

alent reaction between B<sub>10</sub>H<sub>14</sub> and MeAuPEt<sub>3</sub>, which affords the triethylphosphine triple cluster as the only isolable species, presumably *via* a multistage reaction. These points must remain conjectural, however, because of the (unexpected) finding of the OH function terminal to B(9). Since we cannot say whether hydrolysis occurred during reaction or work-up we clearly cannot be totally confident of the precise nature of the reacting species. Nevertheless, we are prompted by the findings reported herein to repeat and extend these synthetic and isolation procedures under strictly anhydrous conditions, and to study the reactions of a wider range of metallasubstituted *nido* and *arachno* boranes with MeAu-PR<sub>3</sub>. The results of these studies will be reported in future publications.

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## Neutron Diffraction Study of Sodium Oxalate Monoperhydrate at 123 K\*

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**Abstract.** Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 168.02, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 3.521 (2), *b* = 8.206 (3), *c* = 8.950 (3) Å,  $\beta$  = 96.63 (3)°, *V* = 257.0 (5) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.17, *D<sub>m</sub>* = 2.09 Mg m<sup>-3</sup>,  $\lambda$  = 1.0559 (2) Å,  $\mu$  = 0.0413 mm<sup>-1</sup>, *F*(000) = 168, *T* = 123.0 (2) K. *R* = 0.0351 for 2873 observations representing two sets of equivalent reflections. The hydrogen peroxide molecule is planar, *i.e.* the H—O—O—H dihedral angle is 180.0°; O—O = 1.467 (1), O—H = 1.0094 (9) Å, and O—O—H = 99.95 (8)°. The oxalate ion is centro-

symmetric and planar, the two C—O distances are 1.2671 (6) and 1.2445 (7) Å, differing by 0.0226 Å, the longer one being the acceptor of the hydrogen bond. The C—C distance is especially long, 1.564 (1) Å.

**Introduction.** The structure of the title compound, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub>, was determined from X-ray film data by Pedersen & Pedersen (1964). The conformation of the H<sub>2</sub>O<sub>2</sub> molecule was also studied by NMR spectroscopy. Both space-group symmetry and NMR spectra led to the conclusion that the dihedral angle of the H<sub>2</sub>O<sub>2</sub> molecule was 180.0°, *i.e.* a planar conformation of the molecule was observed for the first time.

Several compounds containing H<sub>2</sub>O<sub>2</sub> molecules have been studied (Pedersen, 1969, 1972; Adams &

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Pritchard, 1976, 1977; Fritchie & McMullan, 1981) and the dihedral angle has been found to vary between 90 and 180°. Theoretical calculations have shown that the barrier hindering internal rotation about the O—O bond is low, only a few kJ mol<sup>-1</sup>. The conformation of H<sub>2</sub>O<sub>2</sub> molecules in the solid state therefore is believed to be strongly influenced by intercrystalline forces and in particular by hydrogen bonding. We are presently studying the influence of intercrystalline forces on the deformation density of the hydrogen peroxide molecule, both experimentally and theoretically. We have started by collecting low-temperature X-ray data out to  $\sin\theta/\lambda = 1.12 \text{ \AA}^{-1}$  and by the parallel neutron diffraction study at 123 K reported here. The investigations will be used to study the electron density distribution in the H<sub>2</sub>O<sub>2</sub> molecule.

Also of interest is the deformation electron density of the oxalate ion as the deformation electron density of oxalic acid has been the subject of study by several groups.

**Experimental.** Sodium oxalate (p.a. Merck) was dissolved in perhydrol (30% H<sub>2</sub>O<sub>2</sub>). By slow evaporation, crystals of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O<sub>2</sub> were formed. The crystals invariably grew as needles along the *a* axis. The density was measured at room temperature by the flotation method. The crystals were grown in Norway and transported to the BNL High Flux Beam Reactor, USA. A needle of cross section 1.2 × 0.9 mm and of length 4.2 mm was used for data collection. For subsequent application of neutron absorption and extinction corrections, the crystal was described by six boundary planes, ±(0 $\bar{1}$ 1), ±(011), ±(100) enclosing a volume ≈ 4 mm<sup>3</sup>.

The neutron intensity data were collected on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor, operating at 60 MeV, using a neutron beam obtained by 002 reflection from a Be monochromating crystal. The neutron wavelength of 1.0559 (2) Å was determined by a least-squares fit of  $\sin^2\theta$  data for a standard KBr crystal [*a* = 6.6000 (1) Å]. The crystal was glued to a hollow aluminium pin fastened within a sealed aluminium can filled with He gas. The enclosure was cooled by a closed-circle refrigerator† mounted within the diffractometer  $\chi$  circle with the crystal *a*\* axis within a few degrees of the  $\varphi$  axis.

The lattice parameters, Table 1, were determined by a least-squares fit of  $\sin^2\theta$  data for 32 reflections with  $41 < 2\theta < 56^\circ$ . The crystal temperature was set at 123 K and kept within ±0.2° by a temperature controller,‡ monitoring the temperature during the

Table 1. Crystal data (Å and °)

Sodium oxalate hydrogen peroxide, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O<sub>2</sub>, space group *P*2<sub>1</sub>/*c*.

	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$
This work, 123 K	3.5205 (18)	8.206 (3)	8.950 (2)	96.63 (3)
Room temp. (1964)	3.548	8.23	9.01	96.0
X-ray, 123 K (1989)	3.5201 (1)	8.1993 (3)	8.9426 (4)	96.611 (5)
Room temp. (1989)	3.5590 (9)	8.219 (2)	8.987 (4)	96.86 (2)

period of intensity data collection. A total of 2873 reflections (*h, k, l*: 0 to 5, -9 to 12, -9 to 13) were measured, giving data for 1160 independent reflections measured for  $2\theta < 114^\circ$ . The scan range was  $3.0^\circ$  for  $2\theta < 58^\circ$  and  $2.6^\circ + 0.833^\circ \text{tg}\theta$  for  $58 < 2\theta < 114^\circ$ , max.  $(\sin\theta)/\lambda = 0.794 \text{ \AA}$ . Squared structure amplitudes and variances  $\sigma^2(F^2)$  were evaluated from  $F_o^2 = (C - B)\sin 2\theta$ , *i.e.* counts - background.  $\sigma^2 F_o^2 = [\sigma^2 c(F_o^2) + 0.002 F_o^2]$ ,  $\sigma c(F_o^2)$  being based on counting statistics.

An analytically calculated absorption correction was applied, the range of transmission factors was 0.86 to 0.98.

The refinement of atomic parameters was initiated with positions from Pedersen's (1989) low-temperature X-ray study, and assumed isotropic thermal parameters. The neutron scattering lengths 5.805 fm for O, 3.63 fm for Na, 6.648 fm for C, and -3.741 fm for H were taken from Koester (1977). The parameters were refined by least-squares methods. The observations were given weights  $w = \sigma^{-2}(F_o^2)$  where  $\sigma^2(F_o^2)$  are the variances evaluated above. The function minimized was  $\sum w(F_o^2 - F_c^2)^2$ . The indices of fit at convergence ( $\Delta/\sigma \leq 0.02$ ) were  $R(F) = 0.0351$ ,  $wR(F^2) = 0.0515$  and  $S = 1.239$ . A total of 61 parameters were refined, including scale factor, positional and anisotropic thermal parameters for all six atoms. Type 1 model anisotropic extinction correction with a Lorentzian distribution (Becker & Coppens, 1974) and anisotropy of mosaic spread described according to Thornley & Nelves (1974) were also included. Values of the mosaic spread tensor  $Z \times 10^6$  are as follows:  $Z_{11} = 0.6975$ ,  $Z_{22} = 0.5632$ ,  $Z_{33} = 0.6247$ ,  $Z_{12} = -0.2118$ ,  $Z_{13} = -0.2037$ ,  $Z_{23} = 0.2103$ . The final atomic parameters are given in Table 2.\* All calculations were carried out on a VAX computer using programs written or modified for the system by Lundgren (1982).

**Discussion.** The molecular structure is shown in Fig. 1 which also gives the atomic notation. Complete geometrical details and standard deviations are given

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52039 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Air Products and Chemicals, Inc. DISPLEX, Model CS-202.

‡ Lake Shore Cryotronics Inc. Model DRC 80 C, and a Sensor Selector Model SW 10 A.

in Table 3. It is apparent that the O—O distance is significantly longer in the planar hydrogen peroxide molecule than in the molecule with a synclinal conformation. Previous studies have shown the O—O bond to be invariant within 0.004 Å whereas the distance in the planar molecule is 0.009 Å longer than the longest of the previously determined values. The lengthening of the O—O distance probably can be justified from different orbital overlap in the planar and in the nonplanar molecular conformations.

There is also a difference in the O—H bond lengths. The O—H bond in the planar molecule is 0.009 Å longer than in the urea.H<sub>2</sub>O<sub>2</sub> complex (Fritchie & McMullan, 1981) and 0.021 Å longer than in solid H<sub>2</sub>O<sub>2</sub>, see Table 3 for references.

The lengthening of the O—H bond in both Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> and in urea.H<sub>2</sub>O<sub>2</sub> can be attributed to the relatively strong hydrogen bonding in these two compounds. The shortening of the H...O distance is very close to the values expected based on the correlation between bond length and hydrogen-bond distance. Even the small difference in the O—H bonds in the first two compounds can be correlated to the difference in the hydrogen-bond lengths in the two compounds (Ichikawa, 1978).

It will be interesting to look into the deformation electron density of the O—O bond in this compound and in K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> which has also been studied by both neutron and X-ray diffraction at low temperature (Pedersen & Kvick, 1989; Pedersen, 1989). The O—O bond length is 1.4578 (6) Å in potassium oxalate monoperhydrate and is in complete

agreement with O—O in the twisted conformation. The O—H distance is 1.0117 (5) Å, and the hydrogen-bond length is 1.5979 (6) Å. The O—H distance of H<sub>2</sub>O<sub>2</sub> in potassium and sodium oxalate monoperhydrates is 1.0117 (5) and 1.0094 (9) Å, a difference of 0.0023 (10) Å, and hence they are not significantly different.

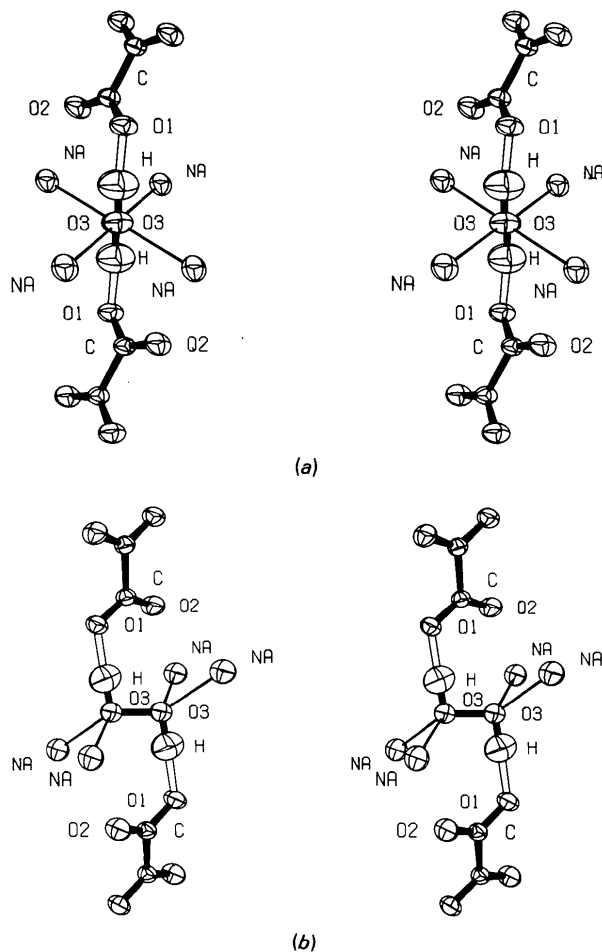


Fig. 1. Stereoscopic views of the planar hydrogen peroxide molecule with hydrogen bonds and Na ion coordination. Probability level of thermal ellipsoids is 99%.

Table 2. Final positional and thermal parameters in Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> at 123 K

$$U_{eq} = 1/3(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Na	0.5033 (1)	0.37629 (7)	0.21952 (7)	0.0074
O1	0.0302 (1)	0.32065 (4)	0.39566 (4)	0.0083
O2	0.3014 (1)	0.11722 (4)	0.12761 (4)	0.0086
O3	0.0307 (1)	0.00639 (4)	0.42057 (4)	0.0089
C	0.0965 (1)	0.41416 (3)	0.50832 (3)	0.0058
H	0.0476 (2)	0.12863 (9)	0.41065 (9)	0.0176

Table 3. Interatomic distances (Å) and angles (°)

Dimensions of the oxalate ion			Dimensions of the hydrogen peroxide molecule			$\varphi$ (°)	T (K)	Reference
C—O1	C—O2	C—C	C—C—O1	C—C—O2	O1—C—O2			
1.2671 (6)	1.2445 (7)	1.564 (10)	115.58 (5)	118.07 (5)	126.34 (4)			
O—O	O—H	O—O—H	H...O	O—H...O				
1.467 (1)	1.0094 (9)	99.95 (8)	1.582 (1)	174.38 (8)	180.00			a
1.4573 (8)	1.0005 (7)	102.53 (5)	1.6196 (6)	174.53 (6)	99.98	81		b
1.458 (4)	0.988 (3)	101.9 (1)	1.786 (5)	168.4 (2)	120.5	110		c
1.453 (7)	0.988 (5)	102.7 (3)	1.825 (6)	167.6 (4)		223–248		d
1.455 (2)	0.978 (2)	102.1 (1)	(2.782 (1))			258		e

References: (a) this work; (b) Fritchie & McMullan (1981); (c) Savariault & Lehmann (1980); (d) Busing & Levy (1965); (e) Prince, Trevino, Choi & Farr (1975).

The oxalate ion is centrosymmetric and planar. The dimensions of the ion are given in Table 3.

We see that there is a slight difference in the two C—O distances of 0.0226 (7) Å, the longest being C—O1 which is the acceptor of a relatively strong hydrogen bond. The unperturbed bond should have C—O distances of equal length. The C—C distance is long, 1.564 (1) Å, and definitely longer than in oxalic acid, 1.554 (1) Å the value determined from low temperature X-ray and neutron diffraction work by Stevens & Coppens (1980). The angles around the C atoms also reflect earlier findings: O—C—O larger than 120° and C—C—O1 smaller than C—C—O2. The sizes of the last two correlate well with the corresponding C—O bond lengths (Pedersen, 1969).

**Sodium coordination.** The Na ion has six nearest neighbours in a distorted octahedral arrangement. The Na—O distances range from 2.336 (1) to 2.465 (1) Å and are of normal length. The O—Na—O angles range from 68 to 94°. These results compare well with corresponding distances and angles determined in sodium carbonate hydrogen peroxide crystals 2.33–2.51 Å and 78–100°. Stereoscopic views are given in Fig. 1.

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## Tetraphenylphosphonium-hexachlorowolfram(V) und die Fehlordnung in tetragonalen $E\text{Ph}_4^+$ -Salzen mit oktaedrischen Anionen

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**Abstract.**  $[\text{P}(\text{C}_6\text{H}_5)_4][\text{WCl}_6]$ ,  $M_r = 736.0$ , tetragonal,  $P4/n$ ,  $a = 12.958$  (3),  $c = 7.764$  (2) Å,  $V = 1303.7$  (8) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.875$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 48.8$  cm<sup>-1</sup>,  $F(000) = 710$ ,  $T = 293$  K,  $R = 0.029$  for 1329 unique observed reflexions. The structure corresponds to the  $[\text{AsPh}_4][\text{RuNCl}_4]$  structure type with octahedral  $\text{WCl}_6^-$  ions on the fourfold rotation axes. Unusual 'thermal' ellipsoids for five of the Cl atoms and a seemingly abnormal short Cl...Cl contact between ions can be explained by positional disorder of the  $\text{WCl}_6^-$  ion in a way such that one Cl atom is situated on the

fourfold axis but the rest of the ion is tilted away from it. Comparison with other isotopic compounds with octahedral anions shows this effect to be common for  $[\text{EPh}_4][\text{MX}_6]$  compounds.

**Einleitung.** In Tetraphenylphosphonium und -arsonium Salzen mit einem Kationen-zu-Anionen-Verhältnis von 1:1 sind die  $E\text{Ph}_4^+$ -Ionen meist zu parallel stehenden Säulen gestapelt (Müller, 1980;  $E = \text{P, As, ...}$ ). Die Hohlräume zwischen den Säulen eignen sich besonders gut zur Unterbringung von quadratisch-pyramidalen Anionen. Der entspre-