

## Preparation and Structure of a Gallium Phosphate Framework Enclosing Isopropylamine: GaPO<sub>4</sub>-14

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**Abstract.** Tetragallium tetrakis(orthophosphate) hydrate–isopropylamine, Ga<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub>OH·C<sub>3</sub>H<sub>10</sub>N·1.09H<sub>2</sub>O, GaPO<sub>4</sub>-14,  $M_r = 755.4$ , triclinic,  $P\bar{1}$ ,  $a = 9.601$  (2),  $b = 9.757$  (2),  $c = 10.701$  (2) Å,  $\alpha = 74.20$  (1),  $\beta = 75.01$  (1),  $\gamma = 88.48$  (1)°,  $V = 930.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.70$  g cm<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 60.5$  cm<sup>-1</sup>,  $F(000) = 732$ , room temperature,  $R = 0.034$  for 3663 reflections. The structure is novel with a powder pattern resembling that of AlPO<sub>4</sub>-14. Units of five- and six-coordinated gallium polyhedra are cross linked *via* gallium and phosphorus tetrahedra to form a framework enclosing isopropylamine molecules. Three atoms of gallium are coordinated to a hydroxyl group in the framework. Its removal produces a hypothetical network of interconnected four-membered rings composed of alternating GaO<sub>4</sub><sup>-</sup> and PO<sub>4</sub><sup>-</sup> tetrahedra outlining a two-dimensional system of channels in (001).

**Introduction.** Series of framework structures with compositions close to AlPO<sub>4</sub> and GaPO<sub>4</sub> have recently been reported (Wilson, Lok & Flanigen, 1982; Wilson, Lok, Messina, Cannan & Flanigen, 1982; Parise, 1985a). The compounds are crystallized by the hydrothermal treatment of synthesis gels which include an amine added as a templating agent. The amine is found to be hydrogen bonded to the framework (Parise, 1984a,b,c; Parise, 1985a,b, 1986; Parise & Day, 1985), suggesting it plays a structure-directing role during the growth of a particular phase. Depending on the experimental conditions and the amine used, a variety of novel structures have been synthesized. These are distinguished using nomenclature introduced by workers at Union Carbide as either AlPO<sub>4</sub>- $n$  or GaPO<sub>4</sub>- $n$ ; here AlPO<sub>4</sub> and GaPO<sub>4</sub> refers to the approximate framework composition and  $n$  refers to a unique structure type.

Details of the structures of some of the members of these families have been reported (references mentioned above) and suggest they can be placed into three broad categories. All have  $M/P$ , where  $M = \text{Al or Ga}$ , equal to one, but differ in the type of  $M$ -centred polyhedra and how these are connected to form an open framework enclosing pores and channels containing the templating amine. Firstly, there are frameworks containing only MO<sub>6</sub> octahedra ( $M^{\text{VI}}$ ) and PO<sub>4</sub> tetrahedra.

These are typified by the dense phases AlPO<sub>4</sub>·2H<sub>2</sub>O, variscite and metavariscite (Knip, Mootz & Vegas, 1977; Knip & Mootz, 1973) and the more open Al<sub>2</sub>[NH<sub>4</sub>](OH)(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O which contains blocks of edge-shared AlO<sub>6</sub> octahedra linked *via* Al–O–P to form tunnels containing NH<sub>4</sub><sup>+</sup> (Parise, 1984b; Bennett, Cohen, Artioli, Pluth & Smith, 1985). A second type consists of corner-linked MO<sub>4</sub> and PO<sub>4</sub> tetrahedra; examples AlPO<sub>4</sub>-5, -11, -17 and -20 (Bennett, Cohen, Flanigen, Pluth & Smith, 1983; Bennett & Smith, 1985; Parise, 1984a). These compounds are synthesized in the presence of an organic amine. The amine is believed to behave as a structure-directing agent since in its absence no open frameworks are formed. Finally, a group of compounds which contain elements of the first two are also synthesized in the presence of organoamine templates (Parise, 1984a; Parise, 1985a,b, 1986). Types 12 (Parise, 1984c, 1985b) and 21 (Parise & Day, 1985; Parise, 1986) contain two distinct structural elements into which five-coordinated Al<sup>V</sup> and Al<sup>IV</sup> are separated.

During investigation of the GaPO<sub>4</sub> system a new structure type was synthesized using isopropylamine (iPrNH<sub>2</sub>) as a template (Parise, 1985a). The structure was found to be related to types 15 (Parise, 1984b) and 12 (Parise, 1984c, 1986) and to have a powder pattern resembling that of AlPO<sub>4</sub>-14 (Wilson, Lok, Messina, Cannan & Flanigen, 1982). Although the compound was designated GaPO<sub>4</sub>-14, a full structural analysis of its AlPO<sub>4</sub> namesake is required to establish any relationship between the structures.

**Experimental.** GaPO<sub>4</sub>-14 synthesized by combining H<sub>3</sub>PO<sub>4</sub> (85%), water, a source of gallium (Parise, 1986) and isopropylamine (iPrNH<sub>2</sub>), to give a gel of composition 1.0iPrNH<sub>2</sub>:Ga<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub>:40H<sub>2</sub>O; gel treated hydrothermally at 473 K for 86 h; sample examined under optical microscope and found to contain blades of GaPO<sub>4</sub>-21 (Parise, 1986) and clear crystal tablets of GaPO<sub>4</sub>-14 (Parise, 1985a); no chemical analysis attempted.

Weissenberg and precession photographs indicated triclinic symmetry. GaPO<sub>4</sub>-14 (iPrNH<sub>2</sub>): tablet 0.13 × 0.15 × 0.03 mm; cell parameters determined from 12 fully centred reflexions with  $24.7 < 2\theta < 30.6^\circ$ ; Picker FACS-1 diffractometer, graphite monochromator

Table 1. Atomic positional ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for non-hydrogen positions in  $\text{GaPO}_4\cdot 14$

	x	y	z	$U_{\text{eq}}^*$
Ga(1)	2234 (1)	7893 (1)	8332 (1)	8
Ga(2)	4779 (1)	2171 (1)	9360 (1)	11
Ga(3)	8188 (1)	10480 (1)	6574 (1)	7
Ga(4)	232 (1)	5061 (1)	11342 (1)	7
P(1)	4982 (1)	9743 (1)	7873 (1)	9
P(2)	2837 (1)	4815 (1)	9024 (1)	8
P(3)	9765 (1)	12074 (1)	3579 (1)	7
P(4)	8184 (1)	2166 (1)	8676 (1)	9
O(1)	1774 (2)	4460 (3)	8311 (2)	11
O(2)	4177 (2)	3934 (2)	8775 (2)	12
O(3)	8140 (3)	1442 (3)	10145 (2)	12
O(4)	4345 (3)	10835 (3)	8623 (3)	23
O(5)	3839 (2)	9223 (3)	7364 (2)	11
O(6)	3429 (2)	6372 (2)	8348 (3)	12
O(7)	10126 (3)	13653 (2)	3003 (2)	10
O(8)	9081 (3)	11824 (3)	5081 (3)	18
O(9)	9572 (2)	13560 (2)	568 (2)	8
O(10)	12200 (2)	14596 (3)	534 (2)	10
O(11)	8760 (3)	11456 (3)	2956 (3)	16
O(12)	6696 (3)	2679 (3)	8544 (3)	17
O(13)	8599 (3)	979 (3)	7967 (2)	14
O(14)	-6269 (2)	-409 (3)	13313 (2)	14
O(15)	14440 (3)	1496 (3)	1178 (3)	18
O(16)	-741 (3)	3413 (3)	8032 (2)	13
O(17)	-1200 (3)	8706 (3)	6598 (3)	19
N	-3443 (4)	6164 (5)	7110 (4)	27
C(1)	-3487 (8)	6078 (8)	5764 (6)	59
C(2)	-3822 (13)	7410 (11)	4936 (9)	132
C(3)	-2288 (10)	5325 (11)	5164 (8)	90
O(W1)	1683 (4)	1680 (3)	9986 (4)	34
O(W2)	1813 (50)	1695 (53)	7554 (49)	†

\*  $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ .

† Thermal parameter fixed at 0.05  $\text{\AA}^2$ , occupancy refined to 0.09 (1).

(take-off angle  $3^\circ$ ), Mo  $K\alpha$  radiation;  $\theta$ - $2\theta$  scans, 10 s background count,  $3 < 2\theta < 55^\circ$ , scan rate  $2^\circ \text{ min}^{-1}$ ; 3 orthogonal reflexions monitored periodically showed no significant variation; data collected for 3836 unique reflexions of which 173 unobserved ( $I < 0$ ) and excluded from structure solution and refinement; absorption correction applied (from 0.9102 to 0.7372); solution in  $P\bar{1}$  using direct-methods package in *SHELX* (Sheldrick, 1976); structure of framework refined isotropically;  $\Delta\rho$  map revealed position of  $\text{iPrNH}_2$  molecule; other scattering centres located in channels presumed to be  $\text{H}_2\text{O}$ ; structure, except hydrogen and water, refined anisotropically to  $wR = 0.039$ ,  $R = 0.034$ ,  $S = 1.10$ ; interatomic distances involving  $\text{iPrNH}_2$  and water molecules constrained during refinement; nitrogen atom assigned on basis of thermal parameters and hydrogen bonding; function minimized:  $\sum w(F_o - F_c)^2$ ;  $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ ,  $\sigma$  based on counting statistics;  $(\text{shift}/e.s.d.)_{\text{max}} = 0.01$  for final cycle of refinement; in final  $\Delta\rho$  map peaks  $-0.21$  to  $+0.21 e \text{\AA}^{-3}$ . Analytical expressions for scattering factors from *International Tables for X-ray Crystallography* (1974), corrected for anomalous dispersion. Calculations carried out on a Digital Equipment Vax 11/750 at The Research School of Chemistry, ANU, Canberra, using programs *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.

**Discussion. Framework.** The structure of  $\text{GaPO}_4\cdot 14$  consists of a framework  $[\text{Ga}_4(\text{PO}_4)\text{OH}]^-$  enclosing pores containing protonated isopropylamine ( $\text{C}_3\text{H}_{10}\text{N}$ )<sup>+</sup> (Fig. 1). Channels, bounded by eight oxygen atoms (8 rings) lead into these pores. These 8-ring channels run in the [010] and [100] directions.

\* Lists of structure factors, anisotropic thermal parameters, hydrogen positional parameters and details of hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42737 (25 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 ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $\text{GaPO}_4\cdot 14$

O(5)-Ga(1)	1.918 (3)	O(7)-Ga(4)	1.909 (3)
O(6)-Ga(1)	1.851 (3)	O(1)-Ga(4)	1.934 (3)
O(3)-Ga(1)	1.861 (3)	O(9)*-Ga(4)	2.084 (3)
O(9)-Ga(1)	2.138 (3)	O(16)-Ga(4)	1.910 (3)
O(11)-Ga(1)	1.842 (3)	O(10)-Ga(4)	1.961 (3)
		O(9)-Ga(4)	2.053 (3)
O(5)-Ga(1)-O(6)	91.2 (1)	O(7)-Ga(4)-C(1)	98.2 (1)
O(5)-Ga(1)-O(3)	94.0 (1)	O(7)-Ga(4)-O(9)*	174.2 (1)
O(5)-Ga(1)-O(9)	178.9 (1)	C(7)-Ga(4)-O(16)	93.9 (1)
O(5)-Ga(1)-O(11)	93.0 (1)	O(7)-Ga(4)-O(10)	92.7 (1)
O(6)-Ga(1)-O(3)	115.6 (1)	O(7)-Ga(4)-O(9)	90.5 (1)
O(6)-Ga(1)-O(9)	89.7 (1)	O(1)-Ga(4)-O(9)*	84.9 (1)
O(6)-Ga(1)-O(11)	123.0 (1)	O(1)-Ga(4)-O(16)	91.9 (1)
O(3)-Ga(1)-O(9)	85.1 (1)	O(1)-Ga(4)-O(10)	165.2 (1)
O(3)-Ga(1)-O(11)	120.7 (1)	O(1)-Ga(4)-O(9)	84.2 (1)
O(9)-Ga(1)-O(11)	87.0 (1)	O(9)*-Ga(1)-O(10)	83.4 (1)
		O(9)*-Ga(4)-O(9)	84.9 (1)
		O(9)*-Ga(4)-O(16)	90.9 (1)
		O(16)-Ga(4)-O(10)	97.3 (1)
		O(16)-Ga(4)-O(9)	174.5 (1)
		O(10)-Ga(4)-O(9)	85.7 (1)
O(2)-Ga(2)	1.798 (3)	O(14)-Ga(3)	1.817 (3)
O(4)-Ga(2)	1.803 (3)	O(17)-Ga(3)	1.808 (3)
O(12)-Ga(2)	1.838 (3)	O(13)-Ga(3)	1.823 (3)
O(15)-Ga(2)	1.820 (3)	O(8)-Ga(3)	1.793 (3)
O(15)-Ga(2)-O(2)	115.0 (1)	O(14)-Ga(3)-O(17)	106.4 (1)
O(15)-Ga(2)-O(4)	111.7 (2)	O(14)-Ga(3)-O(13)	113.4 (1)
O(15)-Ga(2)-O(12)	111.8 (1)	O(14)-Ga(3)-O(8)	109.1 (1)
O(12)-Ga(2)-O(2)	94.4 (1)	O(17)-Ga(3)-O(8)	113.7 (1)
O(12)-Ga(2)-O(4)	105.2 (1)	O(17)-Ga(3)-O(13)	108.6 (1)
O(4)-Ga(2)-O(2)	117.0 (1)	O(13)-Ga(3)-O(8)	105.9 (1)
O(14)-P(1)	1.531 (3)	O(1)-P(2)	1.519 (3)
O(15)-P(1)	1.546 (3)	O(2)-P(2)	1.534 (3)
O(4)-P(1)	1.526 (3)	O(6)-P(2)	1.545 (3)
O(5)-P(1)	1.500 (3)	O(10)-P(2)	1.530 (3)
O(14)-P(1)-O(15)	106.7 (2)	O(10)-P(2)-O(1)	113.8 (2)
O(14)-P(1)-O(4)	110.7 (2)	O(10)-P(2)-O(2)	110.2 (2)
O(14)-P(1)-O(5)	109.5 (2)	O(10)-P(2)-O(6)	109.9 (2)
O(15)-P(1)-O(4)	109.7 (2)	O(6)-P(2)-O(1)	109.1 (2)
O(15)-P(1)-O(5)	111.4 (2)	O(6)-P(2)-O(2)	103.8 (2)
O(4)-P(1)-O(5)	108.9 (2)	O(2)-P(2)-O(1)	109.6 (2)
O(11)-P(3)	1.523 (3)	O(3)-P(4)	1.529 (3)
O(7)-P(3)	1.508 (3)	O(2)-P(4)	1.529 (3)
O(8)-P(3)	1.524 (3)	O(13)-P(4)	1.540 (3)
O(17)-P(3)	1.550 (3)	O(16)-P(4)	1.504 (3)
O(11)-P(3)-O(7)	115.3 (2)	O(16)-P(4)-O(3)	113.8 (2)
O(11)-P(3)-O(8)	109.7 (2)	O(16)-P(4)-O(12)	108.3 (2)
O(11)-P(3)-O(17)	108.9 (2)	O(16)-P(4)-O(13)	110.3 (2)
O(7)-P(3)-O(8)	106.7 (2)	O(13)-P(4)-O(3)	104.1 (2)
O(7)-P(3)-O(17)	107.9 (2)	O(13)-P(4)-O(12)	109.5 (2)
O(8)-P(3)-O(17)	108.2 (2)	O(12)-P(4)-O(3)	110.8 (2)

\* Related to O(9) by the operation  $-x, 1-y, 2-z$ .

Within the framework there are  $\text{PO}_4$  and  $\text{GaO}_4$  tetrahedra cross linking tetramers of Ga-centred polyhedra. These tetramers consist of edge- and corner-linked  $\text{GaO}_4(\text{OH}_2)$  octahedra [Ga(4)] and  $\text{GaO}_4(\text{OH})$  trigonal bipyramids [Ga(1)]; the average angular deviations from these ideal geometries being 3 and 5°, respectively. Similar geometries are to be found in frameworks of types 15 and 12 (Parise, 1984*b*; Bennett, Cohen, Artioli, Pluth & Smith, 1985; Parise, 1984*c*, 1985*b*). In type 15 this grouping consists of two-gallium-centred octahedra which share a common edge. Each of these octahedra then share corners with two additional octahedra (Mooney-Slater, 1966). The common edges and corners consist of hydroxyl groups whilst the remaining atoms coordinating the gallium metal are oxygens. Hydroxyl groups are shared only by gallium, and their removal, along with coordinated water, converts the framework to a hypothetical one consisting of alternating  $\text{PO}_4$  and  $\text{GaO}_4$  polyhedra (Fig. 2*a*).

A similar unit exists in the structure of type 12 (Parise, 1985*b*). Two distinct structural elements, consisting of Ga tetramers cross linked *via*  $\text{PO}_4$  and  $\text{GaO}_4$  tetrahedra, intergrow to build the framework. The sheet is reminiscent of the structure of apophyllite [ $\text{KCa}_4(\text{Si}_4\text{O}_{10})_2\text{F}\cdot 8\text{H}_2\text{O}$  (Bloss, 1971)]. The tetramers in this case are composed of trigonal bipyramids which are cross linked by  $\text{PO}_4$  tetrahedra (Fig. 2*c*). None of the framework oxygen atoms are protonated and removal of the corner linkage between three  $\text{GaO}_5$  polyhedra does not lead to a sensible four-connected net.

In  $\text{GaPO}_4$ -14 an intermediate structure exists. The tetramer (Fig. 2*b*) consists of both six- and five-coordinate gallium. Removal of the hydroxyl corner linkage leads to a continuous four-connected net with alternating  $\text{GaO}_4$  and  $\text{PO}_4$  polyhedra in 4 rings. The dehydrated framework would then outline a two-dimensional 8-ring channel system in (001) (Fig. 1).

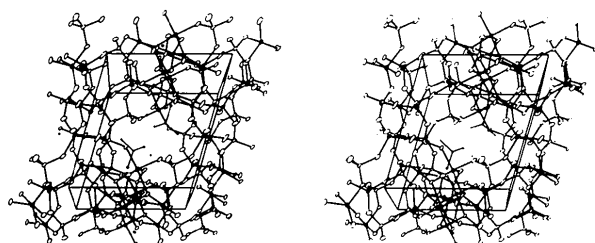
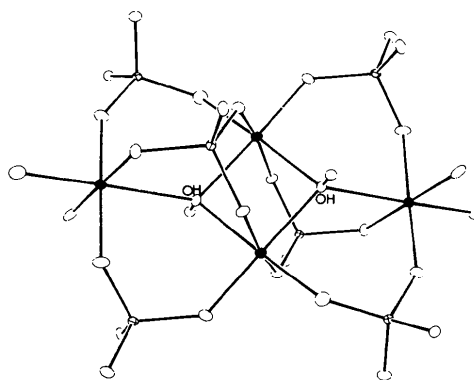
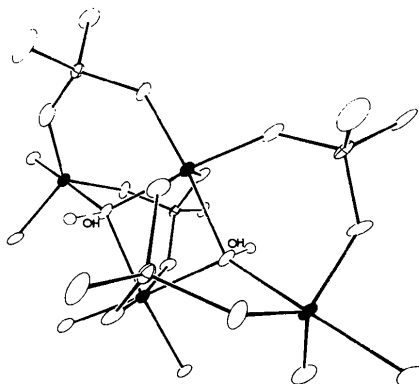


Fig. 1. Stereoscopic ORTEP (Johnson, 1965) drawing of the structure of  $\text{GaPO}_4$ -14. Gallium atoms (in four-, five- and sixfold coordination with oxygen) are represented by solid ellipsoids. Isopropylamine molecules are shown in the channels. The origin of the unit cell (outlined) is in the back left-hand corner with *y* across the page and *z* up. For clarity, hydrogen atoms are omitted.

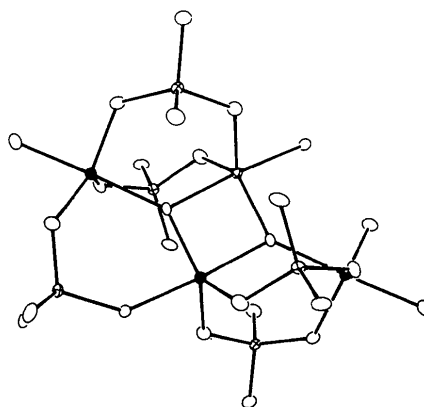
Within the framework of  $\text{GaPO}_4$ -14 the  $\text{GaO}_4$  and  $\text{PO}_4$  polyhedra, which serve to interconnect the tetramers, are tetrahedra with the following average interatomic distances (Table 1): Ga(2)–O, 1.81 (2); Ga(3)–O, 1.81 (1); P(1)–O, 1.53 (2); P(2)–O, 1.53 (1); P(3)–O, 1.53 (2); P(4)–O, 1.53 (2) Å.



(a)



(b)



(c)

Fig. 2. Relationship between the tetramers (see text) found in the structures of (a)  $\text{GaPO}_4$ -15, (b)  $\text{GaPO}_4$ -14 and (c)  $\text{GaPO}_4$ -12. Gallium atoms are represented by filled circles.

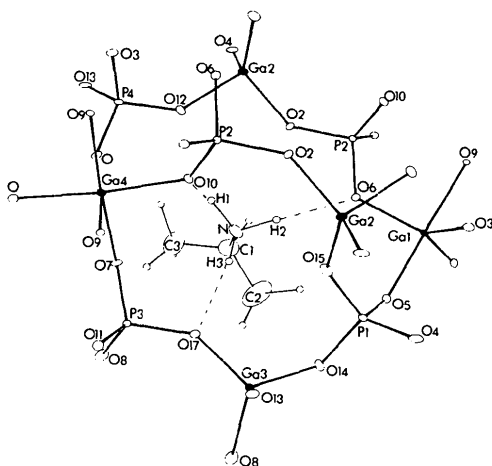


Fig. 3. ORTEP (Johnson, 1965) drawing of the asymmetric unit in  $\text{GaPO}_4\cdot 14$  (see Tables 1 and 2). Hydrogen atoms [H(1)–H(3)] are hydrogen bonded (dotted lines) to oxygen atoms of the framework.

**Template.** The isopropylamine molecule is hydrogen bonded to the framework (Fig. 3) via N–H...O linkages. The geometries of these are as follows: N–H(1)...O(10), 2.29 (3) Å, 123 (5)°; N–H(2)...O(6), 1.99 (2) Å, 166 (5)°; N–H(3)...O(17), 2.18 (2) Å, 166 (5)°; the first figure quoted is the H...O distance and the second the N–H...O angle. This hydrogen-bonding scheme serves to anchor the amine group, which has a low thermal parameter

relative to those for the carbon atoms (Table 1 and Fig. 3).

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## Structural Comparison of (*o*-Phenylenediaminetetraacetato)zinc(II) with its Protonated Complex, $X_2\text{ZnC}_{14}\text{H}_{12}\text{N}_2\text{O}_8\cdot n\text{H}_2\text{O}$ ( $X = \text{K}$ or $\text{H}$ )

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**Abstract.** (1)  $X = \text{K}$ ,  $n = 3$ ,  $M_r = 533.9$ , monoclinic,  $P2_1/a$ ,  $a = 24.140$  (3),  $b = 8.551$  (1),  $c = 9.684$  (1) Å,  $\beta = 97.11$  (1)°,  $V = 1983.7$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.780$ ,  $D_x = 1.788$  g cm<sup>-3</sup>,  $\mu = 59.9$  cm<sup>-1</sup>,  $F(000) = 1088$ , final  $R = 0.037$  for 3113 observed reflections. (2)  $X = \text{H}$ ,  $n = 2$ ,  $M_r = 439.7$ , triclinic,  $P\bar{1}$ ,  $a = 12.851$  (3),  $b = 15.366$  (7),  $c = 9.583$  (2) Å,  $\alpha = 103.48$  (4),  $\beta =$

$89.28$  (2),  $\gamma = 108.67$  (4)°,  $V = 1739$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.682$ ,  $D_x = 1.678$  g cm<sup>-3</sup>,  $\mu = 23.2$  cm<sup>-1</sup>,  $F(000) = 904$ , final  $R = 0.046$  for 5469 observed reflections. For both cases  $\lambda(\text{Cu } K\alpha) = 1.5417$  Å,  $T = 293$  K. In the potassium complex ( $X = \text{K}$ ), the zinc ion is hexacoordinate but the coordination environment deviates markedly from  $O_h$ . In the diprotonated complex ( $X = \text{H}$ ), a coordinated carboxylate O is replaced by a water molecule and the coordination polyhedron retrieves the octahedral geometry.

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