The Crystal Structure of Ammonium Oxalate Monoperhydrate, $(NH_4)_2C_2O_4 \cdot H_2O_2$

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We want to report on the crystal structure of a new perhydrate formed by ammonium oxalate. Similar to the alkali metal oxalates [1-3] also ammonium oxalate has now been found to crystallize as the monoperhydrate from a perhydrol solution (30 % H_2O_2 in H_2O) at room temperature.

Ammonium oxalate monohydrate, the stable phase in equilibrium with a water solution, is known to contain an uncommon, non-planar oxalate ion.[4] The deviation from planarity of the oxalate ion is believed to be caused by the particular hydrogen bond network in the monohydrate. The exchange of the water molecule with the larger hydrogen peroxide molecule will change the hydrogen bond network. Hence, also changes in the shape of the oxalate ion might be expected. To see if the increased stability of the perhydrate relative to the monohydrate could be explained as being due to a less strained oxalate ion in the perhydrate phase, we have determined the crystal structure of this compound from X-ray diffraction data.

Ammonium oxalate monoperhydrate, $(NH_4)_2C_2O_4 \cdot H_2O_2$, crystallizes with orthorhombic symmetry in space group $P2_12_12$ which is the same space group as found for the monohydrate. The unit cell dimensions (in Å) of the two phases are also very similar:

	a	*b*	*c*
Perhydrate:	8.57	10.54	3.81
Hydrate:	8.035	10.310	3.795

A preliminary structure determination, based on visually estimated film intensities, shows the structure of the perhydrate to be closely related to that of the hydrate. A projection of this structure along the *c*-axis is shown in Fig. 1, and may be compared to Fig. 1 of Robertson's paper on the hydrate.[4] The H_2O_2 molecule is sitting on a twofold axis in approximately the same position as the water molecule in the hydrate. The H_2O_2 molecule is bound by hydrogen bonds to neighboring oxalate and ammonium ions, as is the water molecule, but the hydrogen bond acceptor atoms have been pushed somewhat away to give space for the larger H_2O_2 molecule. The hydrogen bond lengths are of normal values ($O-H \cdots O = 2.60$ Å and $N-H \cdots O = 2.87$ Å). The coordination about the ammonium ion is the same in both salts.

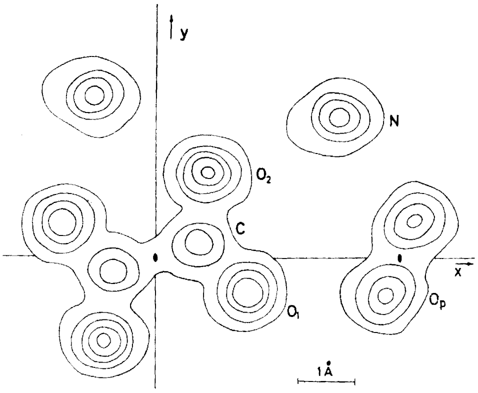

Fig. 1. Fourier projection of $(NH_4)_2C_2O_4 \cdot H_2O_2$ along the *c*-axis.

Surprisingly enough, also the shape of the oxalate ion in the perhydrate is similar to the shape observed in the hydrate. The angle of twist of the two planar CO_2-groups about the $C-C$ bond is found to be 33.3° which is somewhat larger than the value observed in the hydrate, 26.6°. The increased stability of the perhydrate can therefore not be sought in a more favourable shape of the oxalate ion.

A detailed discussion of the structure based on more accurate three-dimensional X-ray diffraction data than presently available will be published later. Standard deviation in the atomic coordinates is at present 0.005 Å.

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