Crystal Structure of the Novel Bleaching Agent Hexaaquomagnesium(II) Bis(2-carboxylato-monoperoxybenzoic acid), $[Mg(H_2O)_6](C_8H_5O_5)_2$

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Currently the two most important industrial bleaching agents used in solid detergents are 'sodium percarbonate' ($Na_2CO_3 \cdot \frac{1}{2}H_2O_2$) and 'sodium perborate' ($Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$). As part of a programme of chemical and structural studies [1–3] on these and related compounds we report the structural characterisation of a novel bleaching agent $[Mg(H_2O)_6](C_8H_5O_5)_2$.

The title compound was prepared by a modification of the published procedure [4]. A dry mixture of magnesium oxide (4.0 g, 0.1 mol) and phthalic anhydride (30 g, 0.2 mol) was slowly added to a 30% hydrogen peroxide solution (12.5 cm^3, 0.1 mol), and the temperature was kept below 15 °C at all times. The resulting mixture was filtered and washed with ethyl acetate and dichloromethane.

The colourless plate-like crystals were suitable for structural study, and have a monoclinic unit cell of dimensions a = 13.053(3), b = 5.375(1), c = 14.931(2) Å, β = 90.44(2)° (at 18 °C), U = 1047.6 $Å^3$, space group $P2_1/a$ and Z = 2. X-ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu-Kα radiation. A total of 1083 independent reflections were measured (to θ = 50°), of which 276 were judged to be 'unobserved'. A combination of direct methods and difference Fourier syntheses yielded the structure, and least-squares refinement has now reached R = 0.050. The program system SHELXTL [5] was used throughout the calculations.

Within the structure, the magnesium atoms lie on centres of symmetry, and each is surrounded by six water molecules to give an octahedral coordination geometry. The other components in the structure are the $(C_8H_5O_5)^-$ anions, and there are two such anions per magnesium atom, as shown in Fig. 1. We have also shown that there is a hydrogen atom attached to the terminal oxygen atom of the peroxy moiety.

The mean Mg–O distance is 2.074 Å [range 2.043(4) to 2.105(5) Å, while the O–Mg–O *cis* angles are in the range 87.6(2) to 92.4(2)°]. In the anions the bond lengths agree well with the limited structural data available on peroxycarboxylic acids [6, 7]. Thus, within the peroxycarboxylic group the O–O distance is 1.442(6) Å, while the C–O (peroxy) distance is longer [1.351(7) Å] than the C–O (terminal) distance 1.202(7) Å. In the 2-carboxylato moiety the two C–O distances are very similar to each other with a mean of 1.260(7) Å. The peroxycarboxylic group lies approximately within the plane of the six-membered ring (dihedral angle 8.6°), while the plane of the carboxylato group is approximately normal to the plane (dihedral angle 79.2°).

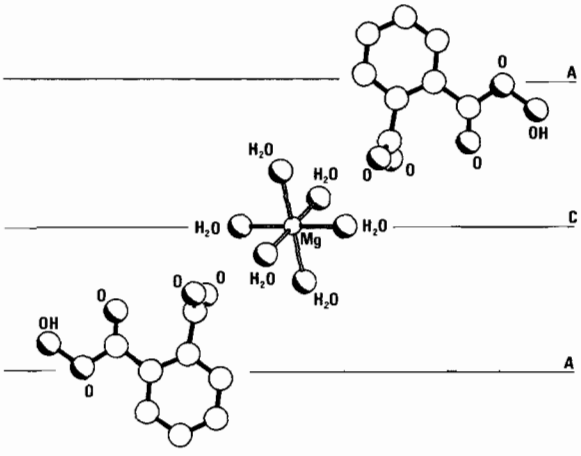

Fig. 1. A formula unit of $[Mg(H_2O)_6](C_8H_5O_5)_2$. Hydrogen atoms have been omitted. The horizontal lines delineate the 'sandwich' referred to in the text.

The $Mg(H_2O)_6$ octahedra lie in a plane (C) sandwiched between two layers (A and A′) of anions (Fig. 1). There is a network of hydrogen bonds of the type O–H···O (O···O distances 2.61 to 2.82 Å), between the water molecules and oxygen atoms of the anions, and also between the anions themselves involving the peroxy group hydrogen atoms, these help to hold the 'sandwich' together. The orientation of the anions is such that the network of hydrogen bonds lies only within a 'sandwich', so that there are no hydrogen bonds between one 'sandwich' and the next.

The Raman spectra of the solid title compound and of magnesium phthalate are in general similar, but in the former a new strong band is observed at 905 cm^{-1} which can be assigned to the O–O stretch of the peroxy group. Similar bands are seen in other peroxy acids [8]. In the infrared spectrum of the title compound a band at 3450 cm^{-1} appears, which is clearly due to the O–H stretch of the OOH group.

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