

MONOHYDRATES OF COBALT AND MANGANESE HYDROGENARSENATES -
A PAIR OF NON-ISOMORPHOUS COMPOUNDS WITH SIMILAR
INFRARED SPECTRA

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ABSTRACT

The infrared spectra of the monohydrates of cobalt and manganese hydrogenarsenates are similar, although the two compounds are not isomorphous (whereas the former is triclinic, the latter has at least monoclinic symmetry). Three, instead of the expected four, bands are found in the OH bending region of the spectrum of cobalt hydrogenarsenate monohydrate, probably because of accidental degeneracy resulting from the similar strength of the hydrogen bonds formed by two of the acidic protons.

INTRODUCTION

Among the members of the series of compounds with the general formula $MHASO_4 \cdot H_2O$ ($M = Co, Mn, Zn$ and Cd) only the structure of the cobalt compound has been determined by crystallographic methods [1] and the vibrational spectra have not received much attention either (In Ref. 1 the infrared spectrum of $CoHASO_4 \cdot H_2O$ is only presented and very briefly discussed).

It was found [1] that $CoHASO_4 \cdot H_2O$ crystallizes in the triclinic system (space group $P\bar{1}$, $Z = 8$). Since the space group is centrosymmetric, four crystallographically non-equivalent hydrogenarsenate ions and four different types of water molecules are present in the unit cell. Group theory shows that under such circumstances each vibrational mode of the polyatomic units is expected to give rise to four infrared and four Raman active components (of A_u and A_g symmetry respectively). As will be seen, the spectral picture does not conform entirely with these predictions, the number of observed bands being less than the expected one.

EXPERIMENTAL

The compounds were prepared as described in the literature [1], the recorded infrared spectrum of the cobalt compound being identical with that reported in Ref. 1. The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer at room and liquid-nitrogen temperature (RT and LNT). The powder X-ray diffractograms were obtained on a JEOL diffractometer.

RESULTS AND DISCUSSION

The infrared spectra of $\text{CoHAsO}_4 \cdot \text{H}_2\text{O}$ recorded at RT and LNT are compared in Fig. 1. Although rather rich in bands, the infrared spectra are not, as seen, exceedingly complex in appearance and the Raman spectrum (Fig. 2) is even simpler.

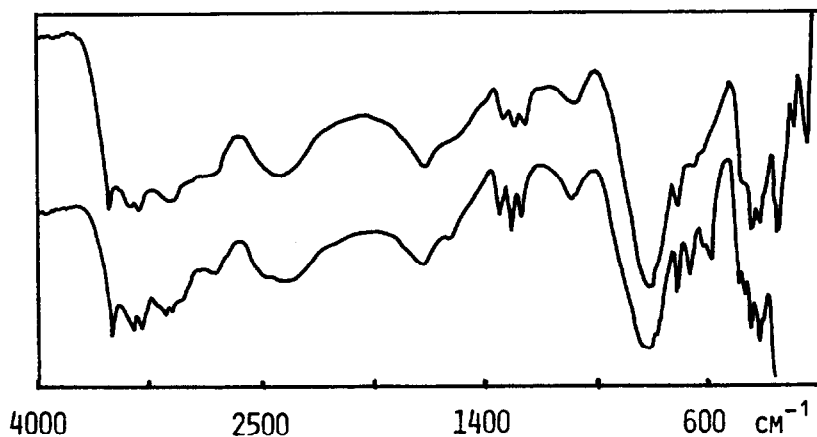


Fig. 1. Infrared (RT and LNT) spectra of $\text{CoHAsO}_4 \cdot \text{H}_2\text{O}$

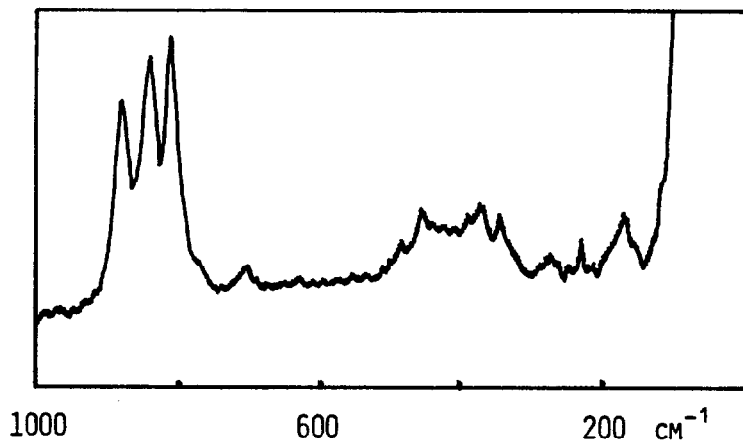


Fig. 2. Raman spectrum of $\text{CoHAsO}_4 \cdot \text{H}_2\text{O}$

Particularly noteworthy is the appearance of only three bands (the middle one being appreciably stronger than those flanking it) in the region where the OH in-plane bending modes of the hydrogenarsenate ions are expected to appear i.e. in the region around 1300 cm^{-1} although, as pointed out earlier, four bands would have been expected. No further splitting is observed even at LNT. Such a picture is even less expected if one considers the fact that the four HAsO_4 ions fall into two classes - two of them,

as far as the OH groups are concerned, act only as proton-donors, whereas in the other two the hydroxylic oxygen is, in addition to that, also an acceptor of a proton from a neighbouring water molecule.

Since two of the hydrogen bonds formed by the acidic protons - those belonging to the hydrogenarsenate ions with As(2) and As(3) - have nearly the same length [1], the assignment would be simplified if the strength of the hydrogen bonds formed by the acidic hydrogen (all of them are quite strong, the O...O distances ranging from 252.3 to 256.5 pm) is taken to be the major frequency-determining factor. The three OH bending bands would then be attributed, in order of decreasing frequencies, to hydrogenarsenate ions containing As(1) (the hydroxylic proton of this ion forms the strongest hydrogen bond); As(2) and As(3) (the bands of the latter two being, apparently, accidentally degenerate as a result of the closeness of the hydrogen bond lengths) and, finally, As(4) (the proton of this one taking part in the least strong of the hydrogen bonds and, hence, giving rise to a band with lowest frequency). As mentioned before, however, the whole neighbourhood of the hydroxylic oxygens of the HAsO_4 ions is different and the hydrogenarsenate anions containing As(2) and As(3) fall each in a different category as far as their environment is concerned.

Of the bands in the OH stretching region the one with highest frequency certainly belongs to almost uncoupled OH vibrations of the water molecules O(3) for which the difference between the two hydrogen bond lengths is largest (the $\text{O}_w\text{...O}$ distances being 268.1 and 300.9 pm). This is confirmed also by the behaviour of this band on increasing the deuterium content in the members of the series of partially deuterated compounds (Fig. 3). Less certain is

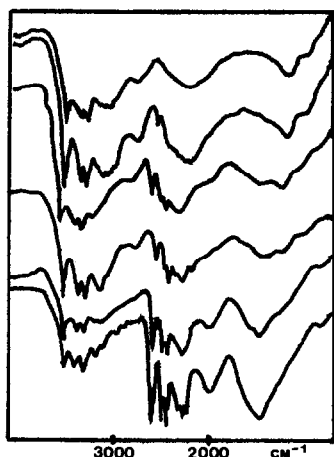


Fig. 3. The OH/OD stretching region in the IR spectra of $\text{CoHASO}_4 \cdot \text{H}_2\text{O}$ and partially deuterated analogues

the precise assignment of the bands in the middle of the complex high-frequency feature (although, undoubtedly, they all are due to water vibrations), whereas the broad bands below 2900 cm^{-1} are certainly related to OH stretches of the acidic hydrogens. Similar bands are, namely, found in many hydrogenarsenates, hydrogenphosphates and similar compounds (see, for example, [2] and references given therein).

As seen in Fig. 4, the infrared spectrum of the manganese compound is quite similar to that of the cobalt one (the Raman spectra are also very much alike) and it would have been easy to conclude that these two monohydrates are isomorphous were it not for the pronounced differences in their X-ray powder diffracti-

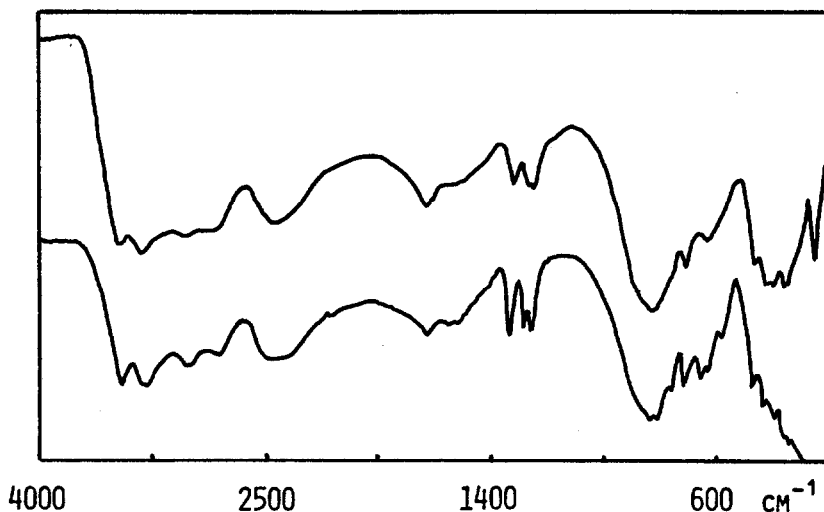


Fig. 4. Infrared spectra (RT and LNT) of $\text{MnHASO}_4 \cdot \text{H}_2\text{O}$

on patterns and the available preliminary crystallographic data which show [3] that the manganese compound is at least monoclinic (and perhaps with higher symmetry, but not triclinic), so that no strict isomorphism is possible. It is quite likely that the similarity of the infrared spectra implies that the basic structural patterns in the two compounds are similar, despite their non-isomorphism, although, as this work has attempted to demonstrate, it may be dangerous to make far-reaching conclusions on the basis of the similarity of the vibrational spectra alone.

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