The crystal structures of adamite and paradamite

Toshio Kato

Institute of Earth Sciences, Faculty of Liberal Arts
Yamaguchi University, Yoshida, Yamaguchi 753

Yasunori Miûra

Department of Mineralogical Sciences and Geology,
Faculty of Literature and Science,
Yamaguchi University, Yoshida, Yamaguchi 753

Abstract

The crystal structures of adamite, $Zn_2(OH)(AsO_4)$, and its dimorph, paradamite have been refined. Adamite is the andalusite-type structure, and paradamite is isostructural with tarbuttite. The structures of these two minerals are compared. Mean bond lengths of these structures are:

	adamite	paradamite
As–O	1.69 Å	1.68 Å
Zn(VI)–O	2.13	—
Zn(V)–O	2.04	$\begin{cases}2.06_5\\2.06\end{cases}$

Introduction

As a part of a detailed study of the crystal structures of arsenate minerals, the crystal structures of adamite and paradamite have been refined. Adamite is the dimorph of paradamite, and each has a chemical formula of $Zn_2(OH)(AsO_4)$. The crystal structure of adamite was determined by Kokkoros (1937) and it was confirmed that adamite is isostructural with andalusite. Paradamite was first described by Switzer (1956). Finney (1966) determined unit cell para-

meters of paradamite and tarbuttite and concluded that these min-
erals are isostructural. The crystal structure of tarbuttite was
determined by Cocco *et al.* (1966). The essential structural differ-
ence between these structures is coordination of Zn polyhedra. In
paradamite, the Zn ions are all five coordinated, while in adamite
half of the Zn ions are five coordinated and the remaining Zn ions
are six coordinated. It is a main purpose of this study to compare
the configuration of As tetrahedra and Zn polyhedra between these
structures.

Experimental

The samples of both minerals from Mapimi, Mexico were used
in this study. The sample of paradamite was provided by British
Museum (BM 1969, 183). An adamite crystal of $0.2 \times 0.2 \times 0.1$ mm in
size and a paradamite crystal of $0.2 \times 0.2 \times 0.17$ mm were chosen for
the refinement.

The unit cell dimensions obtained by least-squares refinement
with a Syntex single crystal diffractometer are given in Table 1,
together with those of previous works.

Correct cell orientation of paradamite was determined using the

Table 1. Unit cell data.

| | adamite | | | paradamite | |
	Kokkoros (1937)	This study		Finney (1966)*	This study
a	8.34 kX	8.386(5) Å	a	5.807 Å	5.830(1) Å
b	8.56	8.552(4)	b	6.666	6.711(2)
c	6.09	6.036(4)	c	5.627	5.648(1)
			α	104°15′	104.73(2)°
			β	92°08′	92.26(1)°
			γ	76°48′	76.81(2)°
Space group		$Pnnm$		$P\bar{1}$	

* β and γ are modified to the supplementary angle.

program UTRDCL written by Takeda (Sakurai, 1967). The α and γ values by Finney (1966) were modified to the supplementary angle, respectively. The unit cell of tarbuttite determined by Cocco *et al.* (1966) also must be modified.

Intensity measurements were made with a Syntex $P\bar{1}$ automated single crystal diffractometer, using MoKα radiation with a graphite monochromator. Only reflections for which $I>3\sigma(I)$ were considered observed. Intensities of 496 reflections for adamite and 970 reflections for paradamite were measured in the 1°–60° 2θ range using 2θ–θ scans in the variable scan-speed mode. The intensities were corrected for Lorentz and polarization effects and for absorption.

Refinement

The atomic coordinates of eveite, $Mn_2(OH)(AsO_4)$, by Moore and Smyth (1968) and those of tarbuttite by Cocco *et al.* (1966) were used for starting parameters of adamite and paradamite, respectively. The full matrix least-squares program, FLS-4 (Sakurai, 1967) was used for the refinement. The final conventional unweighted residuals are $R=0.080$ for adamite and 0.102 for paradamite. Although the precision of residuals is not good, this is attributed to the high absorption effect ($\mu=191.7\,\text{cm}^{-1}$ for adamite and 203.5 cm^{-1} for paradamite).

The atomic coordinates are listed in Table 2. Bond lengths and angles of adamite and paradamite are listed in Tables 3 and 4, respectively.

Discussion

Adamite is isostructural with andalusite, and is characterized by the Zn ions having two different coordinations (Fig. 1). The Zn(VI) ions are coordinated to 4O and 2OH. The Zn(VI) octahedra form chains parallel to the c-axis by sharing edges. The Zn(V) ions are

Table 2. Atomic coordinates.

Adamite

Atom	x	y	z	B
Zn(VI)	0	0	0.2478(3)	0.88(3)
Zn(V)	0.3674(2)	0.1366(2)	0.5	0.59(3)
As	0.2503(2)	0.2582(2)	0	0.47(3)
OH=O(1)	0.394(2)	0.376(1)	0.5	0.96(18)
O(2)	0.424(2)	0.357(1)	0	0.91(18)
O(3)	0.104(2)	0.394(2)	0	1.33(18)
O(4)	0.231(1)	0.1414(9)	0.223(1)	1.09(18)

Paradamite

Atom	x	y	z	B
Zn(1)	0.7505(4)	0.5005(4)	0.3928(5)	0.57(4)
Zn(2)	0.2646(4)	0.1867(4)	0.0213(5)	0.42(4)
As	0.7525(3)	0.2748(3)	0.8313(4)	0.25(4)
O(1)	0.031(3)	0.141(2)	0.762(3)	0.33(22)
O(2)	0.610(3)	0.126(2)	0.944(3)	0.37(22)
O(3)	0.618(3)	0.332(2)	0.578(2)	0.60(22)
O(4)	0.254(3)	0.498(2)	0.955(3)	0.27(22)
OH	0.109(3)	0.299(2)	0.353(3)	0.38(22)

coordinated to 4O and 1OH. The Zn(V) polyhedra, which occur in pairs having a common edge, are connected to the As tetrahedra through O(3) and O(4), thus forming a supporting framework for the octahedral Zn(VI) chains.

In the Zn(VI) octahedra, Zn(VI)-O(4) bond length, 2.28_9 Å, is longer than others, and can be considered to be 4+2 coordinated. The shared edges, OH-OH', 2.76_7 Å, and O(2)-O(2'), 2.75_8 Å, are shorter than others. The mean bond length of Zn(VI)-O is 2.13 Å.

The five coordinated Zn(V) polyhedra can be described as distorted trigonal bipyramid. To stabilize the high energy effects of

Table 3. Bond lengths and angles of adamite.

As tetrahedron

around As

As–O(2)	(×1)	1.684(15) Å	O(4)–O(4′)	(×1)	2.758(15) Å	O(2)–O(3)	(×1)	106.46(70)°
As–O(3)	(×1)	1.689(17)	O(3)–O(2)	(×1)	2.702(24)	O(2)–O(4)	(×2)	112.38(85)
As–O(4)	(×2)	1.684(46)	O(4)–O(3)	(×2)	2.759(62)	O(3)–O(4)	(×2)	109.75(1.41)
			O(4)–O(2)	(×2)	2.798(52)	O(4)–O(4′)	(×1)	106.13(2.93)
Mean		1.69	Mean		2.76	Mean		109.5

Zn(V) polyhedron

around Zn(V)

Zn(V)–OH	(×1)	2.059(9) Å	O(3)–O(3′)*	(×1)	2.516(24) Å	OH–O(3′)	(×1)	167.19(66)°
Zn(V)–O(3′)	(×1)	2.001(17)	O(4)–O(4′)	(×1)	3.334(9)	O(4)–O(3)	(×2)	124.22(39)
Zn(V)–O(3)	(×1)	2.089(17)	O(3)–OH	(×1)	2.904(21)	O(4)–O(4′)	(×1)	111.21(33)
Zn(V)–O(4)	(×2)	2.026(7)	O(4)–OH	(×2)	2.948(54)	O(3′)–O(4)	(×2)	94.78(2.18)
			O(4)–O(3)	(×2)	3.560(18)	OH–O(4)	(×2)	92.35(2.18)
			O(4)–O(3′)	(×2)	3.031(56)	OH–O(3)	(×1)	91.30(68)
						O(3′)–O(3)	(×1)	75.89(67)
Mean		2.04	Mean		3.09			

Zn(VI) octahedron

around Zn(VI)

Zn(VI)–OH	(×2)	2.038(9) Å	OH–OH′*	(×1)	2.767(18) Å	O(2)–O(2′)	84.35(33)°
Zn(VI)–O(2)	(×2)	2.054(7)	O(2)–O(2′)*	(×1)	2.758(15)	OH–OH′	85.55(38)
Zn(VI)–O(4)	(×2)	2.289(50)	O(2)–OH	(×2)	3.033(3)	OH–O(2)	84.35(33)
			O(2)–O(4)	(×2)	3.070(16)	OH–O(4)	81.82(1.23)
			O(2)–O(4′)	(×2)	3.225(59)	OH–O(4′)	92.65(1.14)
			OH–O(4)	(×2)	3.134(18)	O(2)–O(4)	89.80(1.22)
			OH–O(4′)	(×2)	2.839(62)	O(2)–O(4′)	95.76(1.14)
Mean		2.13	Mean		3.01		

* Shared edges.

Table 4. Bond lengths and angles of paradamite.

As tetrahedron

				around As	
As-O(1)	1.668(16) Å	O(1)-O(2)	2.722(27) Å	O(1) O(2)	108.6(9)°
As-O(2)	1.685(21)	O(1)-O(3)	2.774(24)	O(1)-O(3)	110.8(9)
As-O(3)	1.703(19)	O(1)-O(4')	2.754(21)	O(1)-O(4')	110.7(8)
As-O(4)	1.681(16)	O(2)-O(3)	2.765(30)	O(2)-O(3)	109.4(9)
		O(2)-O(4')	2.747(27)	O(3)-O(4')	108.0(9)
		O(3)-O(4')	2.738(25)	O(2)-O(4')	109.4(9)
Mean	1.68	Mean	2.75	Mean	109.5

Zn(1) polyhedron

				around Zn(1)	
Zn(1)-O(3)	2.018(22) Å	O(3)-O(3')*	2.656(27) Å	O(3)-O(3')	79.3(7)°
Zn(1)-O(3')	2.142(16)	O(3)-O(4')	3.659(29)	O(3)-O(4')	132.7(8)
Zn(1)-O(4')	1.977(19)	O(3)-OH	3.135(26)	O(3)-OH	96.3(7)
Zn(1)-OH	2.188(16)	O(3)-OH'	3.189(28)	O(3)-OH'	105.1(8)
Zn(1)-OH'	2.001(18)	O(3')-O(4')	2.872(24)	O(3')-O(4')	88.3(7)
		O(3')-OH'	3.203(25)	O(3')-OH	173.7(7)
Mean	2.06₅	O(4')-OH	2.986(25)	O(3')-OH'	101.2(7)
		O(4')-OH'	3.482(25)	O(4')-OH	91.5(7)
		OH-OH'*	2.814(21)	O(4')-OH'	122.2(8)
				OH-OH'	84.3(8)

Zn(2) polyhedron

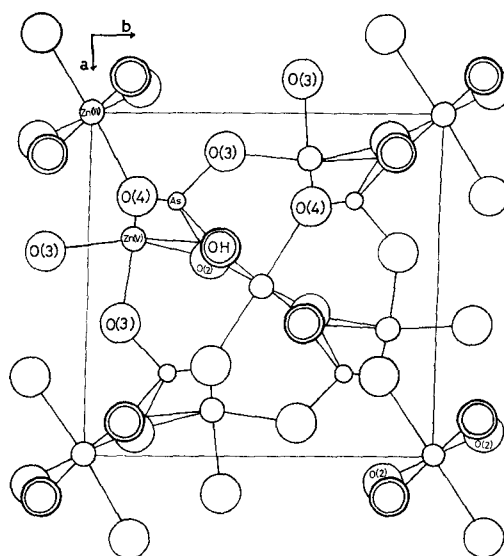|				around Zn(2)	
Zn(2)-O(1)	1.988(18) Å	O(1)-O(2)	3.483(25) Å	O(1)-O(2)	121.6(7)°
Zn(2)-O(2)	2.002(18)	O(1)-O(2')	3.155(26)	O(1)-O(2')	89.2(7)
Zn(2)-O(2')	2.114(18)	O(1)-O(4)	2.939(26)	O(1)-OH	110.8(7)
Zn(2)-O(4)	2.193(19)	O(1)-OH	3.285(25)	O(2)-O(2')	76.3(8)
Zn(2)-OH	2.005(18)	O(2)-O(2')*	2.545(29)	O(2)-O(4)	85.4(7)
		O(2)-O(4)	2.848(23)	O(2)-OH	127.6(7)
Mean	2.06	O(2)-OH	3.596(25)	O(2')-O(4)	161.7(7)
		O(2')-OH	3.046(21)	O(2')-OH	95.4(7)
		O(4)-OH	3.113(30)	O(4)-OH	95.6(7)
OH-O(1)	2.867(25)				

* Shared edges.

Fig. 1.   Projection on (001) of the adamite structure.

edge sharing, the edge shortening (O(3)-O(3'), 2.51_6 Å) occurs. The mean bond length of Zn(V)-O is 2.04 Å. The As tetrahedra can be considered to be regular.

The O(2) and O(3) are coordinated to 2Zn(V) and 1As, while O(4) and OH are to 1Zn(VI), 1Zn(V) and 1As.

On the other hand, paradamite is isostructural with tarbuttite, and the structure is characterized by the fact that the Zn ions are all five coordinated (Fig. 2). The Zn(1) polyhedra form an infinite zig-zag chain along the a-axis. Each of the Zn(1) polyhedra shares three corners, with the Zn(2) polyhedra, and thus form a three-dimensional array. The As tetrahedra, joining together two Zn(2) polyhedra and further connecting the chains of Zn(1) polyhedra.

The Zn ions are bonded to 5O, lying at the corners of a distorted trigonal bipyramid. The average value for the Zn-O bond length is 2.06 Å, which is compared with 2.04 Å for the Zn(V) polyhedra in
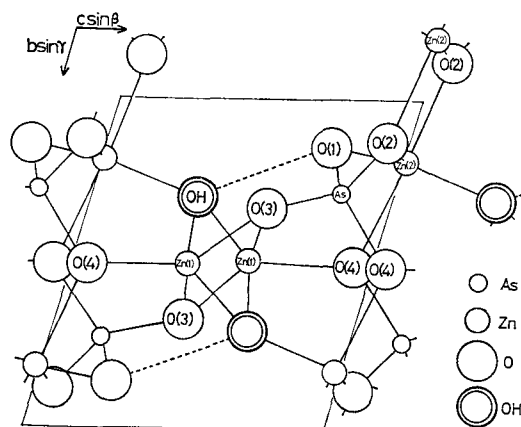
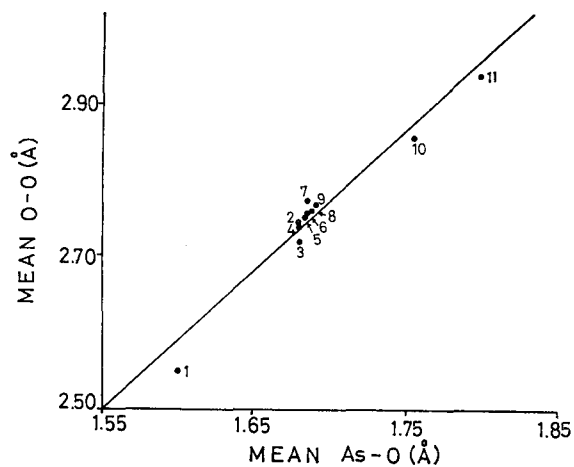Fig. 2. Projection along the a-axis of the paradamite structure. Dotted lines mean the hydrogen bond.

Fig. 3. Plot of O-O *versus* As-O distances for several arsenate minerals. No. 1: retzian (Moore, 1967), 2: alactite (Moore, 1968a), 3: abernathyite (Ross and Evans, 1964), 4: flinkite (Moore, 1967), 5: paradamite (this study), 6: adamite (this study), 7: eveite (Moore and Smyth, 1968), 8: conichalcite (Qurashi and Barnes, 1963), 9: pharmacosiderite (Buerger *et al.*, 1967), 10: stranskite (Plieth and Sänger, 1967), 11: chlorophonecite (Moore, 1968b).

adamite. There is a slight difference between Zn(V) bipyramids in these structures, and those of adamite are more regular.

The oxygen atoms in paradamite, O(1), O(2), O(3), O(4) and OH are coordinated to Zn(2)+As, 2Zn(2)+As, 2Zn(1)+As, Zn(1)+Zn(2)+ As, and 2Zn(1)+Zn(2), respectively.

In Fig. 3, the mean bond length of As–O, against the mean distance O–O for several arsenate minerals which contain isolated As tetrahedra are plotted. A good linear relationship was obtained.

The packing index, volume of cell/Σ anions in cell, is 21.6 Å³/ anion for adamite and 20.4 Å³/anion for paradamite.

REFERENCES

BUERGER, M. J., DOLLASE, W. A. & GARAYCOCHEA-WITTKE, J. (1967)   *Zeits. Krist.*, **125**, 92.

COCCO, G., FANFANI, L. & ZANAZZI, P. F. (1966)   *Zeits. Krist.*, **123**, 321.

FINNEY, J. J. (1963)   *Amer. Miner.*, **48**, 1.

FINNEY, J. J. (1966)   *Amer. Miner.*, **51**, 1218.

HERITSCH, H. (1937)   *Zeits. Krist.*, **98**, 351.

KOKKOROS, P. (1937)   *Zeits. Krist.*, **96**, 417.

MOORE, P. B. (1967)   *Amer. Miner.*, **52**, 1603.

MOORE, P. B. (1968a)   *Amer. Miner.*, **53**, 733.

MOORE, P. B. (1968b)   *Amer. Miner.*, **53**, 1110.

MOORE, P. B. & SMYTH, J. R. (1968)   *Amer. Miner.*, **53**, 1841.

PLIETH, K. & SÄNGER, G. (1967)   *Zeits. Krist.*, **124**, 91.

QURASHI, M. M. & BARNES, W. H. (1963)   *Canad. Miner.*, **7**, 51.

ROSS, M. & EVANS, H. T. (1964)   *Amer. Miner.*, **49**, 1578.

SAKURAI, T. (ed.) (1967)   *Universal crystallographic computation program system.* Cryst. Soc. Japan.

SWITZER, G. (1956)   *Science*, **123**, 1039.