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# THE CRYSTAL STRUCTURE OF DIETZEITE, $Ca_2H_2O(IO_3)_2(CrO_4)$, A HETEROPOLYHEDRAL FRAMEWORK MINERAL

PETER C. BURNS AND FRANK C. HAWTHORNE

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2*

## ABSTRACT

The crystal structure of dietzeite, $Ca_2H_2O(IO_3)_2CrO_4$, monoclinic, *a* 10.118(1), *b* 7.238(1), *c* 13.965(2) Å, β 106.62(1)°, *V* 979.9(3) Å$^3$, *Z* = 4, space group $P2_1/c$, has been solved by direct methods and refined by least-squares methods to an *R* index of 2.8% using 2670 observed [$I_O \geq 2.5\sigma(I_O)$] reflections. The chemical formula of dietzeite has been revised as a result of this determination of the crystal structure. Dietzeite contains two unique Ca positions; Ca(1) is coordinated by six atoms of oxygen and an $H_2O$ group, and Ca(2) is coordinated by eight atoms of oxygen. The single Cr position is tetrahedrally coordinated by oxygen atoms. There are two unique I positions, both of which are present as $IO_3$ triangular pyramids. There are weak bonds to the I(1) position from four additional oxygen atoms and to the I(2) position from three other oxygen atoms; bond-valence considerations for both cations and anions show these interactions to be significant. Dietzeite contains Ca(1)–Ca(2) polyhedral edge-sharing dimers linked by corner-sharing to form chains parallel to [001]. Each Ca polyhedral chain is linked to four other such chains through Cr tetrahedra, I polyhedra and hydrogen bonding, resulting in a heteropolyhedral framework structure.

*Keywords*: dietzeite, crystal structure, iodate, chromate, Atacama Desert, Chile.

## SOMMAIRE

La structure cristalline de la dietzéite, $Ca_2H_2O(IO_3)_2CrO_4$, monoclinique, *a* 10.118(1), *b* 7.238(1), *c* 13.965(2), β 106.62(1)°, *V* 979.9(3) Å$^3$, *Z* = 4, groupe spatial $P2_1/c$, a été déterminée par méthodes directes et affinée par moindres carrés jusqu'à un résidu *R* de 2.8% en utilisant 2670 réflexions observées [$I_O \geq 2.5\sigma(I_O)$]. La formule chimique de cette espèce a été corrigée suite à la détermination de sa structure. La dietzéite contient deux atomes de Ca en positions distinctes; le Ca(1) est entouré de six atomes d'oxygène et d'un groupe $H_2O$, tandis que le Ca(2) est entouré de huit atomes d'oxygène. Le Cr occupe une position unique, en coordinence tétraédrique avec des atomes d'oxygène. Les atomes de I y sont en deux positions distinctes; dans les deux cas, il s'agit de pyramides triangulaires $IO_3$. L'atome I(1) reçoit de faibles liaisons de quatre atomes d'oxygène, et l'atome I(2) en reçoit de trois autres atomes d'oxygène. Une considération des valences de liaison pour les cations et les anions démontre que ces interactions sont importantes. La dietzéite contient des dimères Ca(1)–Ca(2) en polyèdres à arêtes partagées, articulés par partage de coins pour former des chaînes parallèles à [001]. Chaque chaîne de polyèdres de Ca est liée à quatre autres chaînes semblables par les tétraèdres contenant le Cr, les polyèdres contenant l'I, et des liaisons impliquant l'hydrogène; il en résulte une trame hétéropolyédrique.

(Traduit par la Rédaction)

*Mots-clés*: dietzéite, structure cristalline, iodate, chromate, désert de l'Atacama, Chili.

## INTRODUCTION

Dietzeite is a compound iodate–chromate, the formula of which has always been written as $Ca_2(IO_3)_2(CrO_4)$. It was originally found in the nitrate deposits of the Atacama Desert, Antofagasta Province, Chile, and also has been reported from Tocopilla, Chile (Bandy 1937). It forms deep golden yellow crystals that are columnar or occur as fibrous crusts. Earlier morphological and X-ray data (Gossner & Mussgnug 1930) showed dietzeite to be monoclinic with the space group $P2_1/c$.

## EXPERIMENTAL

A columnar crystal of dietzeite from Antofagasta Province, Chile, was mounted on a Nicolet *R*3*m* automated four-circle diffractometer. Twenty-five reflections were centered using graphite-monochromated Mo*K*α X radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the twenty-five automatically aligned reflections by least-squares methods. A total of 3242 reflections were measured, with index ranges $0 \leq h \leq 14$, $0 \leq k \leq 10$, $-18 \leq l \leq 18$ ($3° < 2\theta < 60°$). Two standard reflections were measured every fifty reflections; no significant change in their intensity occurred during data collection. An empirical absorption-correction based on 396 psi-scan reflections was applied, reducing *R* (azimuthal) from 4.3% to 3.0%. The data were corrected for Lorentz, polarization, and background effects, and reduced to structure factors; of the

TABLE 1. MISCELLANEOUS INFORMATION ABOUT DIETZEITE

| | | | |
|---|---|---|---|
| Space Group | $P2_1/c$ | Crystal Size (mm) | 0.12x0.28 x0.22 |
| *a* (Å) | 10.118(1) | Total Ref. | 3242 |
| *b* (Å) | 7.238(1) | $I_o \geq 2.5\sigma(I_o)$ | 2670 |
| *c* (Å) | 13.965(2) | Final *R* | 2.8% |
| β (°) | 106.62(1) | Final *wR* | 3.7% |
| *V* (Å$^3$) | 979.9(3) | *R* (all data) | 3.1% |
| | | *wR* (all data) | 3.8% |
| μ | 8.45 mm$^{-1}$ | | |
| $D_{calc}$ | 3.822 g/cm$^3$ | F(000) | 1040 |

Unit-cell contents: $4[Ca_2H_2O(IO_3)_2(CrO_4)]$

$R = \Sigma ( |F_o| - |F_c|) / \Sigma |F_o|$

$wR = [ \Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^2]^{1/2}$, $w$=1.

3242 reflections measured, there were 2670 unique reflections classed as observed [$I_O \geq 2.5\sigma(I_O)$].

## STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout

TABLE 2. ATOMIC PARAMETERS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (x10$^4$) FOR DIETZEITE

| | x | y | z | $U_{equiv.}$ |
|---|---|---|---|---|
| I(1) | 0.05005(4) | 0.20302(5) | 0.77376(3) | 95(1) |
| I(2) | 0.25614(4) | 0.23921(5) | 0.57448(3) | 103(1) |
| Cr | 0.43076(9) | −0.2029(1) | 0.57850(7) | 113(3) |
| Ca(1) | 0.6994(1) | 0.0852(2) | 0.70392(9) | 119(3) |
| Ca(2) | 0.8994(1) | 0.2563(2) | 0.48855(8) | 117(3) |
| O(1) | 0.1268(5) | 0.4082(6) | 0.8413(3) | 163(13) |
| O(2) | −0.0504(5) | 0.3057(6) | 0.6581(3) | 174(13) |
| O(3) | 0.2744(5) | 0.2999(6) | 0.7033(3) | 170(13) |
| O(4) | 0.4664(5) | −0.0091(6) | 0.6456(3) | 179(13) |
| O(5) | 0.3524(5) | −0.3467(7) | 0.6357(4) | 203(14) |
| O(6) | 0.1290(5) | 0.0595(6) | 0.5639(3) | 162(13) |
| O(7) | 0.6813(5) | 0.1538(7) | 0.5301(3) | 183(13) |
| O(8) | 0.8668(5) | 0.5910(6) | 0.4952(3) | 155(12) |
| O(9) | 0.9060(4) | 0.1831(6) | 0.8250(3) | 134(12) |
| O(10) | 0.5718(5) | −0.2924(8) | 0.5656(4) | 267(16) |
| $H_2O$ | 0.6109(7) | 0.3866(8) | 0.6837(4) | 318(19) |

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS (x10$^4$) FOR DIETZEITE

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 100(2) | 84(2) | 103(2) | 0(1) | 34(1) | −5(1) |
| I(2) | 100(2) | 103(2) | 113(2) | 20(1) | 40(1) | 12(1) |
| Cr | 98(4) | 128(4) | 114(4) | 27(3) | 32(3) | 2(3) |
| Ca(1) | 108(5) | 127(5) | 112(5) | 0(4) | 14(4) | 19(4) |
| Ca(2) | 141(5) | 104(5) | 106(5) | −15(4) | 36(4) | −11(4) |
| O(1) | 189(21) | 164(20) | 138(19) | −74(16) | 52(16) | −91(17) |
| O(2) | 232(22) | 146(20) | 115(18) | 9(16) | 4(16) | 28(17) |
| O(3) | 233(22) | 134(20) | 132(19) | −32(16) | 33(16) | −20(17) |
| O(4) | 161(21) | 178(21) | 166(21) | −8(17) | −4(16) | −46(17) |
| O(5) | 248(23) | 172(21) | 216(22) | 22(18) | 113(19) | −64(18) |
| O(6) | 164(20) | 117(19) | 211(21) | −39(16) | 66(17) | −59(16) |
| O(7) | 177(21) | 239(23) | 117(19) | 1(17) | 14(16) | 9(18) |
| O(8) | 154(20) | 99(19) | 179(20) | 36(16) | −5(16) | 38(16) |
| O(9) | 118(18) | 172(20) | 122(18) | −24(15) | 49(15) | −42(15) |
| O(10) | 240(24) | 342(29) | 277(25) | 121(22) | 166(20) | 126(22) |
| $H_2O$ | 585(37) | 207(25) | 192(24) | 73(20) | 159(24) | 193(25) |

TABLE 4. BOND-DISTANCES (Å), ANGLES (°) AND POLYHEDRAL EDGE-LENGTHS (Å) FOR DIETZEITE

| | | | |
|---|---|---|---|
| I(1)–O(1) | 1.810(4) | Ca(1)–O(4) | 2.364(5) |
| I(1)–O(2) | 1.804(4) | Ca(1)–O(7) | 2.433(5) |
| I(1)–O(9)a | 1.804(5) | Ca(1)–O(9) | 2.390(4) |
| <I(1)–$O_{SHORT}$> | 1.806 | Ca(1)–$H_2O$ | 2.345(6) |
| | | Ca(1)–O(1)g | 2.402(5) |
| I(1)–O(3) | 2.809(5) | Ca(1)–O(3)h | 2.412(5) |
| I(1)–O(1)b | 2.948(4) | Ca(1)–O(5)h | 2.492(6) |
| I(1)–O(2)c | 3.029(5) | <Ca(1)–O> | 2.405 |
| I(1)–O(8)h | 3.197(5) | | |
| <I(1)–$O_{LONG}$> | 2.996 | Ca(2)–O(6) | 2.671(4) |
| | | Ca(2)–O(7) | 2.547(5) |
| I(2)–O(3) | 1.809(5) | Ca(2)–O(8) | 2.451(5) |
| I(2)–O(6) | 1.806(5) | Ca(2)–O(2)i | 2.303(5) |
| I(2)–O(8)d | 1.820(4) | Ca(2)–O(5)f | 2.720(5) |
| <I(2)–$O_{SHORT}$> | 1.812 | Ca(2)–O(6)f | 2.392(5) |
| | | Ca(2)–O(8)i | 2.561(5) |
| I(2)–O(4) | 2.745(5) | Ca(2)–O(9)k | 2.345(5) |
| I(2)–O(5)e | 3.191(5) | <Ca(2)–O> | 2.499 |
| I(2)–O(10)f | 2.992(6) | | |
| <I(2)–$O_{LONG}$> | 2.979 | | |
| | | | |
| Cr–O(4) | 1.668(5) | | |
| Cr–O(5) | 1.647(6) | | |
| Cr–O(10) | 1.623(6) | | |
| Cr–O(7)f | 1.652(4) | | |
| <Cr–O> | 1.647 | | |

I(1) polyhedron

| | | | |
|---|---|---|---|
| O(1)–O(2) | 2.772(6) | O(1)–I(1)–O(2) | 100.2(2) |
| O(2)–O(9)a | 2.646(7) | O(2)–I(1)–O(9)a | 94.4(2) |
| O(9)a–O(1) | 2.721(6) | O(1)–I(1)–O(9)a | 97.7(2) |
| <O–O> | 2.713 | <O–I(1)–O> | 97.4 |
| | | | |
| O(1)–O(3) | 2.865(7) | O(1)–I(1)–O(3) | 73.1(2) |
| O(1)–O(8)h | 3.225(7) | O(1)–I(1)–O(8)h | 74.5(2) |
| O(2)–O(3) | 3.164(7) | O(2)–I(1)–O(3) | 83.6(2) |
| O(2)–O(1)b | 2.980(7) | O(2)–I(1)–O(1)b | 73.2(2) |
| O(9)a–O(1)b | 3.004(6) | O(9)a–I(1)–O(1)b | 94.4(2) |
| O(9)a–O(2)c | 3.075(6) | O(9)a–I(1)–O(2)c | 74.2(2) |
| O(9)a–O(8)h | 2.954(5) | O(9)a–I(1)–O(8)h | 65.7(1) |
| O(1)a–O(2)c | 2.980(7) | O(1)a–I(1)–O(2)c | 55.2(1) |
| <O–O> | 3.031 | <O–I(1)–O> | 74.2 |

I(2) polyhedron

| | | | |
|---|---|---|---|
| O(3)–O(6) | 2.710(6) | O(3)–I(2)–O(6) | 97.1(2) |
| O(3)–O(8)d | 2.842(6) | O(3)–I(2)–O(8)d | 103.1(2) |
| O(6)–O(8)d | 2.664(6) | O(6)–I(2)–O(8)d | 94.6(2) |
| <O–O> | 2.739 | <O–I(2)–O> | 98.3 |
| | | | |
| O(3)–O(4) | 3.212(7) | O(3)–I(2)–O(4) | 87.2(2) |
| O(3)–O(5)e | 2.912(7) | O(3)–I(2)–O(5)e | 64.5(2) |
| O(6)–O(4) | 3.313(6) | O(6)–I(2)–O(4) | 91.1(2) |
| O(8)d–O(5)e | 3.011(6) | O(8)d–I(2)–O(5)e | 67.6(2) |
| O(8)d–O(10)f | 3.503(8) | O(8)d–I(2)–O(10)f | 90.0(2) |
| O(4)–O(10)f | 3.600(7) | O(4)–I(2)–O(10)f | 77.6(1) |
| <O–O> | 3.258 | <O–I(2)–O> | 79.7 |

Cr tetrahedron

| | | | |
|---|---|---|---|
| O(4)–O(5) | 2.689(7) | O(4)–Cr–O(5) | 108.4(3) |
| O(4)–O(10) | 2.697(8) | O(4)–Cr–O(10) | 110.0(3) |
| O(4)–O(7)f | 2.694(6) | O(4)–Cr–O(7)f | 108.5(2) |
| O(5)–O(10) | 2.698(8) | O(5)–Cr–O(10) | 111.2(3) |
| O(5)–O(7)f | 2.641(7) | O(5)–Cr–O(7)f | 106.4(2) |
| O(10)–O(7)f | 2.719(7) | O(10)–Cr–O(7)f | 112.2(3) |
| <O–O> | 2.690 | <O–Cr–O> | 109.4 |

Ca(1) polyhedron

| | | | |
|---|---|---|---|
| O(4)–O(7) | 3.275(7) | O(4)–Ca(1)–O(7) | 86.1(2) |
| O(4)–$H_2O$ | 3.191(7) | O(4)–Ca(1)–$H_2O$ | 85.3(2) |
| O(4)–O(3)h | 3.174(6) | O(4)–Ca(1)–O(3)h | 83.3(2) |
| O(4)–O(5)h | 3.297(6) | O(4)–Ca(1)–O(5)h | 85.5(2) |
| O(7)–$H_2O$ | 2.970(8) | O(7)–Ca(1)–$H_2O$ | 76.8(2) |
| O(7)–O(1)g | 2.857(6) | O(7)–Ca(1)–O(1)g | 72.5(2) |
| O(9)–$H_2O$ | 3.408(7) | O(9)–Ca(1)–$H_2O$ | 92.1(2) |
| O(9)–O(1)g | 3.004(6) | O(9)–Ca(1)–O(1)g | 77.6(2) |
| O(9)–O(3)h | 3.281(6) | O(9)–Ca(1)–O(3)h | 86.2(1) |
| O(9)–O(5)h | 2.830(6) | O(9)–Ca(1)–O(5)h | 70.8(2) |
| $H_2O$–O(5)h | 2.970(7) | $H_2O$–Ca(1)–O(5)h | 75.7(2) |
| O(1)g–O(3)h | 2.865(7) | O(1)g–Ca(1)–O(3)h | 73.0(2) |
| O(3)h–O(5)h | 2.912(7) | O(3)h–Ca(1)–O(5)h | 72.9(2) |
| <O–O> | 3.080 | <O–Ca(1)–O> | 79.8 |

Ca(2) polyhedron

| | | | |
|---|---|---|---|
| O(6)–O(6)f | 2.841(8) | O(6)–Ca(2)–O(6)f | 68.0(2) |
| O(6)–O(8)i | 2.664(6) | O(6)–Ca(2)–O(8)i | 61.2(1) |
| O(6)–O(2)i | 3.093(7) | O(6)–Ca(2)–O(2)i | 76.5(2) |
| O(7)–O(6)f | 3.039(7) | O(7)–Ca(2)–O(6)f | 75.9(2) |
| O(7)–O(2)i | 3.000(6) | O(7)–Ca(2)–O(2)i | 76.2(2) |
| O(7)–O(5)f | 2.641(7) | O(7)–Ca(2)–O(5)f | 60.1(2) |
| O(8)–O(8)i | 2.968(9) | O(8)–Ca(2)–O(8)i | 72.6(2) |
| O(8)–O(2)i | 3.009(6) | O(8)–Ca(2)–O(2)i | 78.5(2) |
| O(8)–O(5)f | 3.011(6) | O(8)–Ca(2)–O(5)f | 71.0(1) |
| O(8)–O(9)k | 3.206(7) | O(8)–Ca(2)–O(9)k | 83.9(2) |
| O(2)i–O(8)i | 3.296(7) | O(2)i–Ca(2)–O(8)i | 85.1(2) |
| O(5)f–O(9)k | 2.830(7) | O(5)f–Ca(2)–O(9)k | 67.5(2) |
| O(6)f–O(9)k | 3.205(6) | O(6)f–Ca(2)–O(9)k | 85.1(2) |
| O(8)i–O(9)k | 2.954(5) | O(8)i–Ca(2)–O(9)k | 73.9(1) |
| <O–O> | 2.983 | <O–Ca(2)–O> | 74.0 |

a = x–1, y, z; b = –x, y–1/2, z; c = –x, y+1/2, –z+1 1/2;
d = 1–x, 1–y, 1–z; e = x, y+1, z; f = 1–x, –y, 1–z;
g = 1–x, y+1/2, –z+1/2; h = 1–x, y–1/2, –z + 1 1/2; i = x+1, y, z;
j = 2–x, 1–y, 1–z; k = x, y–1/2, z+1/2.

TABLE 5. PROPOSED HYDROGEN POSITIONS AND SCHEME OF HYDROGEN BONDING IN DIETZEITE

| | x | y | z |
|---|---|---|---|
| H1 | 0.585 | 0.421 | 0.741 |
| H2 | 0.598 | 0.494 | 0.644 |
| H1–$H_2O$ | 0.94 Å | H2–$H_2O$ | 0.94 Å |
| H1–O4a | 1.87 | H2–O10b | 1.87 |
| H1–H2 | 1.49 | H1–O–H2 | 104.9° |

a = 1–x, y–1/2, –z+ 1 + 1/2, b = x, y–1, z

TABLE 6. BOND-VALENCE* ANALYSIS FOR DIETZEITE

| | I(1) | I(2) | Cr | Ca(1) | Ca(2) | H(1) | H(2) | Σ |
|---|---|---|---|---|---|---|---|---|
| O(1) | 1.454<br>0.162 | | | 0.291 | | | | 1.907 |
| O(2) | 1.476<br>0.143 | | | | 0.371 | | | 1.990 |
| O(3) | 0.201 | 1.458 | | 0.284 | | | | 1.943 |
| O(4) | | 0.223 | 1.432 | 0.319 | | (0.1) | | 2.074 |
| O(5) | | 0.113 | 1.523 | 0.234 | 0.134 | | | 2.004 |
| O(6) | | 1.469 | | | 0.151<br>0.298 | | | 1.918 |
| O(7) | | | 1.501 | 0.270 | 0.204 | | | 1.975 |
| O(8) | 0.112 | 1.418 | | | 0.258<br>0.198 | | | 1.996 |
| O(9) | 1.476 | | | 0.300 | 0.334 | | | 2.110 |
| O(10) | | 0.151 | 1.634 | | | | (0.2) | 1.985 |
| $H_2O$ | | | | 0.334 | | (0.9) | (0.8) | 2.034 |
| Σ | 5.024 | 4.832 | 6.090 | 2.032 | 1.948 | 1.00 | 1.00 | |

* Bond-valence parameters from Brown (1981), bond-valences in v.u.

this study. *R* indices are of the form given in Table 1, and are expressed as percentages.

The space group $P2_1/c$ was verified by examination of systematic extinctions of reflections and by the successful determination and refinement of the structure. The structure of dietzeite was solved by direct methods, with all heavy atoms and five oxygen atoms located in the solution. Least-squares refinement of the positional parameters of the direct-methods solution converged to an *R* index of 13.5%, and all remaining oxygen atoms were located in a difference-Fourier map calculated at this stage. For an isotropic displacement model, the refinement converged to an *R* index of 3.9%. Conversion to a model including anisotropic displacement parameters, together with the refinement of all parameters, resulted in an *R* index of 2.8% and a *wR* index of 3.7%. A model including weighted structure-factors and an isotropic extinction correction was tried at this point, but did not lead to an improved refinement. Final positional parameters are given in Table 2, anisotropic displacement parameters in Table 3, selected interatomic distances, angles and polyhedral edge-lengths in Table 4, a proposed H-bonding scheme in Table 5, and a bond-valence analysis in Table 6. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## CHEMICAL FORMULA

The $H_2O$ content of dietzeite has never been determined directly; in fact, it has always been assumed to be nil. However, the results of the crystal-structure analysis show that an additional anion is present. The electronegativity principle constrains this to be a neutral species, and local bond-valence calculations show this to be an ($H_2O$) group with a sensible and necessary hydrogen-bonding scheme. Thus $H_2O$ is an essential constituent of the structure, and the chemical formula of dietzeite is $Ca_2H_2O(IO_3)_2(CrO_4)$.

## DESCRIPTION OF THE STRUCTURE

### *Ca polyhedra*

There are two unique Ca positions in dietzeite, both of which are located on general positions. Ca(1) is bonded to six oxygen atoms and a single $H_2O$ group, with an average bond-distance of 2.405 Å. Ca(2) is bonded to eight oxygen atoms, with an average bond-distance of 2.499 Å.

### *Cr tetrahedron*

The one unique Cr position in dietzeite is coordinated by four oxygen atoms in a tetrahedral arrangement. The <Cr–O> distance is 1.647 Å, similar to chromate tetrahedra in other structures (*e.g.*, 1.643 Å in tarapacaite: McGinnety 1972)

### *I polyhedra*

Dietzeite contains two unique I positions, both of which occur as triangular pyramidal $IO_3$ groups (Fig. 1). I(1) is bonded to three atoms of oxygen, with an average distance of 1.806 Å and a <O–I–O> angle of 97.4°. I(1) is also relatively close to four other oxygen atoms, with an average distance to these of 2.996 Å (Fig. 1). The bond-valence analysis for the I(1) position indicates that each of these oxygen atoms contributes significant bond-valence to the I(1) atom; the total bond-valence contribution of these ~~four~~ oxygen atoms to the central I(1) is 0.62 v.u. (Table 6). I(2) also is bonded to three oxygen atoms, with an average bond-length of 1.812 Å and a <O–I–O> angle of 98.3°. The I(2) position also is weakly bonded to three other oxygen atoms (Fig. 1), with an average bond-distance of 2.976 Å. The bond-valence sum around the I(2) position from these three distant atoms of oxygen and the three proximal atoms of oxygen is 4.83 v.u. There are two additional oxygen atoms at 3.32 Å and 3.34 Å from I(2), each of which may contribute 0.09 bond-valence units, giving a total sum of 5.01 at the I(2) site. The I coordination polyhedra observed in dietzeite are similar to those observed in bellingerite (Ghose & Wan 1974), lautarite (Ghose et al. 1978) and salesite (Ghose & Wan 1978); all three contain triangular pyramidal $IO_3$ arrangements, with average bond-distances ranging from 1.804 (lautarite) to 1.819 Å (bellingerite). The I positions in these minerals are weakly bonded to variable numbers of other oxygen atoms, with the I coordination ranging from five to seven.

Iodine has the electronic structure [Kr core]$4d^{10}5s^25p^5$; in the pentavalent state, $I^{5+}$ thus has a lone pair of electrons. If this lone pair occupies a *p*-orbital, then the ion is lone-pair stereoactive, and the lone pair of electrons projects out to one side of the ion, preventing the close approach of any ligand. This is the reason why $I^{5+}$ shows such asymmetrical coordination. It normally has three short pyramidal bonds, and the stereoactive lone pair projects out from the $I^{5+}$ in the opposite direction to these anions. However, the three short I–O bonds are insufficient to satisfy the bonding requirements of the $I^{5+}$, and hence additional interactions are necessary. These cannot be strong interactions~~, as~~ the stereoactive lone pair prevents the close approach of a fourth anion, so that several weak I–O interactions are required; the structural data of Ghose & Wan (1974, 1978), Ghose *et al.* (1978) and this study show this to be the case.

### *H-bonding*

A H-bonding scheme for the $H_2O$ position has been derived on the basis of bond-valence criteria, with the resulting positions and bond distances for hydrogen given in Table 5. The proposed scheme of hydrogen bonding is illustrated in Figure 2. The $H_2O$ group is bonded to Ca(1) only, which contributes a bond valence of 0.334 v.u. to the satisfaction of the central oxygen atom (Table 6). This means that there will be two hydrogen bonds of about 0.17 v.u. from the two component hydrogen atoms to neighboring anions. H(1) hydrogen bonds to O(4), and H(2) hydrogen bonds to O(10); both acceptor anions belong to the chromate group (Fig. 2). The observed bond-valence sums in Table 6 suggest that the hydrogen bond from H(1) to O(4) is significantly weaker than the hydrogen bond from H(2) to O(10), and the hydrogen bond-valences (Table 6) are assigned on this basis. Difference-Fourier maps calculated during the final stages of refinement showed weak peaks in the distribution of electron density near the proposed positions of the hydrogen atoms.

### *Structure connectivity*

The $Ca(1)O_6H_2O$ and $Ca(2)O_8$ polyhedra share edges

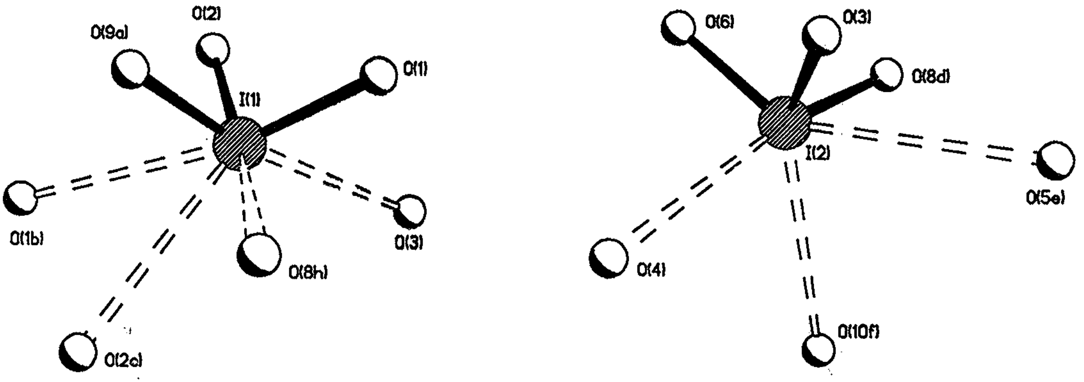

FIG. 1. The I coordination polyhedra observed in dietzeite. Short bonds are given as solid lines, and long bonds are given as broken lines.

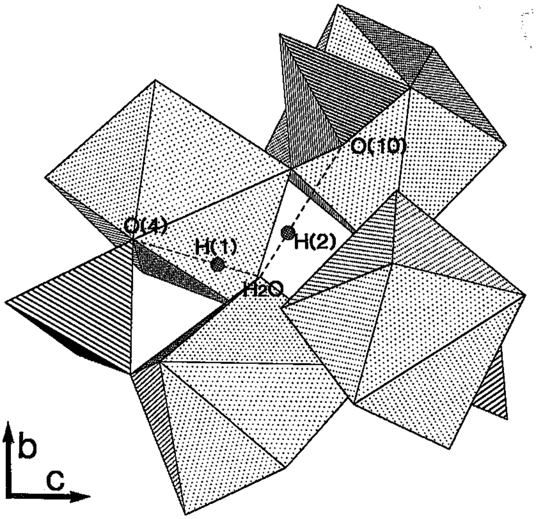

FIG. 2. Proposed scheme of hydrogen bonding in dietzeite. The O–H and H...O bonds are shown as broken lines. Ca polyhedra are shaded with a regular dot pattern, and Cr tetrahedra, with parallel lines.

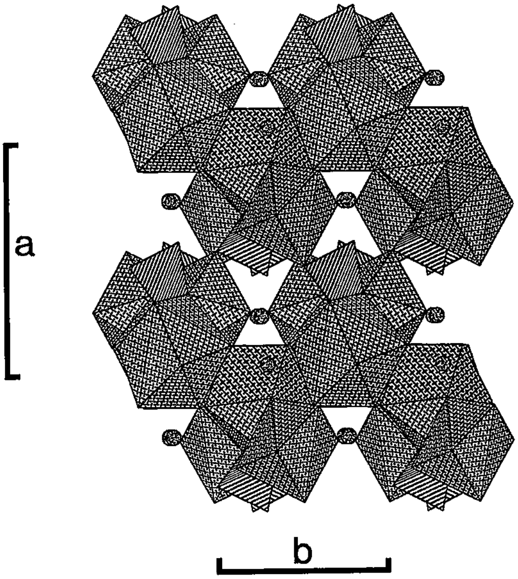

FIG. 4. The dietzeite structure projected onto (001). I atoms are shown as circles shaded with a random dot pattern. The polyhedral shading is as in Figure 2. All I-ϕ bonds have been omitted (ϕ: unspecified anionic group).

to form dimers of composition $[Ca_2O_{12}(H_2O)]^{20-}$. These dimers share corners with adjacent dimers to form chains along [001] (Fig. 3). Each Ca dimer is linked to two Cr tetrahedra, such that the Ca(1) polyhedron shares a corner with an adjacent Cr tetrahedron, and the Ca(2) polyhedron shares an edge with a symmetrically equivalent Cr tetrahedron.

Figure 4 shows the packing of these chains, essentially a *C*-face-centered arrangement with the chains extending along [001]. Each chain links to four adjacent chains to form a complex heteropolyhedral framework, but the details of the cross-linkages can only be seen in different projections of the structure. Figure 5 shows the linkage between chains adjacent along [110] in Figure 4. The chromate groups play an important role here, sharing an edge with a Ca(2) polyhedron of one chain and a corner with a Ca(1) polyhedron of the adjacent chain. Further linkage is provided by the iodate groups, but this involves primarily the long weak I–O bonds. Figure 6 shows the linkage between chains in the [010] direction. Here, the primary linkage involves the iodate groups. For I(1), the strong I–O bonds do not bridge the chains in this direction, the linkage occurring only *via* the long weak I–O bonds. However, for I(2), the three short I–O bonds bridge across the chains (Fig. 6), binding them strongly together.

The overall structure is a very compact heteropolyhedral framework, accounting for the lack of cleavage and the relatively high density ($D_{calc} = 3.822$ g/cm$^3$).

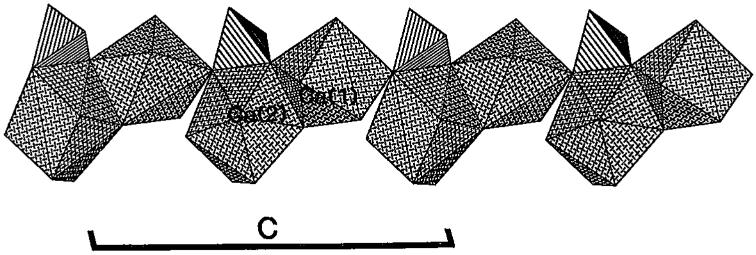

FIG. 3. Chains of Ca(1)–Ca(2) polyhedral dimers that occur in the dietzeite structure. The projection is on (010); Ca polyhedra are shaded with a herringbone pattern, and Cr tetrahedra are shaded with parallel lines.

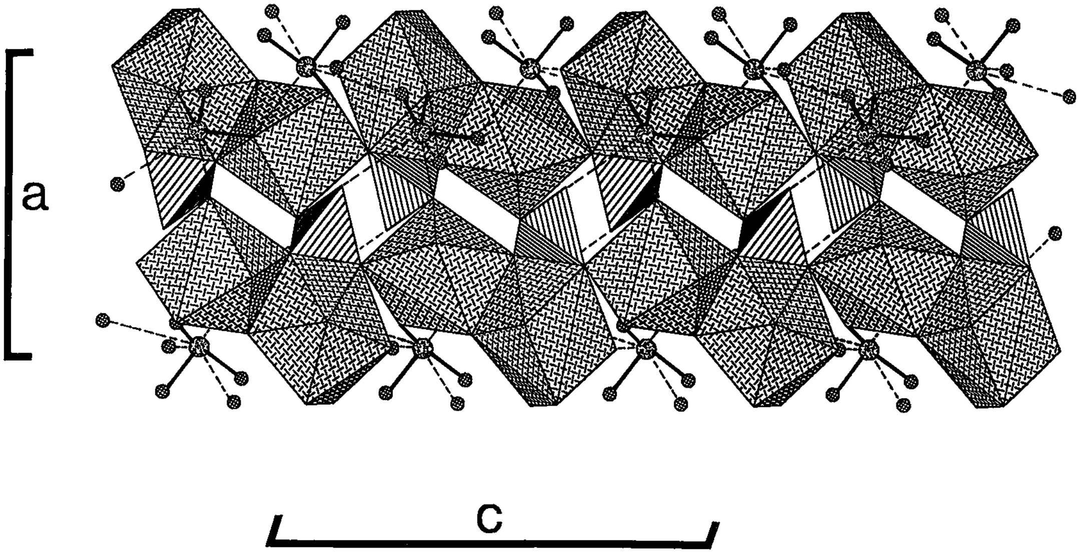

FIG. 5. The dietzeite structure projected onto (010). The polyhedral shading is as in Figure 2. I atoms are given as circles shaded with a random dot pattern, and oxygen atoms are cross-hatched circles. Short I–ϕ bonds are drawn as solid lines, and long I–ϕ bonds, as broken lines (ϕ: unspecified anionic group).

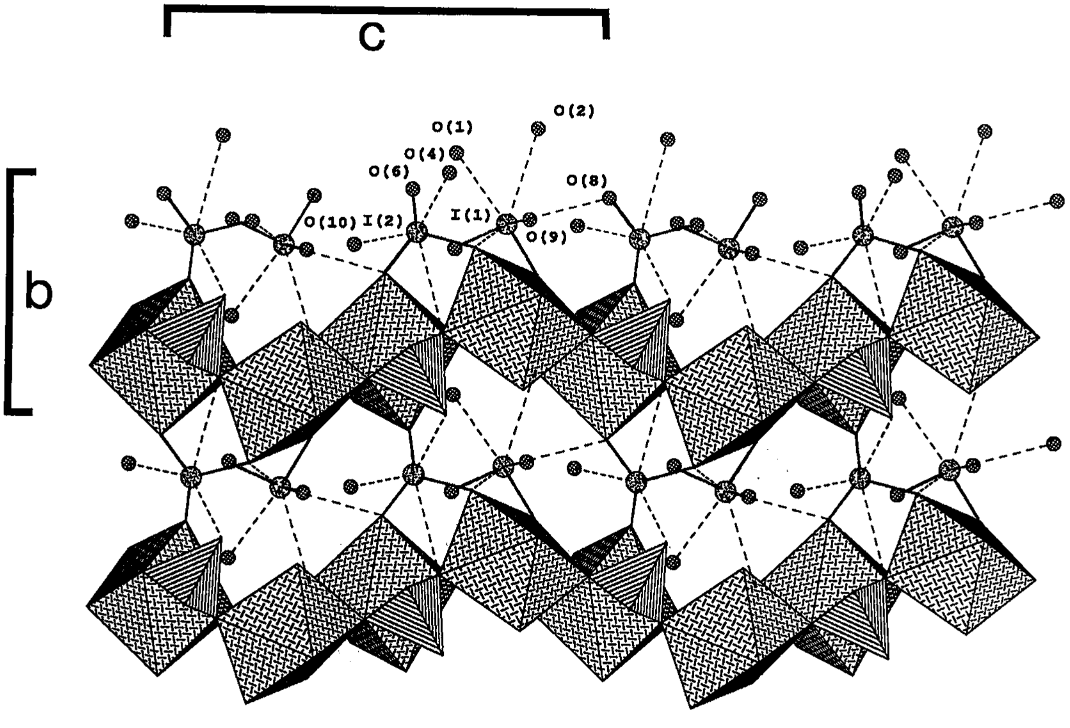

FIG. 6. The dietzeite structure projected onto (100). Legend as in Figure 5.

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