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Symmetrical Hydrogen Bonds in the Crystal Structure of Calcium Bis(dihydrogen arsenate): a Neutron-diffraction Study

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Summary Neutron-diffraction analysis (final R -value 0.025 over 930 independent reflexions) of the crystal structure of calcium bis(dihydrogen arsenate), $\text{Ca}(\text{H}_2\text{AsO}_4)_2$, strongly indicates that inter-ion oxygen–oxygen separations of 2.436(3) and 2.444(3) Å contain symmetrical hydrogen bonds.

CONFIRMATION by neutron-diffraction crystal-structure analysis of the occurrence of symmetrical hydrogen bonds between oxygen atoms of separate approximately tetrahedral oxyanions is uncommon. For the crystal structure of anhydrous calcium bis(dihydrogen arsenate), $\text{Ca}(\text{H}_2\text{AsO}_4)_2$, which crystallises with two formula units in the triclinic space group $P\bar{1}$, single-crystal X -ray analysis¹ revealed two “very short”² inter-ion oxygen–oxygen contacts: $\text{O}(5) \cdots \text{O}(5') = 2.454(8)$ and $\text{O}(8) \cdots \text{O}(8') = 2.455(8)$ Å, both across symmetry centres. In order chiefly to investigate the symmetry or otherwise of the

corresponding hydrogen bonds, an accurate neutron-diffraction analysis of this structure has been carried out. All hydrogen atoms were located unequivocally by Fourier difference syntheses; the positions of all atoms were refined anisotropically by least squares to a final disagreement index, R , of 0.025 over 930 independent reflexions. Assignment of the space group to $P\bar{1}$ rather than $P1$ is supported by the low R -value, the occurrence of a single Fourier-difference peak of acceptable shape, the absence of thermal-parameter anomalies in the least-squares refinement, and the absence of a measured piezoelectric effect. Oxygen–oxygen separations of $\text{O}(5) \cdots \text{O}(5') = 2.436(3)$ and $\text{O}(8) \cdots \text{O}(8') = 2.444(3)$ Å are very close to those derived from the X -ray analysis; $\text{O}(5)\text{--H}(4) = 1.218(3)$ and $\text{O}(8)\text{--H}(5) = 1.222(3)$ Å.

In the two formally symmetrical hydrogen bonds, two kinds of consideration point to centring of the hydrogens, rather than statistical occupation of a pair of sites³ separated

by 0.2 Å or so. First, the thermal parameters of H(4) and H(5) are close to those of O(5) and O(8), rather than being higher than those of nearby atoms. Secondly, for inter-anion hydrogen bonds in a series of acid hydrogen arsenates in which hydrogen positions have been determined directly by neutron diffraction (CaHAsO₄·2H₂O;⁴ Na₂HAsO₄·7H₂O;⁵ and CaHAsO₄·H₂O⁶), we have examined the variation of

several quantities with O...H distance. For the most linear of these graphs, that of the O-H...O angle, the linearity is accurately preserved on the assumption that the O(5)...O(5') and O(8)...O(8') hydrogen bonds in Ca-(H₂AsO₄)_n are genuinely symmetrical.

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