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X-ray Structure of the Peroxodiphosphate Ion $[P_2O_8]^{4-}$ in $\{Na_2(H_2O)_9\}_2[P_2O_8]$

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The peroxodiphosphate ion is one of the strongest oxidants known ($E_0 = 2.07$ V [1]), with applications in organic synthesis [2] and polymerisation initiation [3]. Although several salts have been characterised by elemental analysis [4] and vibrational spectroscopy [5], there is a dearth of structural data. Simon and Richter have reported four forms of the sodium salt, $Na_4[P_2O_8]\cdot xH_2O$ (where $x = 0$, 6, 18, 20) [6], and characterised them by their X-ray powder diffraction patterns. We have determined the crystal structure of $Na_4[P_2O_8]\cdot 18H_2O$, and show that it is $\{Na_2(H_2O)_9\}_2[P_2O_8]$. Despite the presence of disorder affecting the peroxodiphosphate ion, it has been possible to determine its structure unequivocally.

Experimental

Preparation

The preparation is a modification of those reported in the literature [6, 7]. Crude potassium peroxodiphosphate was prepared using the method of Creaser and Edwards [7]: potassium dihydrogen orthophosphate (45.3 g, 0.33 mol), potassium hydroxide (29.7 g, 0.53 mol) and potassium fluoride (18.0 g, 0.31 mol), were dissolved in distilled water to give 80 cm^3 of solution, which was then electrolysed for 6 h on three successive days using a voltage of 6 V and a current of 0.4 A. The anode was a platinum gauze and the cathode a platinum wire. Stirring was continued throughout and the preparation was conducted under a gentle flow of N_2 to prevent the formation of carbonate. The crude $K_4[P_2O_8]$ was filtered off and redissolved in distilled water (100 cm^3); a solution of sodium perchlorate ($NaClO_4\cdot H_2O$, 61 g, 0.43 mol) in distilled water (150 cm^3) was added, followed by methanol (200 cm^3) with stirring. After overnight storage at 5 °C the impure product was filtered off as a white solid. This was then dissolved in the minimum quantity of distilled water (30 cm^3) with stirring. Chilling to 0 °C gave a white precipitate, which was then filtered off at 0 °C and recrystallised by slow evaporation from aqueous solution *in vacuo* over concentrated sulphuric acid.

X-ray Study

Single crystals of the title compound decomposed in approximately 30 min with loss of water if exposed to the atmosphere. Coating with picture varnish was insufficient to delay the process, and data were therefore collected on a crystal enclosed in a Lindemann capillary tube with a drop of mother liquor. The crystals are hexagonal, with $a = 9.186(5)$, $c = 16.696(7)$ Å, $U = 1220.1$ Å^3 (at 20 °C), space group $P6_3$ (no. 173) and $Z = 2$. Intensity data were collected on a Nicolet R3m/Eclipse S140 diffractometer system, using graphite-monochromated Cu Kα radiation. A total of 1024 independent reflections were measured, to $\theta = 55°$, of which 104 were judged to be 'unobserved'.

Initial solution of the structure proved unusually difficult, and required a combination of Patterson, direct, and trial-and-error methods, while refinement was complicated by the threefold disorder of the $[P_2O_8]^{4-}$ ion. Nevertheless, all water hydrogen atoms were located and R has now reached 0.056. The program system SHELXTL [8] was used throughout the calculations.

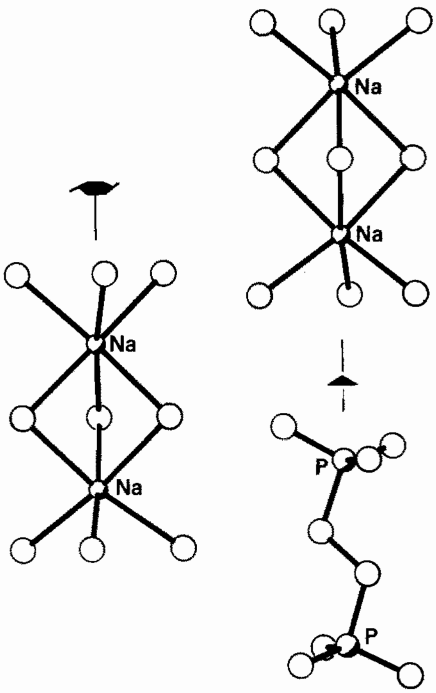

Fig. 1. The three crystallographically independent moieties in the structure of $\{Na_2(H_2O)_9\}_2[P_2O_8]$. Two lie on threefold axes, the other on 6_3 screw axes. The peroxodiphosphate ion is disordered in this structure; for the sake of clarity only one orientation of $[P_2O_8]^{4-}$ is shown.

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Results and Discussion

The crystal structure contains $[P_2O_8]^{4-}$ anions and $\{Na_2(H_2O)_9\}^{2+}$ moieties, as shown in Fig. 1. The peroxodiphosphate ion consists of two phosphate tetrahedra linked by a peroxide bond, with the *anti* O–P–O–O–P–O moiety approximately planar, and the anion having essentially $2/m$ (C_{2h}) symmetry. Terminal P–O distances range from 1.500(10) to 1.512(8) Å, mean 1.506 Å, while the P–O(peroxo) distances are 1.649(9) and 1.654(10) Å, mean 1.652 Å. The O–P–O angles between the terminal atoms are slightly greater than tetrahedral, 113.2(7) to 115.0(7)°, mean 113.9°, while O(terminal)–P–O-(peroxo) angles are 98.5(6)–99.5(6)°, mean 99.0°, for that *anti* to the peroxide group, and 106.0(8)–108.2(8)°, mean 107.3°, for the others. This difference between O(terminal)–P–O(peroxo) angles seems to be a feature for this type of species, and is also found in the $[S_2O_8]^{2-}$ ion in $(NH_4)_2[S_2O_8]$ [9] and the $[HSO_5]^-$ ion in $KHSO_5 \cdot H_2O$ [10, 11].

The peroxide bond length is 1.490(14) Å, similar to that found in $(NH_4)_2[S_2O_8]$, 1.497(8) Å [9], and $K_2[S_2O_8]$, 1.482(6) Å [12]. In peroxoborates these lengths are 1.480(2) Å in $Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$ [13] and 1.477(2) Å in $Na_2[B_2(O_2)_2(OH)_4] \cdot 4H_2O$ [14]. Where one or both atoms attached to the peroxide group are hydrogen, the distance is shorter, e.g. in $KHSO_5 \cdot H_2O$ it is 1.460(3) Å [10], 1.463(1) Å [11], and in solid hydrogen peroxide it is 1.453(7) Å [15]. The P–O–O angles are 107.2(7) and 108.3(7)°, mean 107.8°.

The four sodium ions form two binuclear clusters of type $\{Na_2(H_2O)_9\}^{2+}$, each with six terminal and three bridging water molecules. Each sodium ion has threefold crystallographic point symmetry. For the terminal water molecules, the Na–O bond lengths are in the range 2.338(5)–2.379(6) Å, mean 2.363 Å, while the $Na-H_2O$(bridging) distances are somewhat longer, range 2.402(7)–2.457(6) Å, mean 2.428 Å, giving each sodium ion a distorted octahedral coordination. There is an extensive network of hydrogen bonds, of the type O–H...O, linking the constituent groups.

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