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), $Ca(H_2AsO_4)_2$, 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), $Ca(H_2AsO_4)_2$, which crystallises with two formula units in the triclinic space group $P\bar{1}$, single-crystal X-ray analysis[1] revealed two "very short"[2] inter-ion oxygen–oxygen contacts: O(5) · · · O(5′) = 2·454(8) and O(8) · · · 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 O(5) · · · O(5′) = 2·436(3) and O(8) · · · O(8′) = 2·444(3) Å are very close to those derived from the X-ray analysis; O(5)–H(4) = 1·218(3) and O(8)–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 sites[3] 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 ($CaHAsO_4,2H_2O$;[4] $Na_2HAsO_4,7H_2O$;[5] and $CaHAsO_4,H_2O$[6]), 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 $Ca(H_2AsO_4)_2$ are genuinely symmetrical.

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