

## Preparation and Structure of a Gallium Phosphate Framework with Clathrated Isopropylamine

BY JOHN B. PARISE\*

Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

(Received 11 January 1985; accepted 25 September 1985)

**Abstract.** Trigallium tris(orthophosphate) hydrate–isopropylamine,  $\text{GaPO}_4\cdot 21$ ,  $\text{Ga}_3(\text{PO}_4)_3\cdot \text{C}_3\text{H}_9\text{N}\cdot \text{H}_2\text{O}$ ,  $M_r = 571.2$ , monoclinic,  $P2_1/n$ ,  $a = 8.700$  (1),  $b = 18.146$  (2),  $c = 9.087$  (1) Å,  $\beta = 107.28$  (2)°,  $V = 1369.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.77$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 62.0$  cm<sup>-1</sup>,  $F(000) = 1112$ , room temperature, atoms in the framework refined anisotropically to  $R = 0.047$  for 2385 reflexions with  $I > 2\sigma(I)$ . The structure is essentially as described for the aluminophosphate molecular-sieve precursor,  $\text{AlPO}_4\cdot 21$ , with the exception of the position of the attempted template isopropylamine, which is statistically disordered over two sites within the pores of the structure. The framework is formed by cross linking corrugated sheets composed of ribbons of edge-shared three- and five-membered rings containing five-coordinated gallium polyhedra and phosphorus-centred tetrahedra, with crankshaft-shaped chains of alternating  $\text{GaO}_4$  and  $\text{PO}_4$  tetrahedra. Upon calcination, loss of the hydroxyl group, which forms the bridge between three- and five-membered rings, converts  $\text{GaPO}_4\cdot 21$  to the open-framework structure of  $\text{GaPO}_4\cdot 25$ .

**Introduction.** The synthesis of gallium phosphate frameworks, some of which are related to the series of aluminophosphate compounds reported by workers at Union Carbide Corporation (Wilson, Lok & Flanigen, 1982; Wilson, Lok, Messina, Cannan & Flanigen, 1982) has recently been described (Parise, 1985). This process typically involves the hydrothermal treatment of a galliophosphate gel, to which an amine has been added in an attempt to direct the synthesis towards a particular structure type. Although the exact role of this agent is still in doubt, its presence and aspect in several  $\text{AlPO}_4$  compounds studied to date (Parise, 1984*a,b,c*; Parise & Day, 1985; Parise, 1985) suggest the molecule behaves as a template, its shape dictating the geometry of the framework. The observation that only dense phases form in the absence of amines indicates they may play a crucial role in controlling the gel chemistry, nucleation, crystal growth or a combination of these processes. During the investigation of the synthesis of

framework structures in the  $\text{GaPO}_4$  system, several new compounds were produced (Parise, 1985). From a comparison of Guinier X-ray powder photographs with published data (Wilson, Lok & Flanigen, 1982), some of these were found to be structurally related to the  $\text{AlPO}_4$  family of molecular sieves. One such compound, designated  $\text{GaPO}_4\cdot 21$ , is related to  $\text{AlPO}_4\cdot 21$  (Parise, 1984*c*; Parise & Day, 1985; Bennett, Cohen, Artioli, Pluth & Smith, 1985), the precursor that, upon calcination at above 823 K, is converted into the molecular sieve  $\text{AlPO}_4\cdot 25$  (Wilson, Lok & Flanigen, 1982) with an estimated pore size of between 3.4 and 4.3 Å.

Although the composition of the framework for these compounds is not necessarily  $\text{AlPO}_4$  or  $\text{GaPO}_4$  (see below), it appears as such in the patent literature and will also be used as a forename in designating new frameworks in this and future reports. For example, in  $\text{GaPO}_4\cdot 21$ , 'GaPO<sub>4</sub>' denotes the approximate composition of the framework while '21' denotes the unique structure type.

**Experimental.**  $\text{GaPO}_4\cdot 21$  was synthesized by combining, with stirring,  $\text{H}_3\text{PO}_4$  (85%), water, a source of gallium, and isopropylamine ( $\text{iPrNH}_2$ ), to give a gel of composition close to  $1.0\text{iPrNH}_2:\text{Ga}_2\text{O}_3:\text{P}_2\text{O}_5:40\text{H}_2\text{O}$ . This was then sealed, under a vacuum of better than 0.13 mPa, in a thick-walled Pyrex® glass capsule, placed in a water-jacketed stainless-steel bomb fitted with a Teflon® seal, and heated at 473 K for 86 h.

The sample was examined under the optical microscope and was found to consist of two distinct crystal forms: prisms of  $\text{GaPO}_4\cdot 21$ , up to 1.2 mm, and blades of a second phase. The amount of template clathrated by the framework of  $\text{GaPO}_4\cdot 21$  has been determined from the results of the analysis given below.

Weisenberg and precession photographs indicated monoclinic ( $2/m$ ) symmetry, space group  $P2_1/n$  (No. 14), with absences:  $h0l$ ,  $h+l=2n+1$ ;  $0k0$ ,  $k=2n+1$ ; prism  $0.13 \times 0.05 \times 0.04$  mm; cell parameters determined from 12 fully centred reflexions with  $28 < 2\theta < 31^\circ$ ; Picker FACS-1 diffractometer, graphite monochromator (take-off angle =  $3^\circ$ ), 3113 data collected,  $\theta$ - $2\theta$  scans, 10 s background count on either side of peak,  $3 < 2\theta < 55^\circ$ , scan rate  $2^\circ \text{ min}^{-1}$ , 3 orthogonal reflexions monitored periodically showed no

\* Present address: The Department of Chemistry, New South Wales Institute of Technology, Broadway, Sydney, NSW 2006, Australia.

significant variation; following merging of data ( $R_{\text{int}} = 0.03$ ), deletion of systematic absences and 'unobserved' data [ $I < 2\sigma(I)$ ], 2385 unique data used in structure solution and refinement; absorption correction applied, varying from 0.85 to 0.89; positions for the  $\text{Ga}_3(\text{PO}_4)_3$  O framework inferred from those for  $\text{AlPO}_4\text{-21}$  (Parise & Day, 1985) and refined isotropically before being used to phase difference Fourier map, which revealed position of an H atom attached to O(1) of the framework as well as the  $i\text{PrNH}_2$  moiety in two distinct orientations; refinement of occupation factors for the two possible orientations indicated they were statistically distributed and the occupancy of each atom in the molecules was fixed at 0.5 for the remainder of the refinements. Assignment of N based on thermal parameters and comparison with  $\text{GaPO}_4\text{-14}$  (Parise, 1985); atoms in the framework [with the exception of H(1)] refined anisotropically; H atoms in  $i\text{PrNH}_2$  not located; function minimized:  $\sum w(F_o - F_c)^2$ ,  $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ ,  $\sigma$  based on counting statistics;  $(\Delta/\sigma)_{\text{max}} = 0.05$  for final cycle of refinement, in final difference Fourier map peaks ( $-1.3$  to  $1.1 \text{ e } \text{\AA}^{-3}$ ) are close to Ga positions and near the  $i\text{PrNH}_2$  molecules. During refinement the geometry of the isopropylamine molecule was constrained. Scattering factors from *International Tables for X-ray Crystallography* (1974), corrected for anomalous dispersion; final discrepancy factors: for  $I > 2\sigma(I)$ ,  $R$

$= 0.047$ ,  $wR = 0.052$ ,  $S = 1.27$ . Calculations carried out on a Digital Equipment VAX 11/750 using *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Atomic parameters are given in Table 1\* and a list of selected bond lengths and angles is given in Table 2. The atom numbering is defined in Fig. 1.

\* Lists of structure amplitudes anisotropic thermal parameters and further experimental details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42491 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected interatomic distances (Å) and angles (°)

O(5)—Ga(1)	1.939 (5)	O(13 <sup>b</sup> )—Ga(2)	1.911 (5)
O(4)—Ga(1)	1.873 (5)	O(14)—Ga(2)	1.853 (5)
O(3)—Ga(1)	1.927 (5)	O(12)—Ga(2)	1.888 (5)
O(1)—Ga(1)	1.900 (5)	O(1)—Ga(2)	1.984 (5)
O(2)—Ga(1)	1.848 (5)	O(11)—Ga(2)	1.868 (5)
O(5)—Ga(1)—O(1)	89.8 (2)	O(13 <sup>b</sup> )—Ga(2)—O(14)	95.0 (2)
O(5)—Ga(1)—O(2)	84.9 (2)	O(13 <sup>b</sup> )—Ga(2)—O(12)	92.1 (2)
O(5)—Ga(1)—O(3)	172.4 (2)	O(13 <sup>b</sup> )—Ga(2)—O(1)	165.3 (2)
O(5)—Ga(1)—O(4)	94.5 (2)	O(13 <sup>b</sup> )—Ga(2)—O(11)	85.7 (2)
O(4)—Ga(1)—O(1)	113.3 (2)	O(14)—Ga(2)—O(12)	110.8 (2)
O(4)—Ga(1)—O(2)	106.1 (3)	O(14)—Ga(2)—O(1)	99.7 (2)
O(4)—Ga(1)—O(3)	92.6 (2)	O(14)—Ga(2)—O(11)	105.0 (2)
O(3)—Ga(1)—O(1)	90.1 (2)	O(12)—Ga(2)—O(1)	83.8 (2)
O(3)—Ga(1)—O(2)	90.5 (2)	O(12)—Ga(2)—O(11)	144.2 (2)
O(2)—Ga(1)—O(1)	140.6 (2)	O(11)—Ga(2)—O(1)	89.4 (2)
O(9)—Ga(3)	1.833 (5)	O(12 <sup>b</sup> )—P(1)	1.517 (5)
O(8)—Ga(3)	1.808 (5)	O(13)—P(1)	1.514 (5)
O(6)—Ga(3)	1.802 (5)	O(2)—P(1)	1.515 (5)
O(7)—Ga(3)	1.826 (5)	O(6)—P(1)	1.543 (5)
O(9)—Ga(3)—O(8)	110.2 (3)	O(12 <sup>b</sup> )—P(1)—O(13)	112.2 (3)
O(9)—Ga(3)—O(6)	111.9 (2)	O(12 <sup>b</sup> )—P(1)—O(2)	110.6 (3)
O(9)—Ga(3)—O(7)	111.1 (2)	O(12 <sup>b</sup> )—P(1)—O(6)	108.4 (3)
O(8)—Ga(3)—O(6)	106.6 (2)	O(13)—P(1)—O(2)	106.7 (3)
O(8)—Ga(3)—O(7)	108.4 (3)	O(13)—P(1)—O(6)	109.3 (3)
O(7)—Ga(3)—O(6)	108.4 (2)	O(6)—P(1)—O(2)	109.7 (3)
O(4 <sup>III</sup> )—P(2)	1.517 (5)	O(5 <sup>b</sup> )—P(3)	1.515 (5)
O(9 <sup>a</sup> )—P(2)	1.544 (5)	O(8 <sup>b</sup> )—P(3)	1.534 (5)
O(7)—P(2)	1.537 (5)	O(3)—P(3)	1.538 (5)
O(14)—P(2)	1.522 (5)	O(11)—P(3)	1.531 (5)
O(4 <sup>III</sup> )—P(2)—O(9 <sup>a</sup> )	111.5 (3)	O(5 <sup>b</sup> )—P(3)—O(8 <sup>b</sup> )	111.2 (3)
O(4 <sup>III</sup> )—P(2)—O(7)	109.9 (3)	O(5 <sup>b</sup> )—P(3)—O(3)	109.6 (3)
O(4 <sup>III</sup> )—P(2)—O(14)	108.2 (3)	O(5 <sup>b</sup> )—P(3)—O(11)	107.5 (3)
O(9 <sup>a</sup> )—P(2)—O(7)	106.8 (3)	O(8 <sup>b</sup> )—P(3)—O(3)	110.3 (3)
O(9 <sup>a</sup> )—P(2)—O(14)	110.1 (3)	O(8 <sup>b</sup> )—P(3)—O(11)	106.2 (3)
O(14)—P(2)—O(7)	110.4 (3)	O(11)—P(3)—O(3)	112.1 (3)
C(2)—C(1)	1.585 (42)	C(2*)—C(1*)	1.496 (30)
C(3)—C(1)	1.546 (41)	C(3*)—C(1*)	1.504 (33)
N—C(1)	1.569 (41)	N*—C(1*)	1.558 (30)
C(1*)...C(1)	0.499 (59)	O(4)...N*	2.824 (20)
N...N	1.956 (35)		
C(3)—C(1)—C(2)	111 (3)	C(3*)—C(1*)—C(2*)	121 (2)
N—C(1)—C(2)	106 (2)	N*—C(1*)—C(2*)	114 (2)
N—C(1)—C(3)	114 (3)	N*—C(1*)—C(3*)	109 (2)
N...O(5)	2.99 (2)	O(1)—H(1)	0.86 (9)
N...O(11)	3.01 (2)	O(3 <sup>a</sup> )...H(1)	2.01 (10)
N...O(13)	3.02 (2)	O(3 <sup>a</sup> )...H(1)—O(1)	163 (7)

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

Table 1. Atomic positional ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{GaPO}_4\text{-21}$  ( $i\text{PrNH}_2$ )

$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$				
	x	y	z	$U/U_{\text{eq}}$
Ga(1)	818 (1)	2952 (1)	2911 (1)	7
Ga(2)	1364 (1)	1079 (1)	1610 (1)	7
Ga(3)	5291 (1)	3209 (1)	1966 (1)	10
P(1)	3502 (2)	4268 (1)	3596 (2)	8
P(2)	3148 (2)	2070 (1)	-180 (2)	10
P(3)	2670 (2)	1694 (1)	4965 (2)	8
O(1)	395 (6)	2050 (2)	1800 (6)	13
O(2)	1983 (5)	3812 (2)	3019 (6)	15
O(3)	2606 (5)	2500 (2)	4425 (5)	11
O(4)	-356 (6)	3060 (3)	4323 (6)	19
O(5)	-778 (6)	3439 (2)	1242 (6)	13
O(6)	4712 (6)	4045 (2)	2732 (6)	14
O(7)	3473 (6)	2680 (2)	1048 (6)	17
O(8)	6197 (6)	3483 (2)	500 (6)	20
O(9)	6721 (6)	2665 (3)	3460 (6)	18
O(11)	2627 (6)	1151 (2)	3664 (5)	15
O(12)	-714 (6)	856 (2)	307 (6)	13
O(13)	3015 (5)	5064 (2)	3235 (6)	14
O(14)	2716 (6)	1352 (2)	467 (6)	16
H(1)	-364 (98)	2131 (55)	963 (97)	37 (30)
C(1)	1381 (54)	4557 (32)	8175 (51)	200 (34)
C(2)	993 (35)	4948 (19)	6546 (27)	76 (9)
C(3)	3204 (28)	4587 (18)	9035 (33)	83 (9)
N	291 (21)	4943 (11)	9046 (21)	51 (5)
C(1*)	1459 (37)	4431 (15)	7714 (34)	66 (8)†
C(2*)	1740 (44)	5160 (13)	7069 (38)	86 (10)†
C(3*)	2026 (71)	4287 (22)	9420 (32)	172 (22)†
N*	1872 (23)	3753 (9)	6852 (22)	49 (4)†

† Second molecule of isopropylamine designated C(1\*), C(2\*) etc; each molecule has occupancy 0.5, fixed during refinement.

**Discussion.** The same connectivities exist in the framework of GaPO<sub>4</sub>-21 as occur in AlPO<sub>4</sub>-21. Fig. 2 shows this framework, with channels bounded by eight-membered rings running along [101], as being composed of cross-linked crankshaft-shaped single chains of alternating GaPO<sub>4</sub> and PO<sub>4</sub> tetrahedra and sheets containing five-coordinated Ga<sup>v</sup> and PO<sub>4</sub> tetrahedra. The sheet is composed of ribbons of edge-shared three- and five-membered rings; the edge being formed by Ga atoms sharing a hydroxyl group, O(1), which is hydrogen bonded across a five-membered ring to O(3); see Fig. 1 and Table 2. A more complete description of the way in which the structure type is constructed from the elements of sheets and chains is given by Parise &

Day (1985). There is also separation of Al<sup>v</sup> from Al<sup>iv</sup> (or Ga<sup>v</sup> and Ga<sup>iv</sup>) into discrete structural elements in other phases studied in this system (Parise, 1984b,c).

The geometry of polyhedra within the framework of GaPO<sub>4</sub>-21 is similar to that observed in AlPO<sub>4</sub>-21 (Parise & Day, 1985; Bennett *et al.*, 1985). There are two types of Ga<sup>v</sup> polyhedra present with geometries distorted from the ideal trigonal bipyramidal. Ga(1) has an average angular deviation of 9° from this geometry towards square pyramidal. The distortion is more pronounced in the case of Ga(2), with an average 12° deviation (Table 2). The remaining polyhedra are regular tetrahedra with the following average distances: Ga(3)—O, 1.82 (1); P(1)—O, 1.52 (1); P(2)—O, 1.53 (1); P(3)—O, 1.53 (1) Å.

The assignment of O(1) as a hydroxyl group [rather than a water molecule; see Parise & Day (1985)] implies the structural formula Ga<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>·OH·C<sub>3</sub>H<sub>10</sub>N with positive charge probably residing on the iPrNH<sub>2</sub> molecule. This is consistent with the charged organic amines found in other studies of GaPO<sub>4</sub> compounds (Parise, 1985).

Both ethylenediamine (en) in AlPO<sub>4</sub>-21 (Parise & Day, 1985) and iPrNH<sub>2</sub> in GaPO<sub>4</sub>-21 are statistically disordered over two sites within the pores formed by the framework (Figs. 1 and 2). Unlike en, the N atom in iPrNH<sub>2</sub> does not coordinate to Ga(2) but rather is hydrogen bonded to the framework *via* N\*...O(4) and N...O(5), ...O(11), ...O(13) (Table 2). The bonds C(1)—N and C(1\*)—N\* point towards the centre of the eight- and five-membered rings respectively with the N—N distance (Table 2) across the eight-membered ring precluding full occupancy of the sites designated N, C(1), C(2), C(3).

Upon calcination at 873 K for 48 h GaPO<sub>4</sub>-21 is converted into an orthorhombic phase with cell parameters  $a = 8.40$ ,  $b = 18.5$ ,  $c = 15.0$  Å as measured from photographs taken on a Weissenberg camera of a 'single' crystal with high mosaic spread. The diffraction aspect closely resembles that for AlPO<sub>4</sub>-25 (Wilson, Lok & Flanigen, 1982; Parise, 1984c) and it is likely GaPO<sub>4</sub>-25 also represents a four-connected tetrahedral net, composed of alternating GaO<sub>4</sub> and PO<sub>4</sub> tetrahedra, produced by the loss of the hydroxyl bridge between Ga(1) and Ga(2) (Figs. 1 and 2). This converts the edge-shared three- and five-membered-ring ribbon to a ribbon of six-membered rings.

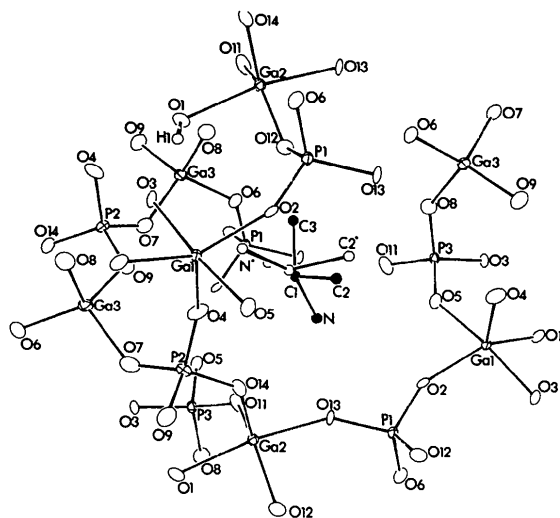


Fig. 1. ORTEP (Johnson, 1965) drawing of the environment around the isopropylamine molecules in GaPO<sub>4</sub>-21. Thermal ellipsoids are drawn at the 50% probability level.

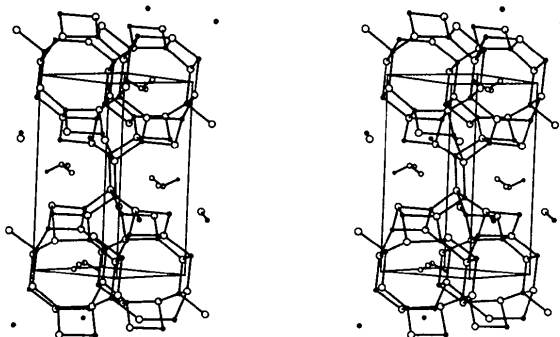


Fig. 2. ORTEP (Johnson, 1965) drawing of the framework of GaPO<sub>4</sub>-21. Only Ga (small dots) and P atoms (large circles) are shown. Oxygen atoms, omitted for clarity, lie approximately at the mid point of the straight-line segment drawn between the metal atoms. Note the five- and three-membered-ring ribbons and the crankshaft chains along [101] point out of the page. The unit-cell origin is in the bottom back corner with  $y$  up,  $x$  left and  $z$  right. Only one of the orientations for iPrNH<sub>2</sub> is shown within the pores. Chains connecting corrugated sheets (Parise & Day, 1985) are out of the page (see text).

## References

- BENNETT, J. M., COHEN, J. M., ARTIOLI, G., PLUTH, J. J. & SMITH, J. V. (1985). *J. Inorg. Chem.* In the press.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 PARISE, J. B. (1984a). *Acta Cryst. C* **40**, 1641–1642.

- PARISE, J. B. (1984b). *J. Chem. Soc. Chem. Commun.* **21**, 1449–1450.  
 PARISE, J. B. (1984c). *International Symposium on Zeolites, Portoroz*. Amsterdam: Elsevier Scientific. In the press.  
 PARISE, J. B. (1985). *J. Chem. Soc. Chem. Commun.* **9**, 606–607.  
 PARISE, J. B. & DAY, C. S. (1985). *Acta Cryst.* **C41**, 515–520.

- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 WILSON, T., LOK, B. M. & FLANIGEN, E. M. (1982). US patent No. 4 310 440.  
 WILSON, T., LOK, B. M., MESSINA, C. A., CANNAN, T. R. & FLANIGEN, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.

*Acta Cryst.* (1986). **C42**, 147–149

## Copper Quinaldinate Monohydrate [Aquabis(2-quinolinecarboxylato)copper(II)]; Pentacoordinate Copper

BY HELMUT M. HAENDLER

*Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824, USA*

(Received 1 August 1985; accepted 24 September 1985)

**Abstract.**  $[\text{Cu}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{H}_2\text{O})]$ ,  $M_r = 425.9$ , monoclinic,  $P2_1/c$ ,  $a = 7.756$  (1),  $b = 7.628$  (2),  $c = 29.573$  (5) Å,  $\beta = 95.31$  (1)°,  $V = 1742.2$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.62$ ,  $D_m = 1.60$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 13.4$  cm<sup>-1</sup>,  $F(000) = 868$ ,  $T = 293$  (1) K,  $R = 0.050$  for 2816 reflections. The Cu atom is pentacoordinate, with its configuration intermediate between that of a trigonal bipyramid and a rectangular pyramid. The ligand–metal–ligand angles are distorted in the direction corresponding to a Berry-type displacement. Comparison of the dihedral angles of the pyramidal faces with the limiting values of the two forms indicates a Berry displacement of 49%. The quinaldinate acts as a bidentate ligand, bonded through an apical N and an equatorial carboxylate O (referred to the trigonal bipyramid). The water molecule occupies the third equatorial position. The copper–ligand distances are 1.954 (3) and 1.962 (3) Å for Cu–O and 2.012 (3) and 2.014 (3) Å for Cu–N; the copper–water distance is 2.143 (3) Å.

**Introduction.** The structure analysis of the title compound is a continuation of the investigation of metal complexes of aromatic and heterocyclic amino acids (Haendler, 1985; Boudreau, Boudreau & Haendler, 1983; Boudreau & Haendler, 1981; Lange & Haendler, 1975). Quinaldinate is a metabolite of tryptophan and has also been suggested as a gravimetric reagent for several metals (Ray & Bose, 1933; Proding, 1940). The Cu complex is an unexpected monohydrate. It contains pentacoordinated Cu and is intermediate between the trigonal-bipyramidal and rectangular-pyramidal structures, analogous to examples discussed in detail by Holmes (1984).

**Experimental.** Crystals were grown by reactive diffusion between a methanol solution of copper(II) acetate monohydrate and an ethanol solution of quinaldinate, in a 1:4 ratio (Martin & Haendler,

1978). Density of a bulk sample was determined pycnometrically in toluene.

The crystal used was an aquamarine rectangular parallelepiped, 0.20 × 0.30 × 0.50 mm. Nicolet four-circle diffractometer, graphite-monochromatized Mo K $\alpha$  radiation. 15 reflections ( $2\theta > 20^\circ$ ) for measurement of lattice parameters at 293 (1) K. No absorption correction ( $\mu = 13.4$  cm<sup>-1</sup>). Max.  $\sin\theta/\lambda = 0.650$  Å<sup>-1</sup>.  $h$  0 to 10,  $k$  0 to 9,  $l$  -38 to 38. 6 check reflections, frequency 300, no indication of deterioration or alignment changes. No extinction correction. 3989 reflections measured, 888 unobserved with  $I < 3\sigma(I)$ . Because of difficulties in interpretation of the Patterson map, Cu atoms located by symbolic addition (Ahmed, 1973); remaining non-hydrogen atoms located by *DIRDIF* (Beurskens & Noordik, 1971; Gould, van den Hark & Beurskens, 1975; van den Hark, Prick & Beurskens, 1976). Least-squares refinement on  $F$ , block-diagonal approximation, isotropic and anisotropic thermal parameters. Positions of the ring H atoms calculated; water H atoms from difference Fourier map after further refinement. Final block-diagonal refinement, with 2816 reflections (285 low-intensity reflections with  $\Delta F/F_o > 0.3$  omitted), anomalous dispersion for Cu, and  $B = 5.0$  Å<sup>2</sup> for H atoms, converged at  $R = 0.050$ ,  $wR = 0.030$ ,  $w = 1/\sigma^2(F_o)$ .  $(\Delta/\sigma)_{\text{max}} = 0.43$ , exclusive of H shifts.  $S = 1.53$ . Final difference map showed max. and min. peaks of 0.89 and -1.34 e Å<sup>-3</sup>. Error analysis showed no systematic errors as functions of  $\sin^2\theta$  or  $F_o$ . No significant correlations. Atomic scattering factors for the nonhydrogen atoms from Hanson, Herman, Lee & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). Correction terms for anomalous dispersion for Cu from *International Tables for X-ray Crystallography* (1974). National Research Council of Canada programs (Ahmed, 1973) were used for all calculations; *ORTEPII* (Johnson, 1976) for the thermal-ellipsoid plot.