

### SPECTROSCOPIC STUDIES OF SALTS OF 4-METHYLBENZENESULFONIC ACID III. THE SPECTRUM OF WATER IN THE HEXAHYDRATE OF COPPER(II) 4-METHYLBENZENESULFONATE

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The appearance of the bands in the O-H and O-D stretching region of the spectra of the title compound and in that of its slightly deuterated analogue indicates a larger spread of the H-bond strengths in the structure of this compound than in that of its cobalt analogue. The numerical values of the  $O_w \cdots O$  distances are not appropriate indicators for the hydrogen-bond strengths. The bands due to water librations were located on the basis of their temperature sensitivity and shift on deuteration.

#### 1. INTRODUCTION

As a part of our spectroscopic studies of salts of 4-methylbenzenesulfonic (or, alternatively, *p*-toluenesulfonic) acid [1-3], we now report the infrared spectra of protiated  $Cu(pTS)_2 \cdot 6H_2O$  and of a series of its partially deuterated analogues (the abbreviation *pTS* stands for the *p*-toluenesulfonate anion).

The title compound crystallizes in the space group  $P2_1/c$ , with two formula units in the unit cell [4]. Each copper(2+) ion in the structure is coordinated with six oxygen atoms from water molecules which form an elongated octahedron.

Three non-equivalent types of trigonally coordinated water molecules exist. Each water molecule forms one stronger and one weaker hydrogen bond. The  $O_w \cdots O$  distances range

from 271.42 to 274.7 pm for the stronger and from 276.70 to 278.90 pm for the weaker bands. It should be borne in mind, however, that five of the six hydrogen bonds involve sulfonate oxygens as proton acceptors and since the negative charge of the anion is, by all means, localized mainly in the  $SO_3$  group, the electron density around the sulfonate oxygens must be higher than that at the water oxygen serving as a proton-acceptor. The two shortest  $O_w \cdots O$  contacts involve, simultaneously, the sulfonate oxygens denoted O(1).

To the best of our knowledge, the only published infrared data for  $Cu(pTS)_2 \cdot 6H_2O$  are those by Laugfeld-erová *et al.* [5]. This work, however, has a rather limited scope and is mainly concerned with the assignment of the bands originating from the  $SO_3$  and *some* of the water modes.

## 2. EXPERIMENTAL

The studied compound was prepared by dissolving copper carbonate in aqueous ( $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  or mixtures of the two) solution of *p*-toluenesulfonic acid. The product was recrystallized several times from water.

The infrared spectra were recorded, at room and liquid-nitrogen temperatures (RT and LNT respectively) and at intermediate temperatures, on Perkin-Elmer 580 and Perkin-Elmer 1720 FT IR spectrophotometers, using KBr pellets, Nujol and fluorolube mulls.

## 3. RESULTS AND DISCUSSION

In agreement with the crystallographic results [4], a complex feature with several resolved maxima is observed in the O-H stretching region of the spectra of copper(II) 4-methylbenzenesulfonate hexahydrate (Fig. 1 a). The half-width of this feature is close to  $400\text{ cm}^{-1}$  whereas in the spectrum of the isomorphous cobalt analogue the half-width of the corresponding complex band does not exceed  $200\text{--}300\text{ cm}^{-1}$ . The overall appearance of the bands in the O-H stretching region therefore indicates a larger spread of the H-bond strengths and, on the average, stronger hydrogen bonds in the structure of the copper compound than in that of its cobalt analogue (the centroid of the complex feature in the spectrum of  $\text{Cu}(\text{pTS})_2 \cdot 6\text{H}_2\text{O}$  lies lower than that in the spectrum of hexaaquacobalt(II) 4-methylbenzenesulfonate). This finding is in accord with the crystallographically determined  $\text{O}_w \cdots \text{O}$  distances in the two cases [4,7]. It should be noted that this is not the only such in-

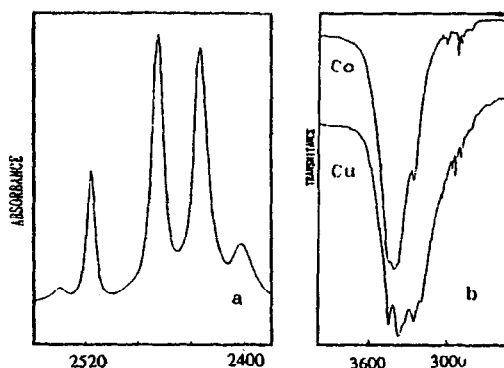


Fig. 1. Comparison of the O-H stretching region in the spectra of  $\text{Cu}(\text{pTS})_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{pTS})_2 \cdot 6\text{H}_2\text{O}$  (a) and the O-D stretching region in the spectrum of slightly deuterated  $\text{Cu}(\text{pTS})_2 \cdot 6\text{H}_2\text{O}$  (b)

stance where a larger spread of the H-bond distances is found in copper compounds than in their isomorphous counterparts containing other  $\text{M}^{2+}$  ions. Such is the case with the Tutton's salts [8] for example where a static Jahn-Teller effect was assumed to be operative.

Even if direct crystallographic data were not available, the observations made above could give a qualitative estimate of the strength of the hydrogen bonds and their distribution in the structure of the title compound compared with that of  $\text{Co}(\text{pTS})_2 \cdot 6\text{H}_2\text{O}$ .

In order to have a clearer insight into the true spectral picture in the O-D stretching region, a difference spectrum was obtained by subtracting the appropriately scaled spectrum of the protiated compound from that of the sample with low deuterium content (Fig. 1 b). As seen, four bands of unequal intensity are found in the  $2560\text{--}2300\text{ cm}^{-1}$  region whereas, as mentioned, six crystallographically non-equivalent protons exist in the structure.

In view of the different intensity of the bands, their number is not entirely surprising and suggests the existence of two pairs of structurally very similar hydrons (in addition to those involved in the formation of one considerably weaker and one stronger hydrogen bond).

Keeping in mind what has been said during the discussion of the crystal structure, it is reasonable to assume that the *weakest* hydrogen bond is that formed between the water oxygen O(4) as a proton donor and the water oxygen O(5) as a proton acceptor, despite the fact that the O(4)-H...O(5) distance is somewhat *shorter* than the distances between O<sub>w</sub>(4) and O<sub>w</sub>(6) on the one hand and the sulfonate oxygens O(3) on the other (the two latter distances are both close to 278 pm). In such a way the appearance of the bands at 2510 and 2464 cm<sup>-1</sup> would be taken into account.

It is more difficult to explain the origin of the unequally intense bands at 2433 and 2402 cm<sup>-1</sup>. If the crystallographic data are taken at face value, then close together are the *shortest* two among the existing O<sub>w</sub>...O contacts, whereas the intensity of the band at 2402 cm<sup>-1</sup> is only half of that characterizing the 2433 cm<sup>-1</sup> band. As mentioned above, however, the two shortest contacts are with the *same* oxygen atom and we submit that these two bonds are somewhat *weaker* than the bond corresponding to the O<sub>w</sub>(4)...O(2) contact, the *shorter* O<sub>w</sub>...O contact notwithstanding.

If the interpretation outlined above is correct and if the crystal structure is considered as reliably solved, then the conclusion which fol-

lows is that the O...O distances are not a proper measure of the hydrogen-bond strength. Of course, this is known, but often forgotten.

Only two δ(HOH) bands could be found (around 1663 and 1648 cm<sup>-1</sup>) in the LNT spectrum of the protiated compound with the higher-frequency component being somewhat broader. In the spectra of the partially deuterated analogues these bands disappear and at lower frequencies δ(HDO) and δ(DOD) bands are found instead (Fig. 2).

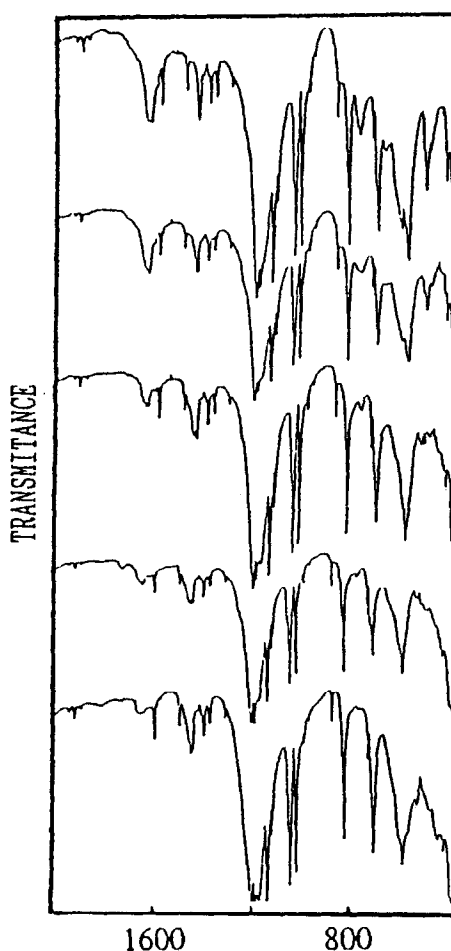


Fig. 2. The effect of deuteration on the medium and low-frequency bands

Using their temperature dependence as a guide [6], the bands at 765, 660, 589, 483 and 464  $\text{cm}^{-1}$  (cf. Fig. 3) may be assigned to water librations and other such bands are probably hidden under the *p*-toluenesulfonate ones and the assignment is confirmed by the analysis of the spectra of the partially deuterated analogues (Fig. 2).

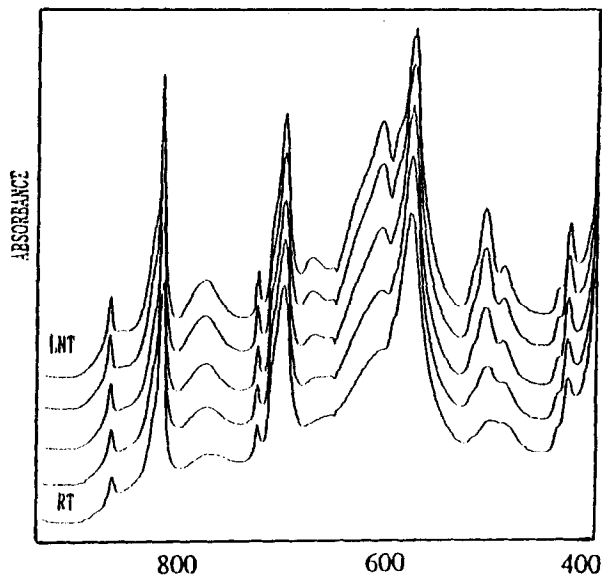


Fig. 3. The effect of the temperature lowering on the bands in the low-frequency region

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