

The crystal structure and infrared properties of adamite

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Abstract

The crystal structure of adamite, $Zn_2(AsO_4)(OH)$, has been solved by direct methods and refined by full-matrix least-squares to $R = 0.0402$ ($R_w = 0.0302$) using 1472 equi-inclination counter data recorded with graphite-monochromatized $MoK\alpha$ radiation. The structure is orthorhombic, $Pn\bar{m}$ (D_{2h}^{12}) with $a = 8.306(4)$, $b = 8.524(6)$, $c = 6.043(3)$ Å and $Z = 4$. Isotypy with andalusite and the members of the olivenite group of minerals is confirmed, the Zn atoms occurring in both six- and five-fold coordination. $ZnO_4(OH)_2$ octahedra share edges to produce chains parallel to the c axis, and share corners with edge-sharing $ZnO_4(OH)$ trigonal bipyramids in the a - and b -axis directions. AsO_4 groups connect the two Zn polyhedron types to produce a dense framework structure in which all O atoms and OH groups are trigonally coordinated.

Introduction

The secondary mineral adamite had early been suggested to be a member of the olivenite group of minerals on the basis of symmetry, cell dimensions and composition, but this relationship was not confirmed until Kokkoros (1937) reported a two-dimensional crystal structure analysis of the species using less than 100 X-ray reflections. Other workers (Strunz, 1936; Heritsch, 1940; Richmond, 1940; Mrose *et al.*, 1948) have concentrated on physical and morphological properties.

Olivenite, $Cu_2(AsO_4)(OH)$, libethenite, $Cu_2(PO_4)(OH)$, eveite, $Mn_2(AsO_4)(OH)$, and adamite are isostructural with the high-temperature mineral andalusite, Al_2SiO_5 (Strunz, 1936; Heritsch, 1940; Moore and Smyth, 1968), and are characterized by the presence of M^{2+} cations in both five- and six-fold coordination. In addition, the component $Co_2(AsO_4)(OH)$ has been found in solid solution with adamite, and a continuous series exists between the synthetic compounds (Keller, 1971).

Experimental

Two fragments of adamite from the Ojuela mine, Mapimi, Durango, Mexico, with (roughly cubic) di-

mensions 0.095 and 0.097 mm were mounted about the a and c directions, respectively. Preliminary Weissenberg photographs established the crystals to be orthorhombic, $Pn\bar{m}$ or $Pnn2$. Space group $Pn\bar{m}$ (D_{2h}^{12}) was subsequently confirmed by the application of statistical tests (Howells *et al.*, 1950; Ramachandran and Srinivasan, 1959) to the X-ray diffraction data. All X-ray data were collected at 21°C on a Stoe automatic Weissenberg diffractometer using $MoK\alpha$ radiation monochromatized with a graphite crystal ($\lambda = 0.7107$ Å). The lattice parameters were determined from ω scans of $h00$, $0k0$, and $00l$ reflections and the results refined by the method of least squares. These values, together with other physical constants for adamite are: $a = 8.306(4)$,² $b = 8.524(6)$, $c = 6.043(3)$ Å, $V = 427.85$ Å³, formula weight = 286.68, $Z = 4$, $F(000) = 536e$, $D_m(\text{water immersion}) = 4.434(8)$ g.cm⁻³, $D_x = 4.45$ g.cm⁻³.

The intensities were measured by the ω -scan technique using a procedure detailed by Snow (1974). Data were gathered for a quadrant of reflections about both crystals (a axis, $0kl-11kl$; c axis, $hk0-hk10$). Standard reflections monitored for each reciprocal lattice layer showed no sensible change. Lorentz and polarization corrections appropriate for use with a highly mosaic monochromator (Whittaker, 1953) were applied, and the data from both axes

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² e.s.d.'s given in parentheses, refer to the last decimal place.

(representing 5258 intensities) were then scaled together by a non-iterative least-squares method (Rae, 1965) to yield 1472 unique reflections. Of these data, 202 had intensities less than three times the standard deviation of the counting statistics and were considered to be "unobserved." No absorption corrections were applied.

Structure determination and refinement

The As and (two) Zn atoms were located by application of the Symbolic Addition Procedure (Karle and Karle, 1966) and refined by least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors and the weights (w) are derived from counting statistics. A subsequent difference map yielded the four O atoms. Isotropic refinement converged with a conventional R index of 0.075. Anisotropic temperature factor refinement³ incorporating the symmetry restrictions of Levy (1956) for the six atoms in special positions reduced R to 0.043.

The high intensity reflections were observed to behave in a manner consistent with the occurrence of extinction, and the observed structure factor was therefore replaced by the expression $F_o K^{-1} [1 + f(\theta) K^2 F_c^2 G]^{1/4}$, where K is the scale factor normally applied to $|F_c|$, $f(\theta)$ is $(1 + \cos^2 2\theta) / [\sin 2\theta (1 + \cos^2 2\theta)]$, and G is a secondary extinction parameter. Full-matrix refinement using only the observed reflections then converged to a final R value of 0.0402 and $R_w^4 = 0.0302$ ($R = 0.050$ and $R_w = 0.031$ for all reflections). The value of G was $5.9(4) \times 10^{-4} e^{-2}$.

From a consideration of the adamite asymmetric unit contents, the hydrogen atom in the formula unit must occur either on the two-fold axis, or on the mirror plane at $z = 0$ or $z = 1/2$. The two-fold position may be eliminated since the proton would then have to exist inside a ZnO_6 octahedron or on one of its shared edges: Baur (1972, 1973) has pointed out that this is an unlikely situation. Difference maps were therefore computed using both the full data set and those data for which $\sin\theta/\lambda < 0.4$, in an attempt to locate the proton on one or other of the mirror planes. One peak was observed on the zero level of the unit cell, in both syntheses, at a distance of 0.77 Å from the O(2) atom and with an intensity appropriate to that of a hydrogen atom. However, least-squares refinement of this H position converged to within 0.5

Å of O(2), indicating that the peak probably represents an accumulation of residual (probably absorption) errors in the data, rather than a physically meaningful atom site. Nevertheless, electrostatic bond strength considerations, presented below, indicate the involvement of the O(2) atom in a bond to H, and for this reason the difference-map-suggested (but not refined) H atom position has been included in the final list of atomic coordinates.

Scattering factors for As, Zn, and O (neutral atoms) were obtained from *International Tables for X-ray Crystallography* (1962) and were corrected for the real part of the anomalous dispersion (Cromer, 1965); for H, the values were those of Stewart *et al.* (1965). Programs used for solution, refinement, and geometry calculations were local modifications of FAME,⁵ MULTAN,⁶ FORDAP,⁷ ORFLS (Busing *et al.*, 1962), ORFFE (Busing *et al.*, 1964) and ORTEP (Johnson, 1965).

The final least-squares parameters of the atoms and their standard deviations (estimated from the inverted full matrix) are given in Table 1. Table 2 presents the anisotropic thermal ellipsoid data from Table 1 transformed to the parameters of dimensions (r.m.s. vibrations in Å) and orientations of principal ellipsoid axes, while the geometry of the structure is given in Table 3. The observed and calculated structure factors are compared in Table 4.⁸

Discussion of the structure

Aside from minor differences in coordinates (when transformed according to the relationship $1/2-x$, $1/2-y$, $1/2-z$), the adamite crystal structure (Fig. 1) is identical to that of andalusite (Burnham and Buerger, 1961), and the members of the olivenite group of minerals (Bragg and Claringbull, 1965). The Zn(1) atoms occur in elongate octahedra which share "equatorial" edges to produce infinite chains in the c -axis direction. These chains share corners with insular AsO_4 tetrahedra and with pentacoordinated Zn(2) atoms. These trigonal bipyramids share an

⁵ Part of the Symbolic Addition Package by E. B. Fleischer, A. L. Stone and R. B. K. Dewar of the University of Chicago, used in this study to calculate a set of normalized E values.

⁶ A program for the automatic solution of crystal structures, the *modus operandi* of which is described by Germain *et al.* (1971).

⁷ A program to execute Fourier summations written by A. Zalkin of the University of California, Berkeley, California.

⁸ To obtain a copy of Table 4, order Document AM-76-027 from the Mineralogical Society of America Business Office, 1909 K St. N.W., Washington, D.C. 20006. Please remit \$1.00 in advance for a copy of the microfiche.

³ The form of the anisotropic thermal ellipsoid is

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

⁴ $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$

TABLE 1. Atomic coordinates and temperature factor coefficients for adamite

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|------------------|----------|----------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|
| As | 25048(6) | 24394(5) | 1/2 | 181(5) | 79(4) | 286(4) | -14(5) | 0 | 0 |
| Zn(1) | 0 | 0 | 24737(10) | 529(8) | 260(6) | 311(10) | -159(7) | 0 | 0 |
| Zn(2) | 13482(7) | 36423(6) | 0 | 267(7) | 128(6) | 444(12) | -1(7) | 0 | 0 |
| O(1) | 0760(4) | 1447(4) | 1/2 | 31(5) | 21(4) | 24(6) | -9(6) | 0 | 0 |
| O(2) \equiv OH | 1079(5) | 1268(4) | 0 | 35(5) | 11(3) | 59(7) | 1(4) | 0 | 0 |
| O(3) | 3960(5) | 1063(4) | 1/2 | 33(5) | 8(4) | 126(9) | -2(4) | 0 | 0 |
| O(4) | 2685(3) | 3615(3) | 2778(4) | 41(4) | 28(5) | 39(5) | -10(3) | -6(3) | 11(3) |
| H | 0.20 | 0.13 | 0 | | | | | | |

Positional parameters and anisotropic temperature factors $\times 10^5$ for As and Zn; $\times 10^4$ for O.

The error in the final figure is indicated in parenthesis.

edge to produce $Zn_2O_6(OH)_2$ dimers within the framework. The three O atoms are each coordinated by (two) Zn and As, while the OH group is trigonally coordinated by Zn alone: all four anions are less than 0.5 Å from the cation plane.

In detail (Table 3) the four As-O bonds are statistically identical, but a significant level of bond angle distortion has resulted in a lowering of the symmetry of the AsO_4 group from $\bar{4}3m$ (ideal tetrahedron) to *m*. The sum of the angles subtended by the As and Zn atoms at O(3) and O(4) is 360° and 358.7° respectively, suggesting that the orbitals on both anions are sp^2 hybridized. However, for O(1) the sum of the angles is 344.5°, halfway between those appropriate to trigonal (360°) and truncated tetrahedron (328°) coordination. For O(1) and O(3) the Zn atoms are situated across shared edges (between octahedra and trigonal bipyramids, respectively) which has resulted in considerably narrower Zn-O-Zn angles (95.5° and 104.3°, respectively) relative to Zn-O-As (average = 126.2°). For O(4) there is no edge sharing and the angles are more regular.

The octahedron contains a Zn(1) atom at the center of an approximately square planar array of two O(1) atoms and two OH groups [previously referred to as O(2)] at an average distance of 2.057 Å. Each octahedron shares an OH-OH and an O(1)-O(1) edge with adjacent octahedra in the *c*-axis direction, the shared edges, as expected (Pauling, 1960), being significantly shorter (by an average of 0.246 Å) than the unshared edge (3.037 Å in length). Two O(4) atoms occur above and below the square plane at a distance of 2.261 Å to complete the octahedron.

The OH group is surrounded by three Zn atoms in a similar manner to the cations bonded to O(1). The

small Zn(1)-O-Zn(1) angle (93.6°) is again a function of the shared edge between Zn atoms, while the 16.6° difference between the sum of the three Zn-O-Zn angles and 360° may be rationalized in terms of the presence of a proton bonded to the central anion to complete an approximate tetrahedral array. In this case the anion orbitals are probably sp^3 hybridized.

The Zn(2) atom is situated 0.075 Å out of the

TABLE 2. Magnitudes and orientation of principal axes of thermal ellipsoids in adamite

| Atom | Axis | Rms displacement Å | Angle, in degrees, to | | |
|-------|------|-----------------------|-----------------------|---------|---------|
| | | | +a | +b | +c |
| As | 1 | 0.053(1) | 81(3) | 8(3) | 90 |
| | 2 | 0.073(1) | 90 | 90 | 180 |
| | 3 | 0.080(1) | 8(3) | 98(3) | 90 |
| Zn(1) | 1 | 0.076(1) | 90 | 90 | 0 |
| | 2 | 0.082(2) | 116(1) | 154(1) | 90 |
| | 3 | 0.146(1) | 26(1) | 116(1) | 90 |
| Zn(2) | 1 | 0.069(2) | 90(3) | 0(3) | 90 |
| | 2 | 0.091(1) | 90 | 90 | 180 |
| | 3 | 0.097(1) | 0(3) | 90(3) | 90 |
| O(1) | 1 | 0.066(9) | 90 | 90 | 0 |
| | 2 | 0.076(16) | 123(11) | 147(11) | 90 |
| | 3 | 0.114(11) | 33(11) | 123(11) | 90 |
| O(2) | 1 | 0.065(10) | 92(10) | 2(10) | 90 |
| | 2 | 0.104(7) | 90 | 90 | 180 |
| | 3 | 0.111(7) | 2(10) | 88(10) | 90 |
| O(3) | 1 | 0.055(12) | 86(9) | 4(9) | 90 |
| | 2 | 0.107(8) | 176(9) | 86(9) | 90 |
| | 3 | 0.153(6) | 90 | 90 | 0 |
| O(4) | 1 | 0.073(8) | 96(8) | 125(12) | 35(13) |
| | 2 | 0.096(7) | 126(8) | 129(10) | 120(14) |
| | 3 | 0.131(5) | 37(7) | 122(7) | 106(4) |

Standard errors indicated in parentheses in terms of last significant figures.

TABLE 3. Adamite interatomic distances and angles

| AsO ₄ tetrahedron | | Zn(1)O ₄ (OH) ₂ octahedron | | Zn(2)O ₄ (OH) trigonal bipyramid | |
|------------------------------|-------------|--|--------------------|---|-------------------|
| As - O(1) | 1.678(4) | Zn(1) - O(1) | 2.062(3) x2 | Zn(2) - OH | 2.036(4) |
| O(3) | 1.684(4) | OH | 2.051(3) x2 | O(3) ^{iv} | 1.999(4) |
| O(4) | 1.682(3) x2 | O(4) ⁱⁱ | 2.261(3) x2 | O(3) ^v | 2.079(4) |
| Average = 1.682(2) | | Average = 2.125(1) | | O(4) | 2.013(3) x2 |
| O(1) - O(3) | 2.678(6) | O(1) - O(1) ⁱⁱⁱ | 2.772(7) | OH - O(3) ^{iv} | 2.876(5) |
| O(4) | 2.788(4) x2 | OH | 3.037(2) x2 | O(4) | 2.933(4) x2 |
| O(3) - O(4) | 2.767(4) x2 | O(4) ^{iv} | 3.057(4) x2 | O(3) ^{iv} - O(3) ^v | 2.504(7) |
| O(4) - O(4) ⁱ | 2.685(5) | O(4) ⁱⁱ | 3.212(4) x2 | O(4) | 3.531(5) x2 |
| Average = 2.746(2) | | OH - OH ⁱⁱⁱ | 2.809(7) | O(3) ^v - O(4) | 3.007(4) x2 |
| | | O(4) ⁱⁱ | 2.823(4) x2 | O(4) - O(4) ^{vi} | 3.358(5) |
| | | O(4) ^{iv} | 3.124(5) x2 | Average = 3.076(2) | |
| | | Average = 3.007(2) | | | |
| O(1) - As - O(3) | 105.6(2) | O(1) - Zn(1) - O(1) ⁱⁱⁱ | 84.5(2) | OH - Zn(2) - O(3) ^{iv} | 90.9(2) |
| O(4) | 112.2(1) x2 | OH | 95.2(1) x2 | O(4) | 92.8(1) x2 |
| O(3) | 110.6(1) x2 | O(4) ^{iv} | 89.9(1) x2 | O(3) ^{iv} | 75.7(2) |
| O(4) | 105.9(2) | O(4) ⁱⁱ | 95.9(1) x2 | O(4) | 123.3(1) x2 |
| Average = 109.5(1) | | OH | OH ⁱⁱⁱ | O(4) | 94.6(1) x2 |
| | | O(4) ⁱ | 81.6(1) x2 | O(4) | 113.0(2) |
| | | O(4) ^{iv} | 92.7(1) x2 | OH | O(3) ^v |
| | | O(4) ⁱⁱ | O(4) ^{iv} | | 166.6(2)* |
| | | Average = 90.1(1) | 172.3(1)* | Average equatorial = 119.9(1) | |
| | | | | Average axial = 90.2(1) | |

Symmetry transformations for atoms outside the asymmetric unit:

- i. x, y, 1-z
 ii. $\frac{1}{2}$ -x, y- $\frac{1}{2}$, $\frac{1}{2}$ -z
 iii. \bar{x} , \bar{y} , z
 iv. x- $\frac{1}{2}$, $\frac{1}{2}$ -y, $\frac{1}{2}$ -z
 v. $\frac{1}{2}$ -x, $\frac{1}{2}$ +y, $\frac{1}{2}$ -z
 vi. x, y, \bar{z}

Distances, in Å, and angles, in degrees, with e.s.d.'s given in parentheses in terms of last decimal place.

*Excluded from the average.

plane formed by O(3) and two O(4) atoms. Another O(3) atom and an OH group occur at slightly greater distances above and below this plane to produce a distorted trigonal bipyramid about the cation. Each of these polyhedra share a "vertex" edge, O(3)-O(3), with another bipyramid to produce discrete Zn₂O₆(OH)₂ groups. The shared edge, of length 2.504 Å (subtending an angle of 75.7° at the Zn(2) atom), is considerably shorter than the unshared edges (of average length 3.147 Å). It appears to be the shortest O-O contact distance documented for any kind of Zn oxyanion. The edge shortening has resulted in the maintenance of a distance of 3.221 Å between Zn cations in adjacent bipyramids without the need to invoke bond stretching. For comparison, the Zn-Zn distances across the O(1)-O(1) and OH-OH shared edges in the octahedron are 3.053 and 2.990 Å, respectively.

The balance of the electrostatic charges, computed with the empirical bond-strength-bond-length curves of Brown and Shannon (1973) is given in Table 5. All

atoms except O(2), and O(4) to a lesser extent, show close agreement between the sum of the bond strengths and valence. The marked charge deficiency on the O(2) atom in adamite suggests that the proton is in a position whereby it is directly bonded to O(2). Assuming that all of the deficiency on O(2) is due to this bond, the Brown and Shannon curves predict an O(2)-H distance of 0.94 Å. This is in reasonable agreement with the "observed" bond distance from the structure factor refinement (0.77 Å).

In the light of these conclusions it is interesting to compare the corresponding bond strength sums for the mineral andalusite (Burnham and Buerger, 1961). As shown in Table 5, all the atoms in andalusite, including the atom (O_a) equivalent to O(2) in adamite, are essentially electrically neutral; there is no need (in the absence of other information) to advocate the presence of H atoms in the structure. Aside from small differences in average bond lengths for analogous polyhedra, the two structures are remarkably alike. The very short O(3)-O(3) distance in ada-

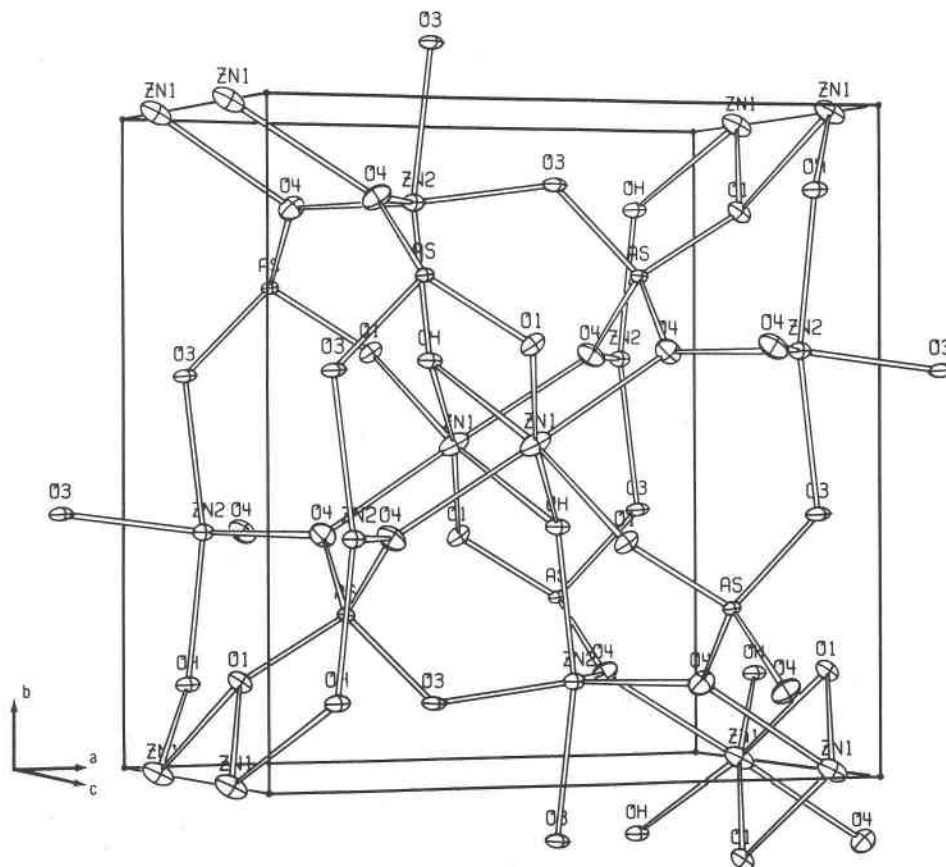


FIG. 1. Unit cell diagram for adamite (with 50% probability thermal ellipsoids).

mite is mirrored by an extremely short O_c-O_c distance (2.247 Å) in andalusite, and by and large the other polyhedron distortions are similar in both structures. Indeed, the charge neutrality of andalusite is a function of the valence of the cations, rather than of any major rearrangement of the anions within the same framework due to cation size differences. In both structures the strongest bonds are those involving the tetrahedral cations, namely As^V and Si^{IV} . In adamite the O(2) atom is the only oxygen atom not bonded to As, and it is unable to counteract the resultant bond strength deficiency by its bonds to divalent Zn. On the other hand, in andalusite, the equivalent atom is able to neutralize the deficiency by forming bonds to the trivalent Al atoms. The andalusite framework can therefore exist without the proton, whereas the additional bond strength inherent in the O(2)-H association is necessary to maintain the stability of adamite.

From the diversity of composition of the members of the olivenite group of minerals, it is apparent that

the structure type is capable of accommodating a wide variety of cations, including Zn^{2+} , Cu^{2+} , Mn^{2+} , Co^{2+} , Al^{3+} (in the octahedral and trigonal bipyramidal sites) and As^{5+} , P^{5+} , and Si^{4+} (in the tetrahedral sites). In regard to the discussion presented

TABLE 5. Brown and Shannon (1973) bond-strength sums (p) for adamite and andalusite

| Atom | Adamite p | Valence | Δ^* | Atom | Andalusite p | Valence | Δ |
|-------|----------------|---------|------------|-----------------|-------------------|---------|----------|
| As | 4.994 | 5 | 0.1 | Si | 3.969 | 4 | 0.8 |
| Zn(1) | 1.994 | 2 | 0.3 | Al ₁ | 2.928 | 3 | 2.4 |
| Zn(2) | 2.044 | 2 | 2.2 | Al ₂ | 3.045 | 3 | 1.5 |
| O(1) | 2.009 | 2 | 0.5 | O _b | 2.019 | 2 | 1.0 |
| O(2) | 1.170 | 2 | 41.5 | O _a | 1.880 | 2 | 6.0 |
| O(3) | 2.039 | 2 | 2.0 | O _c | 2.155 | 2 | 7.8 |
| O(4) | 1.907 | 2 | 4.7 | O _d | 1.944 | 2 | 2.8 |

* The percentage difference between the valence and p .

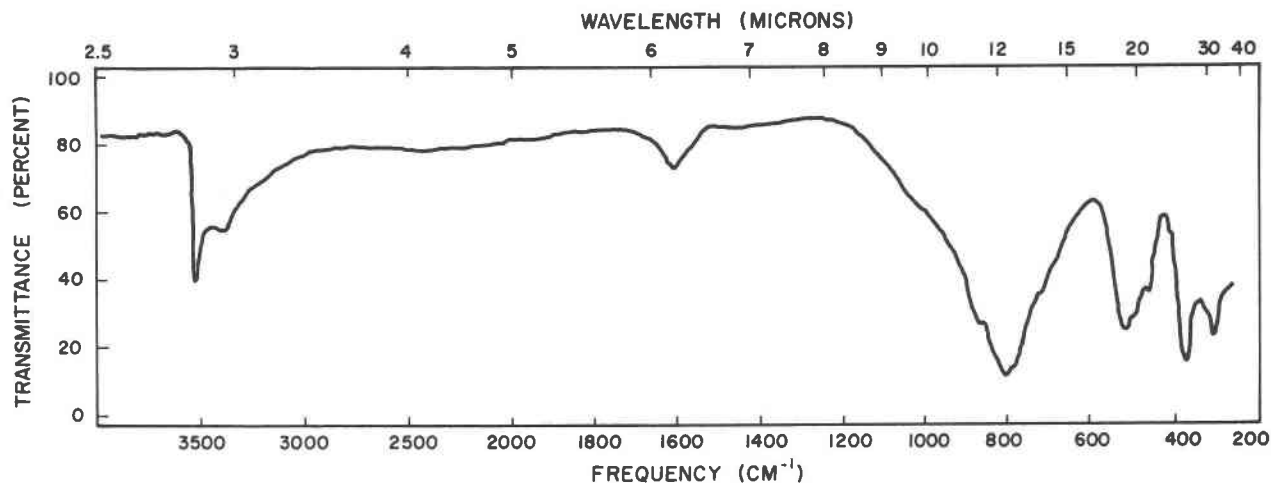


FIG. 2. Infrared absorption spectrum for adamite.

above, all the species containing divalent and pentavalent cations are observed to contain an OH group, despite significant differences in the size of the cations.

Infrared spectrum

Experimental

The spectrum displayed in Figure 2 was obtained on a Perkin-Elmer model 521 Grating Infrared Spectrophotometer. Samples were prepared by gently grinding approximately 1.5 mg of the mineral with 250 mg of AR grade, dessicator-dried, potassium bromide in an agate mortar under alcohol. This blend was then vacuum-pressed for two minutes in a tool-steel die at about 6000 p.s.i. to form a translucent pellet approximately 12 mm in diameter and 1 mm thick. The spectrum was recorded in double-beam mode (KBr standard) for the region 200–4000 cm^{-1} .

Results and discussion

The free arsenate ion belongs to point group $\bar{4}3m$, but in adamite the site symmetry of the ion has been lowered to m . Under these circumstances all degeneracy of the (nine) vibrational modes is lost (Hertzberg, 1945; Adler and Kerr, 1965), and the absorption spectrum is expected to display the full set of nine vibrational modes, represented by three V_3 , one V_1 , three V_4 , and two V_2 bands. The absorption bands in the infrared spectrum of adamite (Fig. 2) have been assigned to various modes of vibration of the AsO_4^{3-} group as displayed in Table 6. They are in agreement with assignments in related compounds (Nakamoto, 1970).

The XY_5 molecules in trigonal bipyramidal configuration (ideal symmetry $\bar{6}m2$) have a possible 12 non-degenerate vibrational modes when their symmetry is lowered, as in adamite. However, frequency assignments for this group could not be located in the literature, despite an exhaustive search.

The relationship between vibrational frequency (ν) and internuclear distance (R) for diatomic molecules as given by the expressions for force constant (Badger, 1934) and frequency (Barnes *et al.*, 1944) is well known. Using the observed values of ν and R for a number of phosphate minerals containing Zn in tetrahedral coordination (Hill, 1975), this relationship has been calibrated for the Zn–O system such that a prediction of the vibrational frequency of Zn in five-fold coordination may be made. The results indicate that for an average Zn–O distance of 2.028 Å in the trigonal bipyramid in adamite, the vibrational frequencies lie in the region below 380 cm^{-1} . An analogous calculation using the frequency (250 cm^{-1}) as-

TABLE 6. Infrared spectral assignments for adamite

| Group | Mode | Frequency (cm^{-1}) |
|----------------|---|--------------------------------|
| O–H | stretching | 3520 |
| Zn–O–H | stretching | 3400 |
| - | combinations | 1620 |
| AsO_4 | $\left\{ \begin{array}{l} v_3 \\ v_1 \\ v_4 \\ v_2 \end{array} \right.$ | 880, 820, 795 |
| | | 730 |
| | | 530, 510, 470 |
| | | - , - |
| ZnO_5 | - | 380, 320 |

signed to Ni-Cl stretching modes involving terminal ligands of a similar pentacoordinate dimer in $[\text{C}_7\text{H}_{16}\text{N}_2]_2[\text{Ni}_2\text{Cl}_8]$ (Goedken *et al.*, 1970) indicates that the equivalent mode in adamite should occur at about 330 cm^{-1} . Moreover, the AsF_6 group, with a close relationship to ZnO_5 in terms of bond length and reduced mass, displays absorption frequencies in the range 809 to 128 cm^{-1} (Nakamoto, 1970). The bands at 380 and 320 cm^{-1} in the adamite spectrum may therefore represent vibrations of the ZnO_5 functional group rather than V_2 modes of AsO_4 . It is interesting to note that a similar array of IR absorption bands in the range 500 to 270 cm^{-1} is obtained for tarbuttite, $\text{Zn}_2(\text{PO}_4)(\text{OH})$, the structure of which also contains pentacoordinated Zn atoms (Hill, 1975).

The large absorption bands at 3400 and 3520 cm^{-1} , with only a minor peak at about 1620 cm^{-1} , indicate the presence of OH groups in the crystal structure, and the absence of crystal-hydrate water (Yukhnevich, 1963; Gillespie and Robinson, 1964; Farmer, 1964). In fact, the small 1620 cm^{-1} peak may represent a combination of lower frequency fundamentals (Farmer, 1964) and does not necessarily correspond to bending modes of water molecules present in trace amounts. Thermal evidence supports this conclusion, dehydration occurring in a single step at 570°C (Hill, 1975).

Since thermal and X-ray evidence indicates the presence of only one structurally distinct OH group in adamite, the two absorption peaks at high frequency are interpreted as having different origins: the sharp peak at 3520 cm^{-1} is assigned to OH stretching vibrations displaced to lower frequencies from their values in the free state by hydrogen bonding effects (Farmer, 1964), while the diffuse band at 3400 cm^{-1} is assigned to stretching vibrations of Zn-O-H groups. The absence of bands in the 1300 and 2700 cm^{-1} regions confirms that no acidic As-OH groups are present in the structure (Hadzi, 1965).

Acknowledgments

The author is grateful to Dr. J. B. Jones for his help in the realization of this work, to Mr. M. Raupach, Division of Soils, C.S.I.R.O., Adelaide, for permitting use of the IR spectrophotometer, and to Mr. J. E. Johnson for supplying the specimens of adamite from his private collection. The research was supported by a C.S.I.R.O. Postgraduate Studentship.

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Manuscript received, September 8, 1975; accepted for publication, February 25, 1976.