

# INFRARED SPECTRA OF SALICYLALDEHYDE COMPLEXES OF SOME ALKALI METALS

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## ABSTRACT

The alkali metal chelates of salicylaldehyde have been prepared and their infrared spectra obtained. The spectra indicate strong bonding between the metal and hydroxy oxygen and only weak co-ordination of the metal to the carbonyl oxygen. For the lithium complexes two M-O stretching frequencies have been observed at about  $590\text{ cm.}^{-1}$  and  $490\text{ cm.}^{-1}$ . The infrared spectra of the complexes have also given indirect evidence towards assignment of the C-OH and aldehydic C-H stretching frequencies.

## INTRODUCTION

ALKALI metals are known to form chelates which are soluble in organic solvents, with salicylaldehyde and methyl salicylate.<sup>1-4</sup> Bis-salicylaldehyde chelates are known for lithium, sodium and potassium and for lithium, hydrated chelates are known with salicylaldehyde and methyl salicylate. In these compounds, it is postulated<sup>5</sup> that the metallion is co-ordinated to four oxygens tetrahedrally. Only limited information is available on the infrared spectra of these compounds. Yamada<sup>6</sup> studied the infrared spectra of sodium complexes of salicylaldehyde and methyl salicylate in the NaCl region. Data on the infrared spectra of the lithium complexes are not available. The infrared spectra of the salicylaldehyde complexes and their deuterio analogues were therefore studied to get information on the structure and the type of bonding, and to determine the extent of co-ordination. Results of these studies are presented in this paper.

## EXPERIMENTAL

The hydrated compounds were prepared by the addition of the required amount of salicylaldehyde to the hydroxide solution. The precipitated complex was purified by recrystallisation from hot alcohol.

Bis-lithium salicylaldehyde was obtained by adding pure, anhydrous lithium hydroxide powder to excess salicylaldehyde and warming over a water-bath. The pale yellow complex was then crystallised from hot salicylaldehyde, washed with cold ether and dried in vacuum. The sodium and potassium compounds were prepared by the addition of the corresponding alcoholate to a cold solution of salicylaldehyde in absolute alcohol. The solid obtained was crystallised from alcohol and dried in vacuum.

The deuterio compounds of lithium were prepared using LiOD and CHO. C<sub>6</sub>H<sub>4</sub>. OD.

The lithium compounds were analysed by converting them to sulphate and taking their weight. The sodium and potassium compounds were analysed by titration against standard hydrochloric acid.

Infrared spectra were obtained with paraffin and fluorolube mulls. A Perkin-Elmer Model-21 spectrophotometer fitted with CaF<sub>2</sub>, LiF, NaCl, KBr and CsBr prisms was employed to obtain the spectra from 4000 cm.<sup>-1</sup> to 300 cm.<sup>-1</sup>

## RESULTS AND DISCUSSION

The spectra of salicylaldehyde and the complexes in the region 1750 cm.<sup>-1</sup> to 1500 cm.<sup>-1</sup> are shown in Fig. 1. It is seen from the spectra that the C=O stretching absorption at about 1668 cm.<sup>-1</sup>, though not shifted much on chelation, shows an increase from 1668 cm.<sup>-1</sup> to 1672 cm.<sup>-1</sup>, 1682 cm.<sup>-1</sup> and 1693 cm.<sup>-1</sup> for the lithium, sodium and potassium compounds respectively. The lower C=O frequency of salicylaldehyde is due to the strong intramolecular hydrogen bonding in the molecule, and on removal of the hydrogen bond in the chelates the C=O frequency increases.

The frequency of the C=O stretch in 'free' aromatic aldehydes<sup>7</sup> is about 1707 cm.<sup>-1</sup> and if we compare the C=O frequencies in the chelates with this value, it is seen that the extent of co-ordination decreases from lithium to potassium. The strength of the M←O=C bond is in the order H, Li, Na and K.

A strong band is observed at about 1540 cm.<sup>-1</sup> in all the complexes. Assignment of this band at present is not quite clear, though Yamada<sup>6</sup> assigned it as a ring vibration, for sodium methyl salicylate. The same assignment may hold in this case, since aromatic ring vibrations appear in this region.

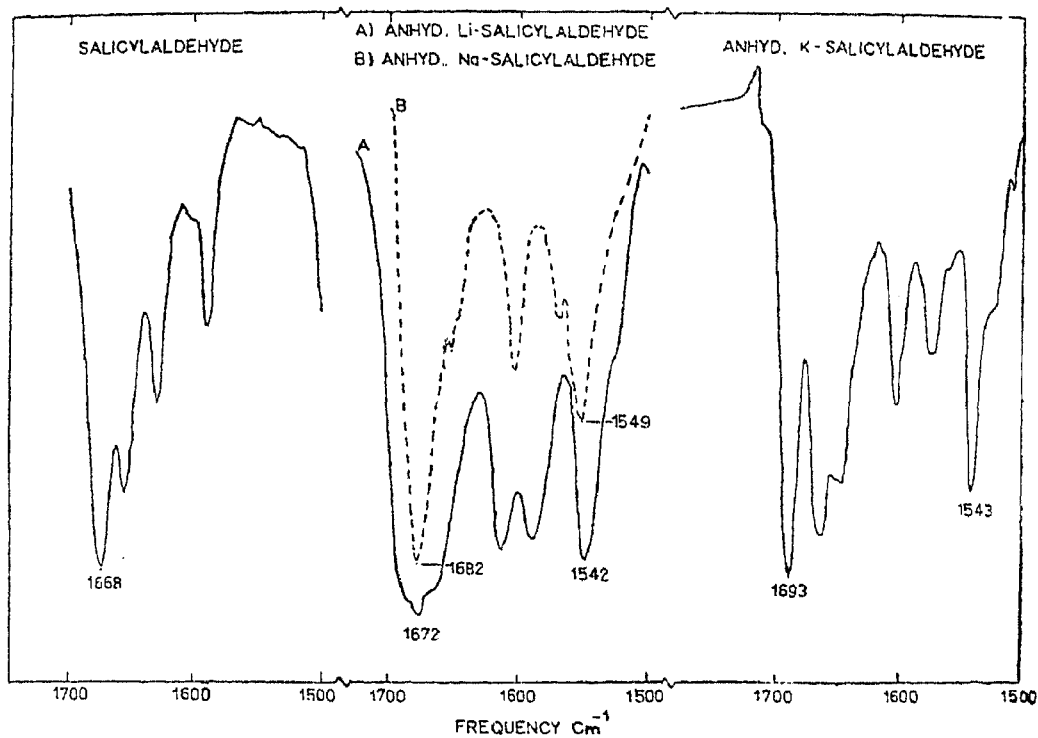


FIG. 1

The spectra of the complexes give an indication of the C-O frequency in salicylaldehyde. This is clear from Fig. 2, where the absorption

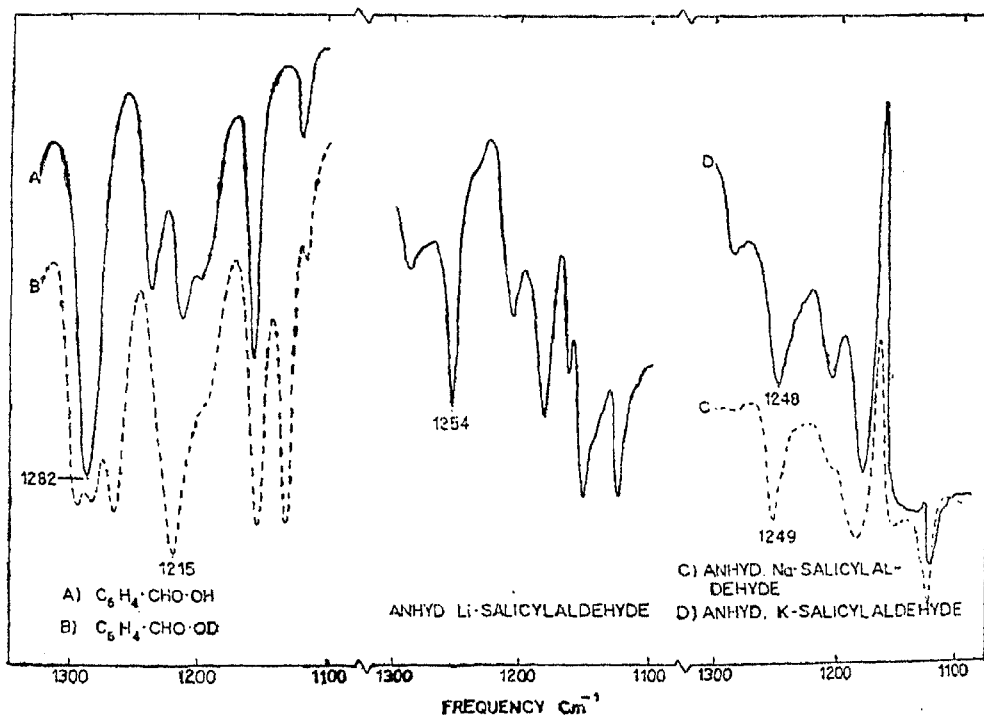


FIG. 2

bands in the region  $1325-1100\text{ cm.}^{-1}$  are shown. The strong band at  $1282\text{ cm.}^{-1}$  in salicylaldehyde is absent in the complexes indicating that this may be the C—OH stretch. This is confirmed from the spectra of salicylaldehyde-OD, where a band of corresponding intensity appears at  $1215\text{ cm.}^{-1}$ . In the complexes the corresponding band may be assigned to the strong band at about  $1250\text{ cm.}^{-1}$  indicating considerable bonding between the metal and C—O.

If we consider the four oxygens co-ordinated to the metal as equivalent, the  $(\text{MO}_4)$  group will have  $T_d$  symmetry and only one M—O stretching frequency will be observed in the infrared. But it is evident that at least for the hydrated compounds this is not likely and we should observe more than one M—O stretching frequency. For lithium the corresponding bands may occur in the region of  $700-500\text{ cm.}^{-1}$ , [while for the other complexes at still lower frequencies. The spectra for the region  $600-500\text{ cm.}^{-1}$  is shown in Fig. 3 for the lithium complex. It is seen that at least two new bands are observed for all the four lithium salicylaldehyde complexes one

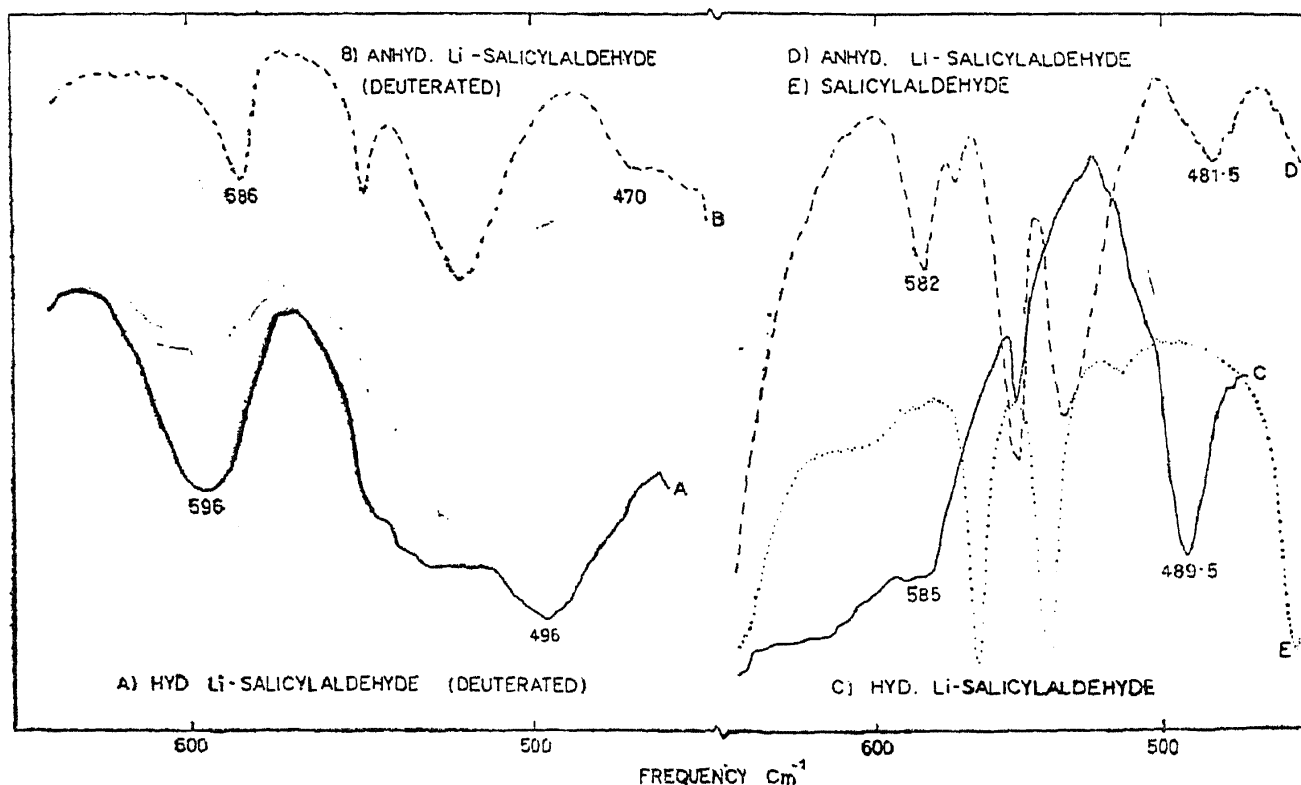


FIG. 3

at about  $590\text{ cm.}^{-1}$  and the other at about  $490\text{ cm.}^{-1}$ . These two bands can, therefore, be reasonably assigned to the metal-oxygen stretching modes.

The present studies show another interesting observation. It is well known that salicylaldehyde shows two bands in the aldehydic C—H stretching region. The high-frequency band in this case is fairly intense, while

the low-frequency band is comparatively weak. There is some uncertainty about which of these should be assigned to the aldehydic C—H stretch. In the series of complexes, it is seen that the weaker low-frequency band increases in intensity, as we proceed from salicylaldehyde to lithium, sodium and potassium compounds. This is shown in Fig. 4. If the low-frequency band is a combination, it is unlikely that its intensity should increase systematically in the series, especially when no such increase is observed for any other bands in the lower frequency range. This can, therefore, be regarded as an indirect evidence for the assignment of the low-frequency band as aldehydic C—H stretching mode. The regular increase in intensity of this band with increase in the C—O frequency is not well understood.

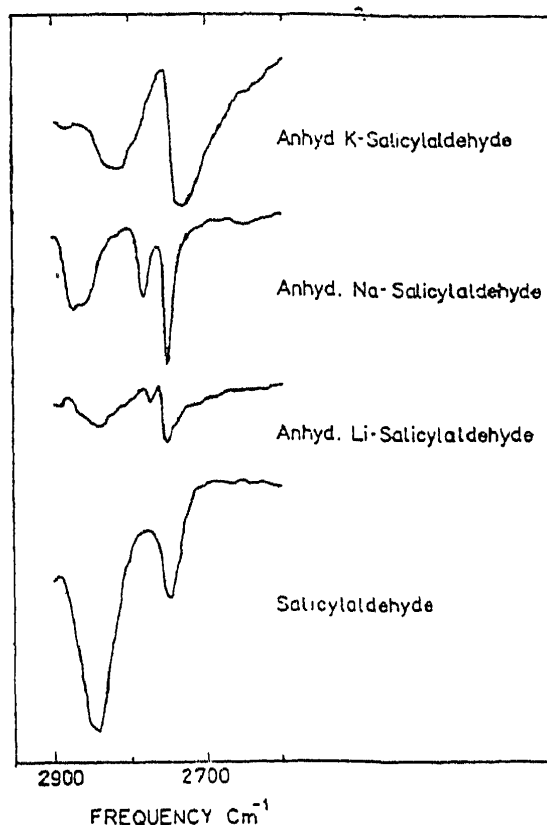


FIG. 4

#### ACKNOWLEDGEMENT

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