alloy (25 wt% Ag)/γ-alumina (6.3 wt%) was prepared by impregnating the Pd/γ-alumina catalyst (5 wt%, powder, Lancaster Chemicals, England) with silver nitrate and calcining at 500°C for 4 h under helium. The oxidation of H_2 in the membrane loop reactor was carried out batchwise with respect to H_2 and liquid medium (0.02 M aqueous H_2SO_4) and continuous with respect to O_2 (50 $cm^3 min^{-1}$) for a period of 3 h (Figure 1a). The liquid medium (60 cm^3) was recirculated continuously by the gas lift mechanism. On the other hand, the H_2 was oxidized by O_2 over the magnetically stirred powdered catalysts in a glass slurry reactor (capacity 250 cm^3) at atmospheric pressure (101 kPa), by using a mixed feed of H_2 and O_2 (1.7 vol% H_2) and H_2SO_4 (150 cm^3, 0.02 M) as the reaction medium. In both cases, the H_2O_2 formed in the reaction was determined by iodometric analysis. The concentration of H_2 in the reactor effluent gases was measured by an online H_2 analyzer. The amount of H_2 that permeated through the membrane catalyst was measured from a decrease in the pressure in the H_2 reservoir, from which the H_2 was supplied to the membrane reactor at a constant pressure. The H_2O_2 was decomposed over the powdered catalysts (0.2 g) by stirring in aqueous H_2SO_4 (105 cm^3, 0.02 M) in the glass reactor; the initial concentration of H_2O_2 in the medium was 0.3 wt%.

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Crystal Structure of Potassium Croconate Dihydrate, after 175 Years

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Potassium croconate dihydrate, $K_2(C_5O_5)\cdot 2H_2O$, was isolated by Leopold Gmelin in 1824 and described as an orange-colored (*pomeranzenfarbige*) crystalline hydrate in 1825.[1] Obtained by heating a mixture of potash and carbon and predating Wöhler's urea synthesis by three years, it thus has a claim to be the first "organic" compound to have been synthesized from inorganic precursors (for an account of early work on oxocarbon compounds, see the chapter by West.[2]) Although some X-ray studies have been reported on other crystalline croconate salts (e.g., ammonium croconate,[3] diethylammonium croconate,[4] ammonium hydrogencroconate,[5] and rubidium hydrogencroconate[5]), the structure of the potassium salt has remained unknown until now.

We have obtained the substance by slow evaporation of an aqueous solution of commercial potassium rhodizonate $K_2(C_6O_6)$[6] in air. This gave a mixture of colorless and orange-yellow needles, of which the former could be identified as potassium oxalate monohydrate,[7] while the latter was shown by X-ray analysis to be potassium croconate dihydrate,[8] both presumably derived from air oxidation of the rhodizonate. Apart from its historical interest, the crystal structure has some noteworthy features. It gives the first reasonably precise dimensions of the aromatic ring system and shows a remarkable stacking of the planar, doubly negatively charged croconate anions.

From the dimensions of the croconate dianion shown in Figure 1, it is evident that it does not deviate much from fivefold symmetry in the crystal environment. The slight differences among the individual distances may be real and attributable to the lower symmetry of the crystal environ-

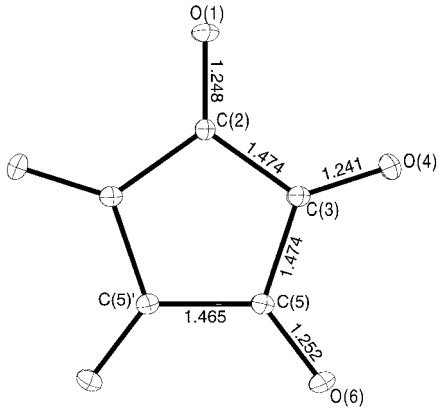

Figure 1. Bond lengths [Å] in the croconate dianion of $K_2(C_5O_5)\cdot 2H_2O$ (estimated standard deviations are ca. 0.003 Å). The dianion has crystallographic C_2 symmetry. The oxygen atoms deviate by up to 0.076 Å from the mean plane of the carbon skeleton (planar to within 0.025 Å). The C-C-C angles are all within 0.5° of 108°, and the C-C-O angles all within 1° of 126°.

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ment. Small deviations of the atoms from the mean plane of the anion (up to 0.025 Å for C atoms, 0.076 Å for O atoms) may arise from the same cause. The most striking feature of the crystal structure is perhaps the stacking of the nearly planar, doubly negatively charged croconate anions along the short *c* axis (Figure 2). With the plane normal tilted 13° from

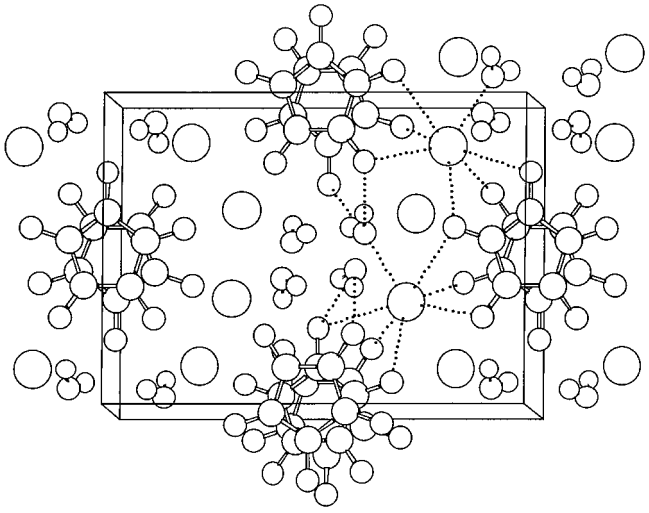

Figure 2. Crystal structure of $K_2(C_5O_5)\cdot 2H_2O$ viewed along a direction nearly parallel to the *c* axis with the *a* axis horizontal. The large circles represent potassium atoms, and dotted interactions correspond to K···O and H_2O···O distances in the range of 2.65 Å to 3.01 Å.

this axis, the interplanar spacing is only 3.30 Å, and individual interatomic distances between neighboring molecules in the stack are as short as 3.28 Å for C···C and 3.34 Å for O···O. These anionic stacks are separated by a complex system of potassium cations and water molecules (Figure 2), in which each K cation is linked to six O atoms of four separate anions in two different stacks (K^+···O 2.79–3.01 Å) and to the O atom of a water molecule (2.65 Å) in an irregular coordination environment. Each water molecule in turn forms hydrogen bonds to O atoms of two adjacent anions in the same stack (O···O 2.79, 2.88 Å), as well as being engaged in the coordination of K^+.

None of the other crystal structures of croconate salts show this pattern; nor does the crystal structure of anhydrous potassium rhodizonate.[9] The simple model in which the doubly negative charge of an individual croconate anion is assumed to be localized on its peripheral oxygen atoms ($q_O = -\frac{2}{5}$) is grossly inadequate for explaining the anion stacking; it would correspond to a potential energy of more than 100 kcal mol^{-1} per pair of anions in the stack. Models involving more localized charges, for example, on the carbon atoms or at the ring centre would be even worse. Perhaps point-charge models are inadequate to describe the observed packing. In any case, the present structure would seem to represent a challenge for advanced crystal structure modelers.

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