

VIBRATIONAL STUDY OF TWO BIPYRIDINE COMPLEXES :
DIAQUA(2,2'-BIPYRIDINE)COPPER(II) SULFATE AND
DIAQUA(2,2'-BIPYRIDINE)NICKEL(II) SULFATE

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In the structure of $[\text{Cu}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ the sulfate ions are more distorted and the hydrogen bonds formed by the water molecules are stronger than those in the structure of the nickel analogue. These structural differences are reflected in the appearance of the infrared spectra of the two title compounds.

INTRODUCTION

The two title compounds are members of the isomorphous series of compounds having the general formula $[\text{M}(\text{H}_2\text{O})_2(\text{bipy})]\text{RO}_4$ where M may be Ni, Co, Mn, Fe or Cu, R is S or Se (the tetrafluoroberyllate analogue of the copper compounds has also been prepared [1]) and bipy stands for 2,2'-bipyridine. To the best of our knowledge, the crystal structures have been determined in detail only for the nickel [2] and copper [3] sulfate compounds (the structure of the copper tetrafluoroberyllate analogue has also been solved [1]). It was found that these compounds crystallize in the space group $C2/c$ with $Z = 4$ (but with only two formula units in the asymmetric unit cell). All water molecules, sulfate ions and bipyridyl ligands are crystallographically equivalent.

In view of our interest for simple and complex hydrated compounds of the first-row *d*-elements, the vibrational spectra of several members of the isomorphous series have been studied in some detail. Other authors [1, 4-6] also give some infrared data. Our results have not been published, however, and those of the other authors are fragmentary and not discussed in detail. This is why we decided to report in the present paper some of our infrared data.

EXPERIMENTAL

The two investigated compounds were prepared following the method outlined by Tedenac and his co-workers [1-3] (it

consists of slow evaporation of equimolar alcoholic solutions of 2,2'-bipyridine and the corresponding metal sulfate). The partially deuterated analogues were prepared by evaporating the solutions of the protiated compounds in H₂O/D₂O mixtures of appropriate composition.

The infrared spectra were recorded from Nujol mulls (the KBr method was also used for the nickel compound) on a Perkin-Elmer 580 spectrophotometer. A VLT-2 variable-temperature cell cooled with liquid nitrogen was used for the low-temperature measurements.

RESULTS AND DISCUSSION

The spectra of the two compounds are, in general, rather similar (as expected for isomorphous compounds) but some clear differences are also present. This is particularly true for the regions of water stretching vibrations (around 3000 cm⁻¹) and water librations as well as that of the sulfate stretching vibrations (the region around 1100 cm⁻¹).

Water stretching region

As seen in Fig. 1, two bands of moderate width are found in the H₂O stretching region of the spectrum of the nickel compound (that at lower frequency is overlapped with the bands originating from C-H stretches of the bipyridine ligands), whereas several much broader bands are observed in the corresponding region of the spectrum of the Cu(II) complex.

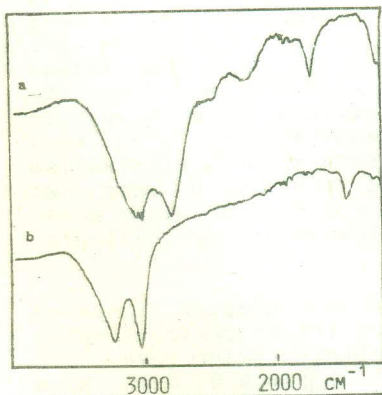


Fig. 1. The H₂O stretching region in the spectra of [Cu(H₂O)₂(bipy)]SO₄ (a) and of [Ni(H₂O)₂(bipy)]SO₄ (b)

In this latter case, namely, broad bands (or shoulders) are found around 2800, 2500 and 2250 cm⁻¹ in addition to the band located in the spectral region where the C-H stretching appear as well. In their paper [1] Tedenac *et al.* also report two H₂O stretching frequencies for the Ni(II) compound, but fail to mention the bands below 2800 cm⁻¹ for the Cu(II) one.

The observed differences for the two compounds are not unexpected. In the structure of the nickel complex, namely, both hydrogen bonds formed by the water molecules are of moderate strength (the corresponding O...O distances are close to 273 and 267 pm [2]) whereas one of the O...O separations in the structure of the copper compound is shorter

(close to 260 pm). Under such circumstances, one would expect a considerable amount of vibrational decoupling of the two water stretching modes, the in-phase one being essentially stretching of the O-H group involved in stronger hydrogen bonding. The appearance of several broad bands below 3000 cm^{-1} is, then, in line with the picture found in other cases where hydrogen bonds of similar strength are formed.

In the O-D stretching region of the spectra of the analogues of both compounds with a high deuterium content, only two bands are found in the region below 2500 cm^{-1} (Fig. 2). Obviously, the conditions for vibrational coupling leading to multiple bands in the spectrum of the protiated compound are less favorable in the case of the deuterated analogues. As expected, the frequencies of the corresponding bands in the spectrum of the copper compound are much lower than those for the nickel analogue.

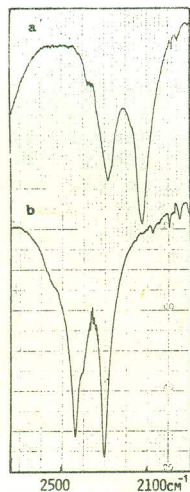


Fig. 2. The O-D stretching region in the spectra of $[\text{Cu}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ (a) and of $[\text{Ni}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ (b)

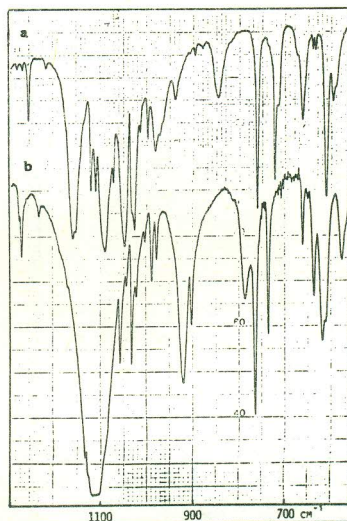


Fig. 3. The low-frequency region in the spectra of $[\text{Cu}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ (a) and of $[\text{Ni}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ (b)

Water librations

The differences in the strengths of the hydrogen bonds in which the water molecules are involved are reflected in the positions of the water librational bands as well (see Fig. 3).

In the spectrum of $[\text{Ni}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ the librational bands of water have (at LNT) frequencies close to 920, 785 and 575 cm^{-1} (the basis for the assignment is the pronounced tempe-

ture sensitivity of the bands and their disappearance on deuteration). The fact that *three* bands of librational origin are found, all of them with non-negligible intensity, suggests a considerable mixing of the librational modes (the twisting mode is symmetry-forbidden for water molecules with C_{2v} symmetry). Such a mixing is made possible by the low site symmetry (C_1) of the water molecules (under the selection rules of the site group, all water modes become of the same symmetry).

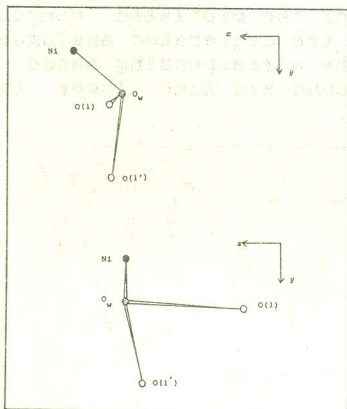


Fig. 4. The surrounding of the water molecules in the structure of $[Ni(H_2O)_2(bipy)]SO_4$ (after [2])

On the other hand, a more precise assignment of these bands is impossible because of the fact that the water molecules belong to the rather peculiar type J of the classification of Ferraris and Franchini-Angela [7] (with the divalent ion situated approximately in the direction of one of the lone pairs around oxygen, the other such position being unoccupied; cf. Fig. 4). With a situation like this, namely, it is difficult to apply the criteria (derived from the model calculations of Eriksson and Lindgren [8]) for assignment of the librational bands since strictly speaking the water molecules are neither trigonally nor tetrahedrally coordinated - the cases treated by Eriksson and Lindgren.

As for the copper compound, the assignment of the bands around 850 and 670 cm^{-1} in the LNT spectrum to H_2O librations is straight-forward: they are both temperature and deuteration sensitive. It should be noted that the above frequencies are *higher* than those of the corresponding bands in the spectrum of the nickel compound in line with the greater strength of the hydrogen bonds in the former case. The assignment of the band found around 980 cm^{-1} is somewhat tentative mainly because of its much lower intensity compared to that of the 920 cm^{-1} band in the spectrum of the nickel compound (Fig. 3).

Water bending region

In the spectrum of $[Ni(H_2O)_2(bipy)]SO_4$ the whole region from 1800 to 1400 cm^{-1} seems to contain bands (probably broad)

which disappear on deuteration. On the other hand, in the spectrum of the sample with the highest deuterium content, several shoulders are observed at the high-frequency side of the intense band which is due to the antisymmetric sulfate stretches (Fig. 5), the band as a whole being considerably broadened.

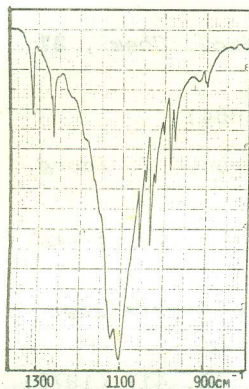


Fig. 5. The sulfate stretching region in the spectrum of deuterated $[\text{Ni}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$.

It would, thus, seem that the water bending modes are involved in vibrational interactions leading to the appearance of several deuteration-sensitive bands. Such a picture (sometime much clearer than in the present case) is observed in the spectra of other compounds containing water molecules (or NH_3 groups) with geometry leading to anharmonicity of the vibrations and, as a consequence, allowing vibrational interactions of various kinds [9,10].

It should be noted that the analysis is complicated by the fact that numerous bipyridine bands are present in the regions where the bands due to H-O-H, H-O-D and D-O-D bendings are expected to occur.

Sulfate vibrations

The crystallographic data [1,2] show that the sulfate ions are considerably more distorted in the case of the copper complex than in $[\text{Ni}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$. Some of the deformation indices [11], namely, are for a whole order of magnitude larger in the former than in the latter complex.

As expected, this is reflected in the infrared spectra. In the spectrum of the nickel complex, the components of the antisymmetric sulfate stretch are close together and give rise to an intense but not very broad band centered around 1100 cm^{-1} . In the spectrum of the copper complex, on the other hand, several bands associated with these modes are found in the $1200 - 1000 \text{ cm}^{-1}$ region (Fig. 3).

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ИЗВОД

ИСПИТУВАЊЕ НА ВИБРАЦИОНИТЕ СПЕКТРИ НА ДВА БИПИРИДИНСКИ КОМПЛЕКСА : ДИАКВА (2,2'-БИПИРИДИН) БАКАР (II) СУЛФАТ И ДИАКВА (2,2'-БИПИРИДИН) НИКЕЛ (II) СУЛФАТ

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Во структурата на $[\text{Cu}(\text{H}_2\text{O})_2(\text{bipy})]\text{SO}_4$ сулфатните јони се повеќе деформирани, а водородните врски образувани од молекулите вода се посилни одошто во соодветното соединение на никел. Овие структурни разлики се одразуваат врз изгледот на инфрацрвените спектри на двете изучувани соединенија.