# Preparation and *X*-Ray Crystal Structure of Guanidinium Oxalate Dihydrate Monoperhydrate: a Novel Example of Crystal Engineering

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*Summary* A simple method of 'burying' molecules of $H_2O_2$ in a thermally stable crystalline solid is described, by the slow crystallization of guanidinium oxalate from $H_2O_2$; the *X*-ray crystal structure of the resulting solid has been determined.

Schmidt and his co-workers[1] have shown how specific kinds of intermolecular or interatomic (non-bonded) forces may be harnessed to produce crystal structures in which a desired orientational, geometric, or symmetry relationship exists between neighbouring molecules to which are attached potentially reactive groups. This approach has enabled the preparation of specially designed solids which subsequently undergo photochemical changes, in the solid state, to yield, *inter alia*, chiral and other types of stereospecific products.[2] We have utilized a similar strategy to design a crystalline hydrate in which molecules of hydrogen peroxide are 'buried' inside the structure of the solid. The basis of our procedure is to use guanidinium cations, which are known[3] to be exceptionally effective for the formation of hydrogen bonds. There is considerable interest in synthesizing stable, oxygen-rich solids (containing either dioxygen complexes or bound $H_2O_2$) which may, by dissolution or other means, be induced to release oxygen.

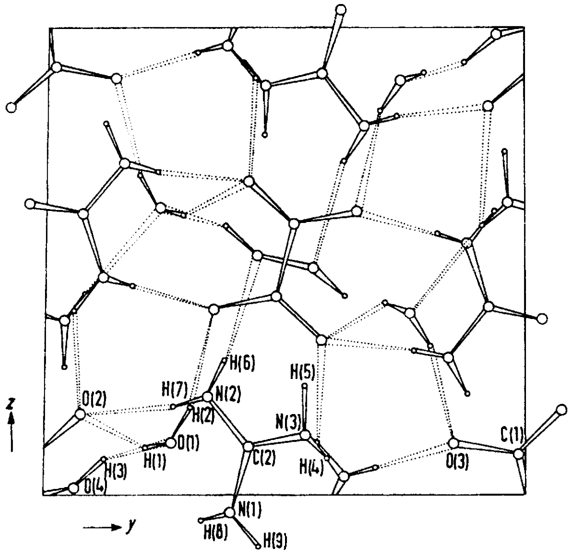

FIGURE. Projection of the structure of guanidinium oxalate dihydrate monoperhydrate down the *a* axis.

Pedersen's work[4] on the perhydrates of alkali metal oxalates was taken as a starting point. In these solids a chain structure linking oxalate to $H_2O_2$ units predominates: this feature is not conducive to thermal stability since it permits easy ingress and egress to reactive species. A compact three-dimensional structure is required. Such a solid is indeed formed when guanidinium oxalate is slowly recrystallised from 30% $H_2O_2$. One view (along the *a* axis) of guanidinium oxalate dihydrate monoperhydrate (GODM) is shown in the Figure. It is to be noted that eight out of the nine possible hydrogen-bonds are formed, a fact which explains why, of all the oxalate perhydrates so far studied, this is the most thermally stable. At room temperature (293 K) the time taken for the release of 20% of the entrapped $H_2O_2$ at a relative humidity of *ca.* 50% is 250 h for GODM whereas ammonium oxalate monoperhydrate takes only 50 h.

Full details of the preparation, analysis, and crystal structure of GODM are to be presented elsewhere.†

We thank the S.R.C. for a studentship to R.G.P.

(*Received*, 2*nd March* 1976; *Com.* 217.)

† The crystal structure was solved by direct methods using 585 reflections (Cu-$K_\alpha$ radiation), $R$ value 6·1%. *Crystal data:* space group: $P2_1/c$; $Z = 2$; $a = 6{\cdot}96(3)$, $b = 9{\cdot}46(3)$, $c = 10{\cdot}13(3)$ Å, $\beta = 114{\cdot}0(1)°$.

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