

INFRARED SPECTRA OF $\text{Ni}(\text{bipy})_3\text{SO}_4 \cdot 7\text{H}_2\text{O}$ AND
 $\text{Ni}(\text{bipy})_3\text{BeF}_4 \cdot 7\text{H}_2\text{O}$

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The general appearance of the infrared spectra of the two title compounds suggests an isomorphism between them. The existing differences in the OD stretching region of the spectra of samples containing small amounts of deuterium are certainly due to the formation, in the course of the deuteration, of a lower hydrate of the sulfate compound. On the basis of the observed OD frequencies of isotopically isolated HDO molecules, the hydrogen bond strength was estimated in the case of the tetrafluoroberrylate.

The complexes of the transition metals with 2,2'-bipyridine (bipy) have been subject of numerous studies /1/. Continuing our work on such compounds (so far usually sulfates and selenates), we now report the infrared spectra (recorded on a Perkin-Elmer 580 instrument) of tris-(bipyridine)nickel(II) sulfate heptahydrate and the corresponding tetrafluoroberrylate compound. The compounds under investigation were prepared using the method described by Tedenac /2/. Heating under reflux was required in order to obtain deuterated products. Unfortunately, in the case of the sulfate compound, the treatment at elevated temperature resulted apparently with a formation of a lower hydrate.

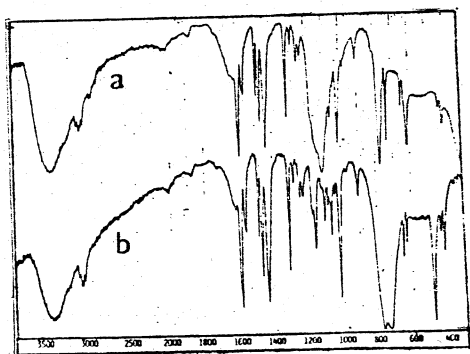


Fig. 1. Spectra of tris-(bipyridine)nickel sulfate heptahydrate (a) and of its tetrafluoroberrylate analogue (b)

RESULTS AND DISCUSSION

The infrared spectra of the two title compounds, recorded at liquid-nitrogen temperature, are shown in Fig. 1. The general appearance of the two sets of spectra is quite similar (with the expected exception of the regions of anion absorption). This, of course, is not surprising in view of the fact that the sulfate and tetrafluoroberrylate compounds of a given type are very often isomorphous. For a pair of supposedly isomorphous compounds, however, one would expect to find not just an overall similarity but also closeness in the appearance of details that are not related to those structural fragments which are

different. One would, for example, expect a high degree of similarity in the parts of the spectra where the vibrations of the bipyridine ligands or the water molecules give rise to bands which are due to vibrations localized predominantly (if not exclusively) within these structural fragments.

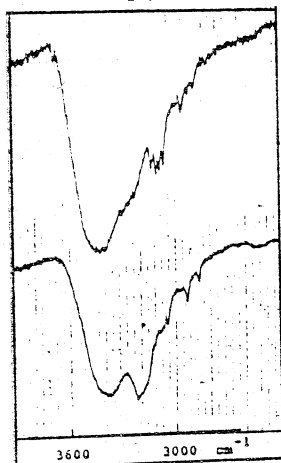


Fig. 2. The OH stretching region in the spectra of the protiated and partly deuterated sulfate

While the expectations are borne out for the bipyridine bands (for which the differences are, in any case, hard to detect), and for the water bands in the protiated compounds, this is not so in the case of the partly deuterated sulfate (Fig. 2). The fact that here a different hydrate is apparently obtained does not permit to follow the similarities also in the OD stretching region of the spectra of samples containing small amounts of deuterium where one would expect to find bands (similar, qualitatively speaking, for the two compounds) whose frequency would reflect the strength of the formed hydrogen bonds (quantitative differences are, hence, certainly anticipated). Unfortunately, because of the change in composition, what we see in the OD stretching region in the case of the sulfate is not the spectrum of the heptahydrate isotopomer.

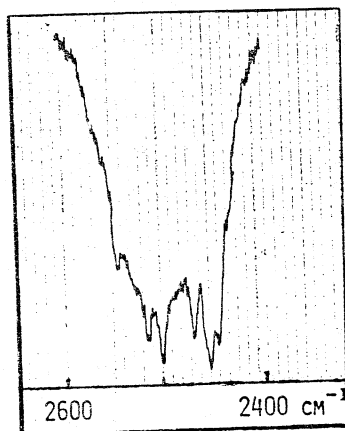


Fig. 3. The OD stretching region in the spectrum of the partly deuterated tetrafluoroberrylate

Since, on the other hand, the basic features of the tetrafluoroberrylate spectrum do not seem to have changed, the frequencies of the OD stretching bands of isotopically isolated HDO molecules (Fig. 3) could be used in this case to estimate the strength of the hydrogen bonds. Using the empirical relation given by Berglund et al. /3/, it could be concluded that the hydrogen bonds (O...O and/or O...F) in the tetrafluoroberrylate compound are equivalent to O...O hydrogen bonds of lengths close to 290, 286, 284, 280, 278 and 277 pm.

The assignment of the bipyridine bands is easy to make on the basis of the published work on similar compounds and is not reported here.

REFERENCES

1. M. Trpkovska, *MS Thesis*, University of Skopje, 1980 and references given therein.
2. J. C. Tedenac, *PhD Thesis*, Science and Technics University of Languedoc, Montpellier, 1974.
3. B. Berglund, J. Lindgren and J. Tegenfeldt, *J. Mol. Struct.* **43**, 167 (1978).