Interpretation of Infrared Spectra of Solid Alkali Metal Oxalates, their Hydrates and Perhydrates

BERIT F. PEDERSEN

Central Institute for Industrial Research, Blindern, Oslo 3, Norway

Infrared absorption spectra of the following compounds have been recorded from 650—4000 cm^{-1}: $Li_2C_2O_4$, $Li_2C_2O_4 \cdot H_2O_2$, $Na_2C_2O_4$, $Na_2C_2O_4 \cdot H_2O_2$, $Na_2C_2O_4 \cdot D_2O_2$, $K_2C_2O_4 \cdot H_2O$, $K_2C_2O_4 \cdot D_2O$, $K_2C_2O_4 \cdot H_2O_2$, $K_2C_2O_4 \cdot D_2O_2$, $Rb_2C_2O_4 \cdot H_2O$, $Rb_2C_2O_4 \cdot D_2O$, $Rb_2C_2O_4 \cdot H_2O_2$, $Rb_2C_2O_4 \cdot D_2O_2$, $Cs_2C_2O_4 \cdot H_2O$, and $Cs_2C_2O_4 \cdot H_2O_2$.

By intercomparison of the IR-spectra of the alkali metal oxalates, their hydrates and perhydrates, the different bands are interpreted in detail and ascribed to either the oxalate ion, the water molecule, or the hydrogen peroxide molecule.

The O—O stretch and the OH-bend bands of the H_2O_2 molecule have been observed in the spectra of potassium and rubidium oxalate monoperhydrates, where the H_2O_2 molecule is known to possess the skew conformation. In sodium oxalate monoperhydrate the H_2O_2-molecule is known to be *trans* planar, and these bands are not observed as expected. From the presence of these two bands in the spectrum of cesium oxalate monoperhydrate we predict that the H_2O_2 molecule is in the skew conformation in this compound, and from the absence of these bands in the spectrum of lithium oxalate monoperhydrate we predict the H_2O_2-molecule to possess the *trans* planar conformation in this compound.

The observed shifts of the OH stretching frequencies in the spectra of the different hydrates and perhydrates investigated indicate hydrogen bond lengths in good agreement with calculated values from the known crystal structures.

As a natural extension of a current study at this institute of the structural chemistry of alkalimetal oxalate monoperhydrates [1,2] by X-ray diffraction and NMR methods, we have recorded the infrared spectra of these and closely related compounds. Contrary to earlier IR-investigations of crystalline perhydrates, the obtained spectra consist of well resolved bands giving us a firm experimental basis.

The interpretation of infrared absorption spectra of solids in general is made complicated by the presence of lattice bands, and only few attempts have been made to characterize perhydrates by this technique. [3,4] However, the interpretation of the IR-spectra of the alkalimetal oxalate monoper-

hydrates is greatly simplified by the information we already have on the crystal structures of some of these and closely related compounds.

By intercomparison of the IR-spectra of the alkalimetal oxalates, their hydrates and perhydrates, we will show how it is possible to interpret the different bands in detail and ascribe them to either the oxalate ion, the water molecule, or the hydrogen peroxide molecule.

The H_2O_2 bands thus deduced will be shown to fit with the structural information we already have on the H_2O_2 molecule conformation and the length of the hydrogen bonds formed between the H_2O_2 molecule and the oxalate ion in the sodium-, the potassium-, and the rubidium oxalate mono-perhydrates. We are therefore encouraged to predict the conformation of the H_2O_2 molecule and the hydrogen bond lengths in the lithium- and the cesium-oxalate monoperhydrates from the observed H_2O_2-bands and their positions in the IR-spectra.

EXPERIMENTAL

Infrared absorption spectra of $Li_2C_2O_4$, $Li_2C_2O_4 \cdot H_2O_2$, $Na_2C_2O_4$, $Na_2C_2O_4 \cdot H_2O_2$, $Na_2C_2O_4 \cdot D_2O_2$, $K_2C_2O_4 \cdot H_2O$, $K_2C_2O_4 \cdot D_2O$, $K_2C_2O_4 \cdot H_2O_2$, $K_2C_2O_4 \cdot D_2O_2$, $Rb_2C_2O_4 \cdot H_2O$, $Rb_2C_2O_4 \cdot D_2O$, $Rb_2C_2O_4 \cdot H_2O_2$, $Rb_2C_2O_4 \cdot D_2O_2$, $Cs_2C_2O_4 \cdot H_2O$, and $Cs_2C_2O_4 \cdot H_2O_2$ have been recorded on a Perkin Elmer, Model 21 infrared spectrophotometer, equipped with NaCl optics.

The region from 650 cm⁻¹ to 4000 cm⁻¹ was examined, and the spectra obtained by the KBr disc technique were checked against nujol mull spectra. The deuterated samples were ground in nitrogen atmosphere to reduce the exchange of deuterium with protium. X-Ray diffraction powder patterns of all compounds were taken immediately before the
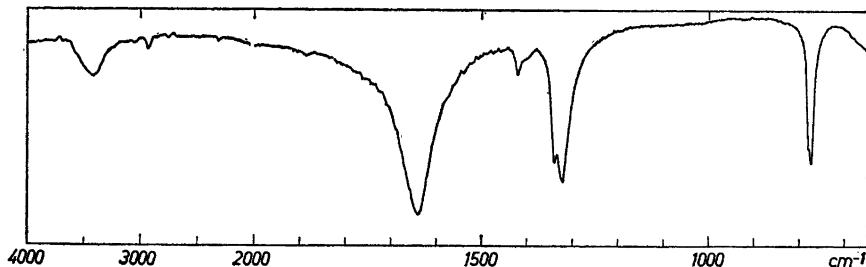

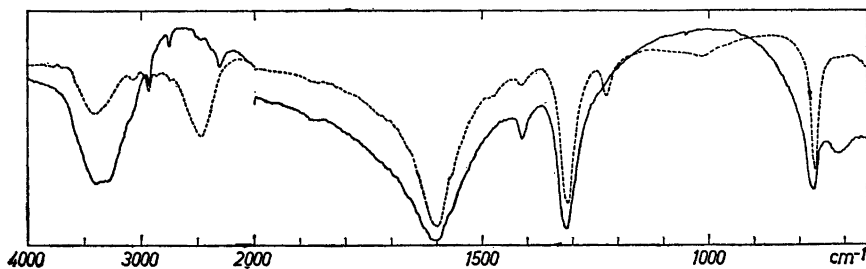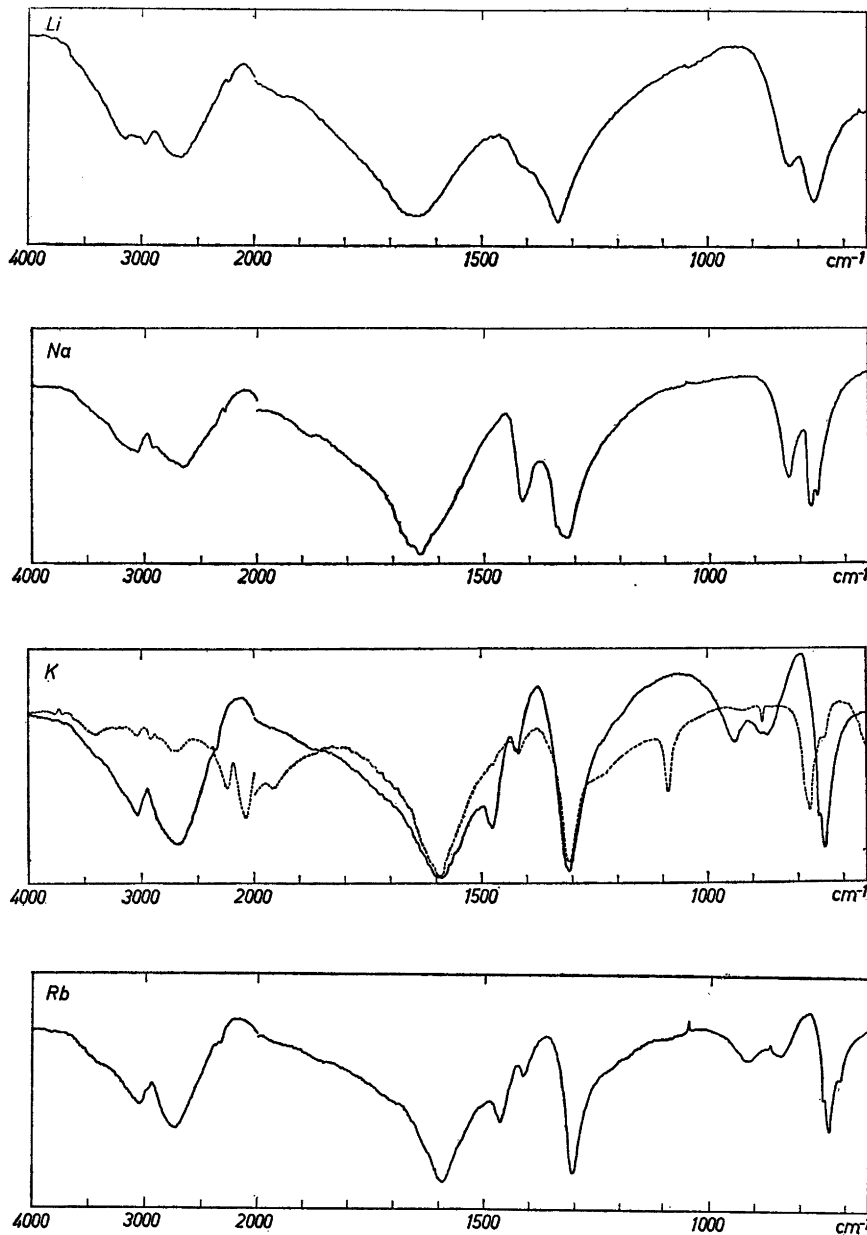*Fig. 1.* Infrared spectrum of sodium oxalate.

Fig. 2. Infrared spectrum of potassium oxalate monohydrate. - - - Infrared spectrum of potassium oxalate monodeuterate.

infrared absorption spectra were recorded, to ascertain that no decomposition of the compounds had taken place.

The frequencies observed are given in Tables 1—4, and the spectra are shown in Figs. 1—3.
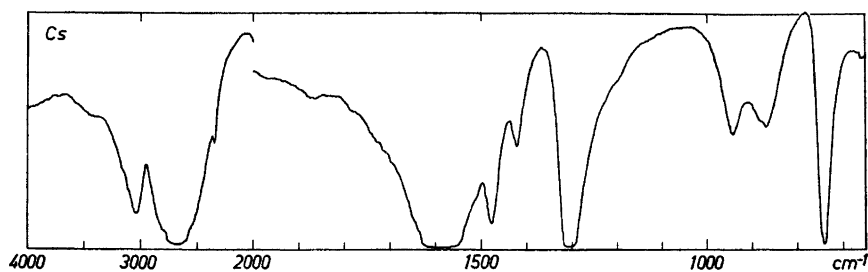
Fig. 3. Infrared spectra of the alkalimetal oxalate monoperhydrates. - - - Infrared spectrum of potassium oxalate perdeuterate.

ASSIGNMENT OF FREQUENCIES

1. Oxalate bands. X-Ray investigations of $Li_2C_2O_4$,[5] $Na_2C_2O_4$,[6] $Na_2C_2O_4 \cdot H_2O_2$,[1] $K_2C_2O_4 \cdot H_2O$,[7] $K_2C_2O_4 \cdot H_2O_2$,[2] $Rb_2C_2O_4 \cdot H_2O$,[8] and $Rb_2\ C_2O_4 \cdot H_2O_2$[2] have shown that the oxalate ion is planar and centrosymmetric in all these compounds. The two C—O distances are equal within the experimental uncertainty, and the O—C—C angles are approximately equal in all the compounds; hence the oxalate ion possesses (*mmm*) point group symmetry (V_h) or very nearly so.

Normal vibration calculations carried out by Schmeltz, Miyazawa, Mizushima, Lane, and Quagliano[9] and by Murata and Kawai,[10] give the following frequencies for the oxalate ion with this symmetry:

			Schmeltz *et al.* cm^{-1}	Murata *et al.* cm^{-1}
A_g (R)	ν_1	(O—C—O)	1407	1422
	ν_2	(C—C)	973	928
	ν_3	(O—C—O)	412	421
A_u	ν_4	C—C torsion	inactive	
B_{1g} (R)	ν_5	(O—C—O)	1595	1714
	ν_6	CO_2 rocking	432	550
B_{1u} (I)	ν_7	CO_2 wagging	—	
B_{2g} (R)	ν_8	CO_2 wagging	—	
B_{2u} (I)	ν_9	(O—C—O)	1544	1600
	ν_{10}	CO_2 rocking	222	295
B_{3u} (I)	ν_{11}	(O—C—O)	1335	1375
	ν_{12}	(O—C—O)	777	757

Very likely the compounds studied are ionic, and the only coupling that might destroy the oxalate ion symmetry is hydrogen bond formation in some of the compounds, whereby the centre of symmetry is retained, thus resulting in $2/m$ symmetry, (C_{2h}), but giving the same infrared active vibrational modes.

No hydrogen bonding occurs in $Li_2C_2O_4$ and $Na_2C_2O_4$, and therefore the pure oxalate ion frequencies are the only ones present in the spectra of these two salts. Table 1 shows that there are no bands above 1660 cm^{-1}. The strong

bands at 1658 and 1635 cm^{-1} are ν_9, the antisymmetric O—C—O stretching frequency, the strong bands at 1340, and 1325 cm^{-1} are ν_{11}, the symmetric O—C—O stretching frequency, and the strong bands at 775 and 770 cm^{-1} are ν_{12} the in plane O—C—O deformation frequency.

These three bands are strong absorption bands in all the compounds examined, and are found to lie between 1658—1587 cm^{-1}, 1340—1305 cm^{-1}, and 775—740 cm^{-1} in the different compounds.

According to calculations,[9],[10] these three frequencies should be the only active infrared frequencies observable in this region; however, from Tables 1—4 it can be seen that all the compounds studied show a weak band around 1400 cm^{-1}. This band was also observed by Schmeltz et al., but no interpretation was given. The data strongly suggest that also this band must be attributable to the oxalate ion. The oxalate ion has a strong Raman line at 1407 cm^{-1}, which may have become infrared active.

2. *Water bands.* By comparing the infrared spectra of the hydrate and the deuterate of potassium and rubidium oxalate, the —OH bands can be identified. The OH-stretching frequency at 3350—3400 cm^{-1} observed in the hydrates

Table 1. Observed frequencies for $Li_2C_2O_4$ and $Na_2C_2O_4$ in cm^{-1}.*

Assignment	$Li_2C_2O_4$	$Na_2C_2O_4$
ν_{12} ox	775 s	770 s
ν_{11} ox	1340 s	1325 s
ν_1 ox	1430 w	1420 w
ν_9 ox	1658 s	1635 s

* vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, ox = oxalate ion.

Table 2. Observed frequencies for the hydrates and deuterates of K, Rb, and Cs oxalates in cm^{-1}.

Assignment	$K_2C_2O_4 \cdot H_2O$	$K_2C_2O_4 \cdot D_2O$	$Rb_2C_2O_4 \cdot H_2O$	$Rb_2C_2O_4 \cdot D_2O$	$Cs_2C_2O_4 \cdot H_2O$
ν_{12} ox	712 m 770 s	765 s	710 s 763 s	762 s	740 sh 753 s 820 m 848 m
ν_2 D$_2$O		1225 m		1207 m	
ν_{11} ox	1315 s		1310 s		1307 s
ν_1 ox	1410 m	1413 w	1405 m	1412 w	1405 w-m
ν_9 ox	1605 vs	1600 s	1595 vs	1595 vs	1597 s
ν_3 D$_2$O		2470 s-m		2520 s	
ν_3 H$_2$O	3350 s		3400 vs		3410 s

Table 3. Observed frequencies for $Li_2C_2O_4\cdot H_2O_2$, $Na_2C_2O_4\cdot H_2O_2$, and $Na_2C_2O_4\cdot D_2O_2$ in cm⁻¹.

Assignment		$Li_2C_2O_4\cdot H_2O_2$	$Na_2C_2O_4\cdot H_2O_2$	$Na_2C_2O_4\cdot D_2O_2$
			760 sh	
ν_{12}	ox	765 s	775 s	775 s
$\nu_4 +$	ν_{Ry} H₂O₂	820 m	825 m	
ν_{11}	ox	1330 s	1320 s	1320 s
ν_1	ox	1410 vw	1415 m	1412 w
ν_9	ox	1645 s	1640 s	1645 s
ν_5	D₂O₂			2080 w
ν_5	H₂O₂	2670 m-s	2640 s	
	H₂O₂	2970 w		
	H₂O₂	3140 w	3060 m	

Table 4. Observed frequencies for the perhydrates and perdeuterates of K, Rb, and Cs oxalates in cm⁻¹.

Assignment	$K_2C_2O_4\cdot H_2O_2$	$K_2C_2O_4\cdot D_2O_2$	$Rb_2C_2O_4\cdot H_2O_2$	$Rb_2C_2O_4\cdot D_2O_2$	$Cs_2C_2O_4\cdot H_2O_2$
			715 sh		
$\nu_4+\nu_{Ry}$ D₂O₂		745 sh		745 sh	
ν_{12} ox	740 s	775 s	735 s	770 s	740 s
	755 sh		750 sh		
ν_{Rx} H₂O₂	870 w		850 w		870 w
ν_3 H₂O₂	880 w	880 w	880 w sh	880 w	880 w sh
$\nu_4+\nu_{Ry}$ H₂O₂	940 w		920 w		940 w
ν_2 D₂O₂		1090 m		1080 m	
ν_{11} ox	1310 s	1310 s	1305 s	1310 s	1305 s
ν_2 ox	1420 w	1420 w	1415 w	1415 w	1420 w
ν_3 H₂O₂	1475 m		1465 m		1475 m
ν_9 ox	1590 s	1595 vs	1590 s	1600 s	1587 s
ν_5 D₂O₂		2080 m		2100 m	
ν_5 H₂O₂	2680 s		2740 s		2680 s
D₂O₂		2240 m		2240 m	
H₂O₂	3040 m-s		3045 m-s		3040 m-s

is, according to expectations, shifted to lower frequencies by deuteration,[11] the fractional shift OH/OD being 1.36 for the potassium and 1.35 for the rubidium compound. The OD-bend bands are observed at 1225 and 1207 cm⁻¹ in the two compounds, which shows that the OH-bend frequencies in the hydrates must be masked by the oxalate bands at 1605—1595 cm⁻¹.

The bands at 710 and 712 cm⁻¹ in the hydrates are absent in the deuterates, and therefore must be shifted to frequency values below 650 cm⁻¹, hence this band must be caused by water molecule.

Boutin and Prask[12] have studied $K_2C_2O_4\cdot H_2O$ using inelastic scattering of low energy neutrons, and find that the neutron spectrum exhibits torsional peaks at 560, 624, and 736 cm⁻¹. The peak observed at 710—712 cm⁻¹ may therefore be assigned to a torsional frequency of the water molecule.

3. *Hydrogen peroxide bands*. Comparison of the infrared spectra of the perhydrates with the corresponding spectra of the anhydrous salts and the hydrates leads to the assumption that the frequencies given in Table 5 must be frequencies caused by the hydrogen peroxide molecule. The intramolecular hydrogen peroxide frequencies caused by the OH-groups can be identified by intercomparison of the perhydrate-spectra with those recorded for the perdeuterates.

Table 5.

$Li_2C_2O_4 \cdot H_2O_2$	$Na_2C_2O_4 \cdot H_2O_2$	$K_2C_2O_4 \cdot H_2O_2$	$Rb_2C_2O_4 \cdot H_2O_2$	$Cs_2C_2O_4 \cdot H_2O_2$
	760 sh.w			
820 m	825 m	870 w-m	850 w	870 m-w
		880	880	880
		940 m-w	920 w-m	940 m
		1475 s	1465 s	1475 s
2670 vs	2640 vs	2680 vs	2740 vs	2680 vs
2980	3060 s	3040 s	3045 s	3040 s
3140 m-s				

The frequencies at 2680 cm^{-1} and 3040 cm^{-1} are shifted to lower frequencies: 2080 cm^{-1} and 2240 cm^{-1} upon deuteration, and the band at 1475 cm^{-1} is shifted to 1090 cm^{-1}; the fractional shifts are accordingly of the magnitude to be expected for isotopic substitution.

The O—O stretching frequency for the hydrogen peroxide molecule is found to lie at 880 cm^{-1} by several authors.[13-18] This band is most clearly observed in the perdeuterates of potassium and rubidium, but is also present in the perhydrate spectra of potassium, rubidium, and cesium oxalates. The sodium and lithium salts, however, do not show the characteristic absorption line at 880 cm^{-1}.

The spectra of the perhydrates of the first three compounds show two additional absorption lines in this region at 870 cm^{-1} and 940 cm^{-1}, whereas the deuterates show one at 745 cm^{-1}, and possibly one in the region just below 650 cm^{-1}. These frequencies are of the order to be expected for intermolecular or lattice vibrations.[19,20]

Absorption lines in this region are difficult to assign with certainty, as the combination and interaction of the vibrational motions of the different entities building up the crystal has to be considered. However, these absorption lines can be accounted for by hindered translations and rotations of the hydrogen peroxide molecule in the compounds. The line at 940 cm^{-1} may be a combination of ν_4, the torsional oscillation and one of the low frequency librations ν_{Ry}, which is of the correct symmetry type. If these frequencies are taken from the work by Giguère and Chapados,[14] $\nu_4 = 690$ cm^{-1} for H_2O_2 and 511 cm^{-1} for D_2O_2, whereas $\nu_{Ry} = 259$ cm^{-1} for H_2O_2 and 244 cm^{-1} for D_2O_2, thus giving 949 cm^{-1} for H_2O_2 and 755 cm^{-1} for D_2O_2, and hence of the correct magnitude for the lines observed. The 870 cm^{-1} absorption line can be ac-

counted for by a high frequency libration ν_{R_x} about the minor axis of the molecule, which by the same authors are found to lie at 809 cm^{-1}.

The crystal structure of solid H_2O_2 and of the compounds considered in this study are different, however, and no immediate reason for corresponding torsional and librational vibrations can be given.

The 820 cm^{-1} and 825 cm^{-1} absorption lines observed in lithium and sodium oxalate monoperhydrates may also arise from hindered rotational and translational motions of the H_2O_2 molecule, and hence may be assigned to ν_4 coupled with a low frequency libration. If ν_{R_y} is estimated to be 250 cm^{-1}, it gives a torsional frequency of 575 cm^{-1}, which is lower than for the potassium, rubidium, and cesium salts, but this is not unexpected as the H_2O_2-molecular conformation is energetically different in the two kinds of compounds.

The three strong lines at 1475, 1465, and 1475 cm^{-1} observed in the K-, Rb, and Cs-compounds undoubtedly must be assigned to the ν_2-OH bending vibration, shifted somewhat to higher frequency than for an isolated molecule because of hydrogen bonding effects.[19] This frequency is absent in the spectra of the sodium and lithium compounds.

From Table 5 it is seen that two bands are observed in the OH-stretching region for all the perhydrates studied. The appearance of two bands in the spectra of all the compounds is difficult to understand, and the interpretation of these two bands spaced about 350 cm^{-1} is somewhat dubious.

However, the strongest frequency line observed at about 2650 cm^{-1} is interpreted as the ν_5-antisymmetric OH-stretching band, shifted to lower frequency than for an isolated molecule, by influence of the hydrogen bonding. A support for this interpretation are the derived hydrogen bond distances which are in accordance with X-ray diffraction experiments (*vide infra*).

The interpretation of the *other* band around 3050 cm^{-1} is uncertain. In solid H_2O_2 two bands with a frequency difference of 110 cm^{-1} are observed, and interpreted as the symmetric and antisymmetric OH-stretching frequencies.[13] However, in sodium oxalate monoperhydrate the H_2O_2-molecule is *trans*-planar, and the symmetric OH-stretching frequency is not expected to be infrared active, further the actual band has a fairly large intensity.

The OH-stretching frequency has in several investigations been found to broaden and split into several peaks by going from a gas to a solid phase.[20,22] This splitting is often explained as arising from coupling between spatially different —OH groups in the unit cell,[20] or from a double-minimum potential for the hydrogen atom along the O—O bond,[31] but none of these explanations seems adequate here.

DISCUSSION

We will now try to extract the structural information concealed in the IR spectra as interpreted in detail above. We will first discuss the conformation of the H_2O_2-molecule, and then the lengths of the hydrogen bonds formed by this molecule and the water molecule to the oxalate oxygens.

1. Conformation of the H_2O_2 molecule. It has been shown that the hydrogen peroxide molecule can give rise to two different infrared absorption spectra

depending on the conformation of the H_2O_2-molecule in the compound studied. On this basis the conformation of the H_2O_2-molecule in $Li_2C_2O_4 \cdot H_2O_2$ and $Cs_2C_2O_4 \cdot H_2O_2$ can be predicted.

The infrared spectrum of $Li_2C_2O_4 \cdot H_2O_2$ strongly indicates that the conformation of the H_2O_2-molecule in this compound is *trans* planar with a dihedral angle of 180°. We rest our conclusion on the similarity of the infrared spectra of sodium and lithium oxalate monoperhydrates, and on the difference between these two spectra and those obtained of the potassium and rubidium oxalate monoperhydrates, *i.e.* the frequencies about 880 cm^{-1} and 1470 cm^{-1}, which are the O—O stretching and the ν_2 OH-bending vibrations are absent in the spectra of the lithium and sodium compounds. These vibrations should be infrared inactive for the *trans* planar conformation of the H_2O_2-molecule.[23] X-ray crystal structure determination of $Na_2C_2O_4 \cdot H_2O_2$ have further shown that the H_2O_2-molecule possesses the *trans* planar conformation with a dihedral angle of 180° in this compound.

The spectrum of $Cs_2C_2O_4 \cdot H_2O_2$ on the other hand shows a close resemblance to the spectra of the potassium and the rubidium oxalate monoperhydrates, showing the characteristic O—O band at 880 cm^{-1} and the OH-bend band at 1475 cm^{-1}. The conformation of the hydrogen peroxide molecule in this compound must therefore be the same as the H_2O_2-molecule conformation in potassium and rubidium oxalate monoperhydrates and can not possess a centre of symmetry. We therefore conclude by stating that the conformation of the H_2O_2-molecule in this compound is the skew conformation. Crystal structure determination of potassium and rubidium oxalate monoperhydrates shows that the conformation of the hydrogen peroxide molecule in these two compounds is the skew conformation with a dihedral angle of approximately 103°.

2. Hydrogen bond lengths. Several authors [24-28] have correlated OH···O distances in hydrogen bonded crystals and the frequencies of infrared absorption bands attributed to the OH-stretching motions. Pimentel and Sederholm [27] in their paper present a plot of OH···O crystal distances, R vs. frequency shifts, $\Delta\nu$, of the stretching motions of the hydrogen bond. $\Delta\nu$ is defined as $\nu_O - \nu_H$, where ν_O is the OH-stretching frequency of the monomer observed in the gas phase or in dilute solution, and ν_H is the infrared OH-stretching frequency of the same molecule observed in the hydrogen bonded solid considered. These authors have found a linear relationship between $\Delta\nu$ and R, and the equation to the line of least mean square deviation from the experimental points is $\Delta\nu = 4.43 \times 10^3 \ (2.84 - R)$. $(\sigma\Delta\nu = 199 \ cm^{-1}.)$

Using this formula the hydrogen bond lengths in the different perhydrates and hydrates investigated here have been determined from their infrared spectra. The values derived are listed in Table 6, together with values obtained from X-ray diffraction studies. In this table are also included the corresponding values for $(NH_2)_2CO \cdot H_2O_2$, which is the only perhydrate structure determined earlier.[29]

The infrared spectrum of the compound published by Aida [4] gives an OH-stretching frequency of 2740 cm^{-1}. Redington, Olson, and Cross [30] have given the following observed OH-stretching frequencies for the hydrogen peroxide molecule: $\nu_1 = 3599 \ cm^{-1}$, $\nu_5 = 3608 \ cm^{-1}$. We have used the mean value

Table 6.

	ν_H	$\Delta\nu$	ΔR	$R_{IR}(\text{Å})$	R_{XR} (Å)
$Li_2C_2O_4 \cdot H_2O_2$	2670	934	0.21	2.63 ± 0.04	
$Na_2C_2O_4 \cdot H_2O_2$	2640	964	0.22	2.62	2.588 ± 0.006
$K_2C_2O_4 \cdot H_2O_2$	2680	924	0.21	2.63	2.591 ± 0.009
$Rb_2C_2O_4 \cdot H_2O_2$	2740	864	0.20	2.64	2.635 ± 0.012
$Cs_2C_2O_4 \cdot H_2O_2$	2680	924	0.21	2.63	—
$(NH_4)_2CO \cdot H_2O_2$	2740	864	0.20	2.64	2.63 ± 0.03
$Cs_2C_2O_4 \cdot H_2O$	3410	340	0.08	2.76	—
$K_2C_2O_4 \cdot H_2O$	3350	400	0.09	2.75	2.746 ± 0.011
$Rb_2C_2O_4 \cdot H_2O$	3400	350	0.08	2.76	2.785 ± 0.019

3604 cm^{-1} as ν_0 for the hydrogen peroxide molecule and 3750 cm^{-1} for the water molecule.

Table 6 shows that the hydrogen bond lengths derived from the infrared spectra are equal to the values determined from X-ray structure analyses within the standard deviations given for the use of the empirical formula. Accordingly the formula can be used for estimating hydrogen bond distances involving the hydrogen peroxide molecule as well as the water molecule.

All the hydrogen bond lengths involving the hydrogen peroxide molecule are found to be fairly equal and relatively short, 2.59—2.63 Å, compared to the hydrogen bonds in the corresponding hydrates, 2.75—2.78 Å. On the basis of this calculation we estimate the lengths of the hydrogen bonds in lithium and cesium oxalate monoperhydrates to be of the order of 2.60 Å.

REFERENCES

1. Pedersen, B. F. and Pedersen, B. *Acta Chem. Scand.* **18** (1964) 1454.
2. Pedersen, B. F. *Acta Chem. Scand.* **21** (1967) 779.
3. Vannerberg, N. G. *Arkiv Kemi* **14** (1959) 107.
4. Aida, K. *J. Inorg. Nucl. Chem.* **25** (1963) 165.
5. Beagley, B. and Small, R. W. H. *Acta Cryst.* **17** (1964) 783.
6. Jeffrey, G. A. and Parry, G. S. *J. Am. Chem. Soc.* **76** (1954) 5283.
7. Pedersen, B. F. *Acta Chem. Scand.* **18** (1964) 1635.
8. Pedersen, B. F. *Acta Chem. Scand.* **19** (1965) 1815.
9. Schmeltz, M. J., Miyazawa, T., Mizushima, S., Lane, T. J. and Quagliano, J. V. *Spectrochim. Acta* **9** (1957) 51.
10. Murata, H. and Kawai, K. *J. Chem. Phys.* **25** (1956) 589.
11. Herzberg, G. *Molecular Spectra and Molecular Structure,* Vol. 2. Van Nostrand, New York 1962.
12. Boutin, H. and Prask, H. J. *Bull. Am. Phys. Soc.* **10** (1965) 687.
13. Giguère, P. A. and Harvey, K. B. *J. Mol. Spectry.* **3** (1959) 36.
14. Giguère, P. A. and Chapados, C. *Spectrochim. Acta* **22** (1966) 1131.

15. Miller, R. L. and Hornig, D. F. *J. Chem. Phys.* **35** (1961) 265.
16. Simon, A. and Kriegsmann, H. *Naturwiss.* **42** (1955) 12.
17. Taylor, R. C. *J. Chem. Phys.* **18** (1950) 898.
18. Bain, O. and Giguère, P. A. *Can. J. Chem.* **33** (1955) 527.
19. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*, Freeman, San Francisco 1960.
20. Mitra, S. S. *Solid State Phys.* **13** (1962) 7.
21. Hunt, R. H., Leacock, R. A., Peters, C. W. and Hecht, K. T. *J. Chem. Phys.* **42** (1965) 1931.
22. Shephard, N. In Hadži, D. *Hydrogen Bonding*, Pergamon, London 1959.
23. Ebsworth, E. A. V. In Davies, M. *Infrared Spectroscopy and Molecular Structure*, Elsevier, London 1963.
24. Rundle, R. E. and Parasol, M. *J. Chem. Phys.* **20** (1952) 1487.
25. Lord, R. C. and Merrifield, R. E. *J. Chem. Phys.* **21** (1953) 166.
26. Lippincott, E. R. and Scroeder, R. *J. Chem. Phys.* **23** (1955) 1131.
27. Pimentel, G. C. and Sederholm, C. H. *J. Chem. Phys.* **24** (1956) 639.
28. Nakamoto, K., Margoshes, M. and Rundle, R. E. *J. Am. Chem. Soc.* **77** (1955) 6480.
29. Lu, C. S., Hughes, E. W. and Giguère, P. A. *J. Am. Chem. Soc.* **63** (1941) 1507.
30. Redington, R. L., Olson, W. B. and Cross, P. C. *J. Chem. Phys.* **36** (1962) 1311.
31. Schwarzmann, E. and Marsmann, H. *Naturwiss.* **53** (1966) 349.