position of the K^+ salt in this family. The structural evolution of the different salts will be discussed later.

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A Refinement of Zinc Dichloride–Hydrochloric Acid–Water (2:1:2)*

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Abstract. $HCl.2ZnCl_2.2H_2O$, orthorhombic, *Fdd*2, $Z = 8$, $a = 9{\cdot}243$ (1), $b = 22{\cdot}885$ (1), $c = 8{\cdot}886$ (1) Å, $V = 1879{\cdot}7$ Å^3 at 279 K. The structure contains symmetrical, staggered $H_5O_2^+$ ions [O···O 2·377 (9) Å]. Each ion is hydrogen bonded to four equivalent Cl atoms [O···Cl 3·151 (5) and 3·156 (4) Å]. Each Zn atom is tetrahedrally surrounded by four Cl atoms. These tetrahedra are joined at their corners to form a three-dimensional network with composition $Zn_2Cl_5^-$.

Introduction. The crystal structure of $HCl.2ZnCl_2.2H_2O$ was determined by Follner (1970). This study indicated the presence of $H_5O_2^+$ ions in the structure. A neutron diffraction study of the structure has been planned in order to obtain more detailed information on the geometry of this ion and the hydrogen-bond system. As a preliminary to this study, a new refinement of X-ray data has been made.

Crystals of the compound were found to be stable only when in contact with their mother liquor or dry HCl gas, which made it difficult to obtain crystals ideally mounted for intensity data collection. Soda-glass capillary tubes were filled with a concentrated aqueous solution of $ZnCl_2$ supersaturated with HCl gas, and carefully sealed. Crystallization was induced by cooling this liquid with dry ice. Crystals were grown using a zone-melting technique. Cell dimensions and intensity data were measured at 279 K using a semi-automatic Stoe–Philips Weissenberg diffractometer (Ni-filtered Cu $K\alpha$ radiation), modified for low-temperature work. The cell dimensions were determined from 38 θ values measured using two crystals rotated about [010] and [101] respectively. Intensity data out to $\sin\theta/\lambda = 0{\cdot}63$ Å^{-1} were collected using a cylindrical crystal (diameter 0·22 mm, length 0·27 mm) rotating about [101]. One end of the crystal was in contact with its mother liquor, the other end with a gas bubble. Six layers of data were collected using an ω–2θ scan technique. Three test reflections were monitored periodically within each layer. The zero-layer test reflections were remeasured before each new layer. The intensities of the test reflections showed an approximately linear decline with respect to elapsed time. An appropriate correction was subsequently applied to all intensities. The total decrease in intensity was about 11%. The intensities were corrected for Lorentz,

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