

## INFRARED SPECTRA OF THE MONOHYDRATES OF TETRAAMMINECOPPER(II) TETRAFLUOROBERYLLATE AND TETRAAMMINECOPPER(II) SULFATE

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The similarities between the infrared spectra of the two title compounds indicate that structural similarities exist as well.

It is known that sulfate and tetrafluoroberyllate compounds of a given type could be isomorphous. However, the two title compounds which are of the same overall composition and crystallize in the same, orthorhombic, system [1-3] can not be strictly isomorphous since the unit cell of the tetrafluoroberyllate compound is, according to Tedenac *et al.* [2,3], approximately four times that of the sulfate and, correspondingly, the number of formula units in the unit cell is also four times larger (16 and 4 respectively).

A parallel study of the infrared spectra of these compounds was nevertheless undertaken hoping that the structural differences between them are not large. Namely, if this is indeed so, then from a spectroscopic point of view this pair is quite suitable for such a study since the bands due to the anion vibrations fall into quite different spectral regions (for example, the very strong bands originating from the antisymmetric stretches of the two anions absorb around 1100 and 800  $\text{cm}^{-1}$  respectively). This, on the other hand, means that the bands due to the vibrations of the remaining structural units (water and ammonia molecules) could be detected even if they overlap with those originating from vibrations of one of the two anions.

## EXPERIMENTAL

The investigated compounds were prepared by adding an excess of aqueous ammonia to an aqueous solution of copper(II) sulfate or copper(II) tetrafluoroberyllate respectively (the latter prepared from copper carbonate, beryllium fluoride and hydrofluoric acid) and letting the resulting solutions to crystallize slowly. The solution of the deuterated analogues were prepared by recrystallization from deuterium oxide or  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures.

The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer of sodium chloride pellets. A parallel study of such discs and of mulls in Nujol and hexachlorobutadiene, namely, showed no detectable differences between the two sets of spectra. The more common method of recording spectra of KBr discs was found to be inapplicable since the samples reacted with the matrix.

## RESULTS AND DISCUSSION

The spectra of tetraamminecopper(II) sulfate monohydrate, recorded at room temperature (RT) and liquid-nitrogen temperature (LNT) are shown in Fig. 1a, whereas the corresponding spectra of the analogous tetrafluoroberyllate compound are given in Fig. 1b. The similarity between the spectra of the

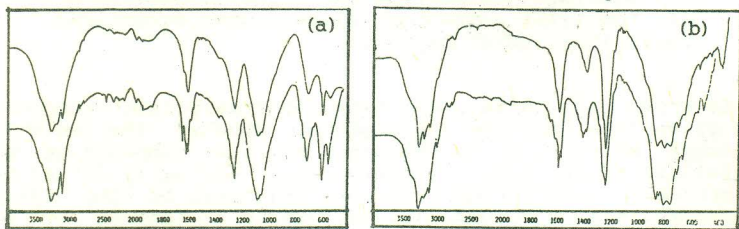


Fig. 1. RT and LNT infrared spectra of tetraamminecopper(II) sulfate monohydrate (a) and tetraamminecopper(II) tetrafluoroberyllate monohydrate (b)

two compounds, both in the X-H stretching region and in the region of water and ammonia bending vibrations, is apparent immediately. As seen in Fig. 2, the resemblance persists in the

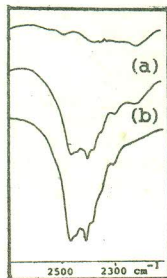


Fig. 2. The X-D stretching region of the LNT spectra of the sulfate (a) and the tetrafluoroberyllate (b)

the X-D stretching region of the spectra of deuterated samples with a low deuterium content (the unmarked curve in this figure is the corresponding part of the spectrum of the protiated sulfate compound). All these spectral similarities are indicative of structural similarities as well.

Thus, although the crystal structures may not be identical (recall the reported differences in the unit cell parameters), the basic structural features must be very similar, at least as far as the molecules of crystal water and coordinated ammonia are concerned. Unfortunately, it is not possible to verify such a conclusion since for the tetrafluoroberyllate only the parameters of the unit cell have been determined [2,3], the complete

structure being still unknown. As far as the spectra are concerned, the only significant difference was found in the region around  $1400\text{ cm}^{-1}$  where in the spectrum of the tetrafluoroberyllate compound a band of non-negligible intensity was observed, whereas only a shoulder is seen in the spectrum of the sulfate.

In the spectrum of the sulfate, the lowering of the temperature produces significant changes in the regions where the bending H-N-H and H-O-H vibrations are expected to appear. Thus, the feature around  $1650\text{ cm}^{-1}$  is clearly split into at least five components and several new bands develop also in the  $1300\text{ cm}^{-1}$  region. Keeping in mind the unit-cell selection rules, such a splitting is not unexpected.

At LNT, the band around  $720\text{ cm}^{-1}$  (assigned by Schmidt and Muller [4] to the ammonia rocking modes) is also, as expected, split into several components but, surprisingly enough, is not shifted towards higher wavenumbers to any significant degree. On the other hand, the rather broad band which in the RT spectrum appears around  $555\text{ cm}^{-1}$  not only becomes narrower at LNT (Fig. 1a) but exhibits a negative temperature coefficient (the shift towards higher wavenumber values, typical case about  $10\text{ cm}^{-1}$  on going from RT to LNT). All above-mentioned bands are deuteration-sensitive, several new bands appearing at lower frequencies (Fig. 3a). Particularly worthwhile mentioning is the doublet centered around  $450\text{ cm}^{-1}$  which seems to suggest that a band of librational origin may overlap, in the spectrum of the protiated analogue,

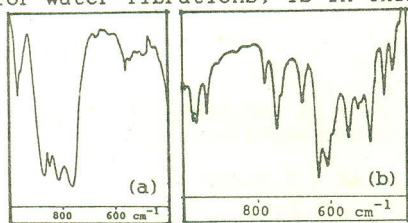


Fig. 3. The low-frequency region of the spectra of the deuterated analogues of the sulfate (a) and the tetrafluoroberyllate (b)

with that due to sulfate antisymmetric bending.

The situation in the case of the tetrafluoroberyllate compounds is, in many respects, similar to that already discussed. Here too the lowering of the temperature produces (cf. Fig. 1b) splitting of some of the bands, as well as a shift towards higher frequency and an increase in intensity of the water librational band around  $530\text{ cm}^{-1}$  (in the RT spectrum the corresponding band is quite weak and, were it not for the spectrum of the sulfate, could be easily missed). The rocking  $\text{NH}_3$  modes give rise to bands appearing on the low-frequency side of the tetrafluoroberyllate stretching bands (around  $720\text{ cm}^{-1}$  and, perhaps,  $680\text{ cm}^{-1}$ ; the latter band may also be due to some water libration). Such a conclusion is supported by the appearance of the spectra of the deuterated compound (Fig. 3b) in which the corresponding region is void of bands. Several new bands appear in the

latter spectrum in the region from 1200 to 950  $\text{cm}^{-1}$  which, it should be recalled, in the spectrum of the sulfate is dominated by the sulfate stretching bands.

All the facts discussed above show, once again, the usefulness of the parallel study of the spectra of structurally closely related compounds which differ in the nature of the anions.

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#### ИЗВОД

#### ИНФРАЦРВЕНИ СПЕКТРИ НА МОНОХИДРАТИТЕ НА ТЕТРААМИНБАКАР(II) ТЕТРАФЛУОРОБЕРИЛАТ И ТЕТРААМИНБАКАР(II) СУЛФАТ

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Инфрацрвените спектри на двете изучувани соединенија покажуваат низа сличности. Спектралните сличности се такви што сугерираат големи сличности и во структурата, макар што двете соединенија можеби и не се стриктно изоморфни. Уште еднаш е покажано дека во случај на изотипни соединенија што се разликуваат по полиатомскиот анјон што го содржат, паралелното изучување на спектрите помага полесно да се лоцираат ленти што потекнуваат од вибрациите на другите структурни елементи.