

Neutron Diffraction Studies of Polyiodides. III. Calcium Decaiodide Heptahydrate

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Abstract

The crystal structure of $\text{CaI}_{10} \cdot 7\text{H}_2\text{O}$ has been determined from both X-ray and neutron diffraction data, giving $R_F = 0.093$ for 1157 neutron reflections. This compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.830$ (14), $b = 15.192$ (12), $c = 9.572$ (8) Å, $\alpha = 91.42$ (2), $\beta = 108.77$ (3), $\gamma = 93.03$ (3)°, $Z = 2$. The structure consists of a novel heptahydrated Ca^{2+} ion and two I_5^- anions. The water molecules are arranged around the Ca^{2+} ion in the form of a distorted monocapped trigonal prism, while the I_5^- ions are the usual V shape.

Introduction

Calcium polyiodide was described by Berzelius (1830) as dark-green crystals with a metallic lustre obtained when a solution of I_2 in aqueous CaI_2 was evaporated. No serious attempt to characterize this compound was made, however, until Snook (1967) studied the ternary system $\text{CaI}_2\text{--I}_2\text{--H}_2\text{O}$ and proposed $\text{CaI}_8 \cdot 10\text{H}_2\text{O}$ as the formula. This phase-equilibrium study was re-examined by one of us (RT) and it was shown that the correct formula is $\text{CaI}_{10} \cdot 7\text{H}_2\text{O}$. A similar system has also been studied in a number of organic solvents by Gorenbein, Zaika, Skorabogat'ko & Pivnutel (1974), who found evidence for the species CaI_6 and CaI_{10} in solution, but no examination of the solid phase was made.

Experimental

$\text{CaI}_2 \cdot 6\text{H}_2\text{O}$ was prepared from analytical grade CaCO_3 and HI. The solid hexahydrate was mixed with I_2 in the ratio 30:50 by weight and dissolved in a minimum of water to give a saturated solution on the solubility arc of the polyiodide as indicated by the phase diagram. Evaporation of this solution gave needle-like crystals ($\text{Ca} = 2.89$, $\text{I}_2 = 70.24$, $\text{H}_2\text{O} =$

8.76% ; $\text{CaI}_{10} \cdot 7\text{H}_2\text{O}$ requires $\text{Ca} = 2.79$, $\text{I}_2 = 70.75$, $\text{H}_2\text{O} = 8.77\%$). To grow a large crystal suitable for neutron diffraction, a seed crystal was suspended in the saturated solution on a two-pronged stirrup formed on the end of a silica rod. The crystal was grown completely around the stirrup, which on inversion became the crystal holder. The crystals so grown tended to be up to 50 mm long. To obtain sufficient thickness, a very large crystal was grown and this was shortened by cutting it off on both sides of the stirrup, to produce a crystal $2 \times 7 \times 11$ mm. Moisture was excluded with a silica cap similar to that described in part I of this series (Thomas & Moore, 1980).

The structure was determined from both X-ray and neutron diffraction data collected on four-circle diffractometers provided by the Australian Institute of Science and Engineering (AINSE) at the Australian Atomic Energy Commission (AAEC) research establishment. Mo radiation ($\lambda = 0.7107$ Å) was used to collect the X-ray data, while the wavelength of the neutrons, $\lambda = 1.240$ Å, was obtained from diffraction measurements of a LiF crystal ($a = 4.0262$ Å). The cell dimensions were refined from the orientation angles of some fifty selected reflections. The density, determined by displacement of paraffin oil saturated in I_2 , was 3.45 (5) Mg m^{-3} , compared with a calculated density of 3.52 Mg m^{-3} for $Z = 2$. The neutron linear absorption coefficient ($\mu = 0.0996$ mm^{-1}) was calculated from the sum of the values for the absorption and scattering cross sections of Ca, O and I (Bacon, 1975) (3.48 , 4.24 , 8.04×10^2 fm^2 respectively at $\lambda = 1.24$ Å) and the value for the slow-neutron cross section for H in water (Melkonian, 1949) (40×10^2 fm^2 at $\lambda = 1.24$ Å). The corresponding values for the X-ray linear absorption coefficient ($\mu = 11.74$ mm^{-1}) were obtained from *International Tables for X-ray Crystallography* (1974). Two sets of equivalents were collected for $2\sigma < 75^\circ$, corrected for absorption, analysed and combined to give 1806 independent neutron reflections, of which 1157 have $F^2 > 3\sigma(F^2)$, and 2677 independent X-ray reflections.

Structure determination and refinement

The values used for the coherent neutron scattering length (Shull, 1972) were 4.66, 5.80, 5.28 and -3.74 fm for Ca, O, I and H respectively, while the corresponding X-ray scattering lengths were obtained from *International Tables for X-ray Crystallography* (1974). *MULTAN* 76 (Main, Woolfson, Lessinger, Germain & Declercq, 1976) failed to solve the structure from either the neutron or the X-ray set of data. This appeared to be caused by the rows of I atoms parallel to *c*, which resulted in a systematic high intensity for the *hkl* reflections where *l* = 3*n*. Consequently, only this variety of reflection was chosen for the starting set of phases instead of a more random selection. Attempts to vary the conditions under which the program was run were not successful. However, because the X-ray diffraction pattern is primarily due to the I atoms, there are only one third as many effectively contributing atoms in this compared to the neutron diffraction data. Consequently, the Patterson plot obtained from the X-ray diffraction data contained relatively few peaks and was readily interpretable. Once the I atom

Table 1. *Positional parameters and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> (Å ²)
I(1)	0.0825 (6)	0.1394 (4)	-0.0314 (5)	6.70 (18)
I(2)	0.0690 (5)	0.1431 (3)	0.2541 (5)	5.30 (16)
I(3)	0.0565 (5)	0.1480 (3)	0.5854 (4)	5.00 (17)
I(4)	0.3087 (6)	0.0197 (3)	0.6891 (4)	5.38 (17)
I(5)	0.5537 (7)	-0.0728 (3)	0.7939 (8)	8.66 (23)
I(6)	0.1826 (6)	0.4327 (3)	0.7733 (4)	4.87 (15)
I(7)	0.1788 (6)	0.4282 (3)	0.4835 (4)	4.87 (15)
I(8)	0.1683 (6)	0.4259 (3)	0.1302 (4)	4.97 (15)
I(9)	0.4730 (6)	0.3555 (3)	0.2442 (4)	5.20 (17)
I(10)	0.7465 (6)	0.2895 (3)	0.3517 (6)	6.54 (18)
Ca	0.3716 (7)	0.7464 (3)	0.2143 (6)	5.44 (20)
O(1)	0.5670 (11)	0.7765 (9)	0.4473 (9)	7.50 (30)
O(2)	0.5768 (10)	0.7577 (6)	0.1265 (6)	6.57 (26)
O(3)	0.3025 (11)	0.8713 (6)	0.3373 (11)	6.33 (27)
O(4)	0.3087 (10)	0.8545 (7)	0.0256 (11)	6.85 (27)
O(5)	0.1521 (19)	0.6850 (7)	0.2486 (15)	11.27 (53)
O(6)	0.2458 (21)	0.6561 (8)	0.0071 (12)	18.13 (58)
O(7)	0.4337 (29)	0.6048 (7)	0.3269 (15)	11.71 (61)
H(1)	0.617 (4)	0.747 (2)	0.509 (3)	21.7 (1.3)
H(2)	0.602 (4)	0.812 (1)	0.483 (3)	17.1 (1.3)
H(3)	0.626 (4)	0.723 (2)	0.105 (4)	23.3 (1.5)
H(4)	0.619 (4)	0.790 (2)	0.117 (4)	26.4 (1.9)
H(5)	0.296 (4)	0.917 (2)	0.320 (3)	17.1 (1.2)
H(6)	0.270 (4)	0.877 (2)	0.403 (3)	27.2 (1.9)
H(7)	0.309 (4)	0.855 (2)	-0.053 (2)	22.3 (1.4)
H(8)	0.285 (3)	0.903 (2)	0.031 (3)	20.0 (1.3)
H(9)	0.152 (3)	0.658 (2)	0.310 (4)	23.1 (1.6)
H(10)	0.068 (2)	0.692 (3)	0.205 (4)	24.1 (2.2)
H(11)	0.241 (4)	0.657 (2)	-0.086 (2)	25.3 (1.3)
H(12)	0.197 (5)	0.616 (2)	0.009 (3)	44.7 (2.8)
H(13)	0.371 (3)	0.560 (2)	0.305 (3)	22.8 (1.3)
H(14)	0.508 (3)	0.593 (2)	0.363 (3)	21.1 (1.3)

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

Symmetry code: (') *x, y, z* - 1.

Ca-O(1)	2.444 (16)	I(1)-I(2)	2.778 (9)
Ca-O(2)	2.422 (18)	I(2)-I(3)	3.212 (8)
Ca-O(3)	2.447 (16)	I(3)-I(4)	3.156 (10)
Ca-O(4)	2.423 (13)	I(4)-I(5)	2.767 (11)
Ca-O(5)	2.428 (22)	I(6)-I(7)	2.761 (8)
Ca-O(6)	2.335 (15)	I(7)-I(8)	3.350 (8)
Ca-O(7)	2.448 (18)	I(8)-I(9)	3.098 (10)
		I(9)-I(10)	2.802 (11)
O(1)-H(1)	0.80 (4)		
O(1)-H(2)	0.65 (4)	I(8)...I(6')	3.468 (8)
O(2)-H(3)	0.79 (4)	I(1)...I(3')	3.600 (8)
O(2)-H(4)	0.65 (4)		
O(3)-H(5)	0.72 (4)	H(11)-I(10)	2.72 (3)
O(3)-H(6)	0.79 (4)	H(13)-I(8)	2.85 (4)
O(4)-H(7)	0.75 (3)	H(14)-I(7)	2.99 (5)
O(4)-H(8)	0.79 (4)		
O(5)-H(9)	0.72 (5)	I(1)-I(2)-I(3)	179.5 (3)
O(5)-H(10)	0.81 (4)	I(2)-I(3)-I(4)	91.9 (2)
O(6)-H(11)	0.88 (4)	I(3)-I(4)-I(5)	172.4 (3)
O(6)-H(12)	0.76 (4)	I(6)-I(7)-I(8)	178.7 (4)
O(7)-H(13)	0.87 (4)	I(7)-I(8)-I(9)	85.8 (2)
O(7)-H(14)	0.74 (4)	I(8)-I(9)-I(10)	178.7 (4)
		H(1)-O(1)-H(2)	90 (4)
O(1)-Ca-O(2)	79.4 (4)	H(3)-O(2)-H(4)	90 (4)
O(2)-Ca-O(3)	122.0 (6)	H(5)-O(3)-H(6)	93 (3)
O(3)-Ca-O(4)	76.3 (7)	H(7)-O(4)-H(8)	97 (3)
O(4)-Ca-O(5)	108.6 (8)	H(9)-O(5)-H(10)	105 (4)
O(5)-Ca-O(6)	71.5 (8)	H(11)-O(6)-H(12)	103 (3)
O(6)-Ca-O(7)	82.8 (8)	H(13)-O(7)-H(14)	114 (3)

coordinates had been determined the positions of the other non-hydrogen atoms were found from a Fourier map and the H atoms from a difference map obtained with the neutron diffraction data. The positions of all atoms were refined with *LINUS* (Coppens & Hamilton, 1970). To obtain convergence, it was found necessary to hold some of the parameters constant while refining others in a cyclic pattern. A final refinement with anisotropic temperature factors for all the atoms and an isotropic extinction correction, for the data where $F^2 > 3\sigma(F^2)$, gave $R_{F^2} = \sum w|F_o^2| - |F_c^2| / \sum |F_o^2| = 0.136$ and $R_F = 0.093$. The positional and thermal parameters are listed in Table 1, bond lengths and angles in Table 2.*

Discussion

The structure consists of hydrated Ca²⁺ cations which reside in a box formed by I₅⁻ anions (Fig. 1). The Ca²⁺ ion is coordinated to seven equivalent water molecules and represents the first example of a heptahydrated cation. The Ca-O distances, when averaged over

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36146 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

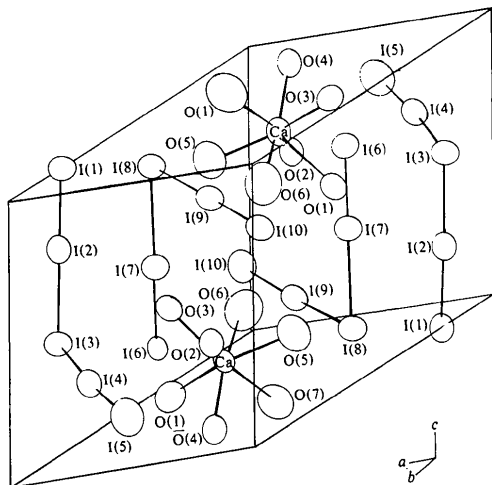


Fig. 1. A perspective view of the structure of calcium decaiodide heptahydrate.

thermal motion (ORFFE, Busing, Martin & Levy, 1964), fall in the range 2.42–2.49 Å indicating that all the water molecules are equally bonded. Likewise, when the O–H distances are averaged over thermal motion more reasonable bond lengths in the range 0.9–1.4 Å are obtained.

The water molecules are arranged in the form of a distorted capped trigonal prism (CTP) (Fig. 2). For O(7) as the capping atom the δ' angles are 7.5, 50.2, 0.0, 13.7° compared to 41.5, 41.5, 0.0, 0.0° for the ideal polyhedron (Muetterties & Guggenberger, 1974). In his review of seven-coordination chemistry, Drew (1977) has examined some 161 structural studies of seven-coordinated monomers. Of these, only nine examples are of a metal ion coordinated to seven equivalent ligands but these do not include an ion coordinated to seven water molecules. Ca does, however, occur in a seven-coordinated state in $\text{Ca}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ (Hsu & Schlemper, 1978), $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (Leclaire & Borel, 1979), and CaV_3O_7 (Bouloux & Galy, 1973).

The I_5^- ions are of the normal V-shaped variety, as opposed to the linear type which has been proposed as the structure of the iodine moiety in the channel-inclusion starch iodine complex (Teitelbaum, Ruby & Marks, 1978; Bowmaker, 1978), and in the iodine

complex with trimesic acid (Herbstein & Kapon, 1972). The I_5^- ion has a planar, right-angular form when it is not constrained by its environment and this has been shown to be the more stable configuration (Wiebenga & Kracht, 1969). There are two crystallographically different I_5^- ions in this structure (Fig. 3) but their structural details are similar to the three other examples of the I_5^- ion previously examined (Table 3). One arm of each of the I_5^- ions forms part of a linear chain of I atoms parallel to *c*, and in this direction the I_5^- units are only 3.60 and 3.47 Å apart. This distance is shorter than the sum of the van der Waals radii of 4.24 Å (Bondi, 1964), and indicates a weak interaction between the iodine units. The minimum distance between members of the two chains of I_5^- anions is, however, such that no interaction between these exists.

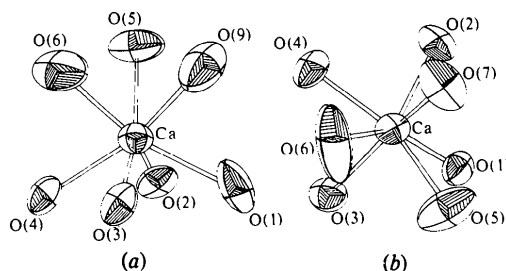


Fig. 2. Two views of the heptahydrated Ca^{2+} ion in calcium decaiodide heptahydrate: (a) along *a* and (b) along *b*.

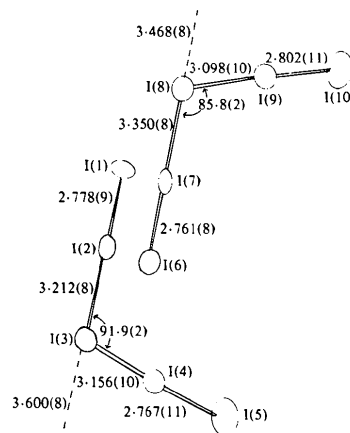


Fig. 3. The two I_5^- ions in calcium decaiodide heptahydrate. (Distances in Å, angles in degrees.)

Table 3. Bond lengths (Å) and angles (°) in I_5^- ions

	I(1)–I(2)	I(2)–I(3)	I(3)–I(4)	I(4)–I(5)	I(2)–I(3)– I(4)	Reference
KI_3 , KI_5 , valinomycin	2.760	3.080	3.080	2.760	83.8	(1)
$[(\text{CH}_3)_4\text{N}]\text{I}_5$	2.81 (1)	3.71 (1)	3.17 (1)	2.81 (1)	95	(2)
$[\text{Fe}(\text{HDF})_2(3\text{-MePy})_2]\text{I}_5$	2.776 (5)	3.131 (6)	3.039 (6)	2.814 (5)	93.7	(3)
$\text{CaI}_{10} \cdot 7\text{H}_2\text{O}$	2.778 (9)	3.212 (8)	3.156 (10)	2.767 (11)	91.9 (2)	(4)
$\text{CaI}_{10} \cdot 7\text{H}_2\text{O}$	2.761 (8)	3.350 (8)	3.098 (10)	2.802 (11)	85.8 (2)	(4)

References: (1) Neupert-Laves & Dobler (1975). (2) Broekema, Havinga & Wiebenga (1957). (3) Dvorkin, Simonov, Malinovskii, Bulgak & Batyr (1977). (4) This work.

Because the charge on the anion is diffuse, there is a minimum of interaction between the anion and the hydrated cation in this compound. In fact, there are only three I—H distances which are less than the sum of the van der Waals distances of 3.15 Å (Bondi, 1964) and this lack of hydrogen bonding has resulted in high thermal parameters for the H atoms. Thus it would seem that, where a hydrated Ca²⁺ ion is free to fill an interstice in the structure with a minimum of interaction, it coordinates to seven water molecules rather than six which is normal for a hydrogen-bonded situation.

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The Structure of (*o*-Phthalato)bis(pyridine)copper(II) with Bridging and Chelating *o*-Phthalate Anions

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Abstract

[Cu(C₅H₅N)₂(C₈H₄O₄)], *M_r* = 385.9, is monoclinic, space group *P*2₁/*c*, with *a* = 18.199 (6), *b* = 11.991 (14), *c* = 17.923 (8) Å, β = 119.98 (2)°, *V* = 3388 (4) Å³, *Z* = 8, *D_x* = 1.51, *D_m* = 1.51 Mg m⁻³, *F*(000) = 1576, λ(Cu *K*α) = 1.54178 Å, μ(Cu *K*α) = 1.999 mm⁻¹. *R* = 0.055 for 5425 observed reflections.

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The structure consists of two crystallographically independent square-pyramidal [Cu(C₅H₅N)₂(C₈H₄O₄)] complexes linked in polymeric chains by bridging phthalate anions which also act as chelating ligands through two O atoms from one carboxylate group. Pentacoordination of Cu involves two N atoms (one at the apex of the pyramid) from two pyridine molecules, one O atom from the monodentate carboxylate of an

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