

PARALLEL STUDY OF ISOMORPHOUS COMPOUNDS AS AN AID  
IN LOCATING WATER LIBRATIONAL BANDS

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In the case of compounds containing polyatomic groups which give rise to intense bands with frequencies falling in the region where the water librations are also expected to appear, the location of water librations is facilitated if a pair (or series) of isomorphous salts differing in the nature of the anion (for example, sulfates and selenates) are studied. The study of isomorphous compound differing in the nature of the cation may also be of help.

INTRODUCTION

When water molecules become a part of a crystal (such as a crystallohydrate), their rotations and translations are transformed into motions which are vibrational in nature. The hindered rotations become *librations* and the former translational motions of water molecules coordinated to a metal cation turn into modes which are essentially *metal-oxygen stretchings*. Needless to say, the resulting modes may not be pure librations or metal-to-water stretchings and *mixing* between these modes themselves or with other modes may take place.

Numerous studies have been performed on various aspects related to the water librations. The majority of this work has been summarized in the recent review by Tayal *et al.* [1] and, less extensively, in the review article by Lutz [2].

The first step in any kind of a more detailed study is, of course, the *location* of the librational bands in a given spectrum. The *sensitivity to deuteration* and the *temperature sensitivity* of the observed bands are usually taken as criteria for locating the librational bands.

Being essentially water motions, namely, the librations are sensitive to the exchange of protons with deuterons and the frequencies of the D<sub>2</sub>O modes are, as a rule, lower than those of their H<sub>2</sub>O counterparts. When, on the other hand, the temperature is lowered, the water librational bands become appreciably sharper, their intensity increases (at least apparently)

and, moreover, they shift towards higher frequencies [1,2].

It does not seem that among the methods applied to the problem of location of water librational modes, the *study of isomorphous compounds* has been reported. It is exactly this latter method to which the present paper is mainly devoted. As an introduction, examples of assignments based on the deuteration behaviour and/or temperature sensitivity will be shown.

### EXPERIMENTAL

The investigated compounds were, as a rule, prepared by standard methods. The details of the preparation methods were either reported previously [3] or will be given in our future articles, those in which the detailed studies of the investigated compounds will be reported.

The infrared spectra were recorded, at room temperature (RT) or at the boiling temperature of liquid nitrogen (LNT) on a Perkin-Elmer Model 580 spectrophotometer. When necessary, the spectra were recorded at intermediate temperatures as well.

For the copper compounds, mulls in Nujol have been employed. The rest of the spectra were recorded from KBr pellets, after checking that these spectra are identical with those recorded from mulls.

### RESULTS AND DISCUSSION

#### $M(\text{bpy})\text{XO}_4 \cdot 2\text{H}_2\text{O}$ ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}; X = \text{S or Se}$ )

The crystal structures of  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and of its copper analogue (bpy denoting the 2,2'-bipyridine ligand) have been determined by Tedenac and his collaborators [4,5]. It was found that these compounds crystallize in the space group  $C2/c$  with four formula units in the crystallographic unit cell. The number of formula units in the spectroscopic unit cell, however, will be only two. Since the cell is centrosymmetric, the number of infrared active factor-group modes will be equal to that expected on the basis of the site-group approximation.

To the best of our knowledge, the structure of the selenate analogue has not been determined but the selenates are known to be, as a rule, isomorphous with the corresponding sulfates.

The infrared spectra of these compounds have been treated in detail by one of us [6]. In the present context only the librational bands will be considered.

On the basis of their temperature sensitivity, three librational bands can easily be located in the spectra of the  $M(\text{bpy})\text{XO}_4 \cdot 2\text{H}_2\text{O}$  type compounds when  $M = \text{Mn}, \text{Fe}, \text{Co}$  or  $\text{Ni}$  and

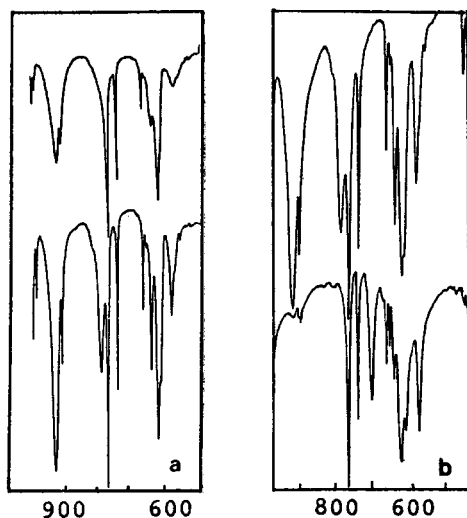


Fig. 1. RT and LNT spectra of  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (a) and LNT spectra of protiated and deuterated  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (b)

$X = \text{S}$  or  $\text{Se}$ . As an example, Fig. 1 a gives the RT and LNT spectra of  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  in the  $1000 - 500 \text{ cm}^{-1}$  region. It can be easily seen that the water librational bands which are clearly visible at LNT are much less pronounced at RT and it would be rather difficult to locate them in absence of LNT spectra.

The assignment of the temperature-sensitive bands to water librations is confirmed by their shift on deuteration (cf. Fig. 1 b).

The situation is similar in the infrared spectra of  $\text{Co}(\text{bpy})\text{XO}_4 \cdot 2\text{H}_2\text{O}$ , of the sulfate compound of iron and of the  $\text{Mn}(\text{bpy})\text{XO}_4 \cdot 2\text{H}_2\text{O}$  analogues with the notable exception of the frequen-

cies and the general appearance of the librational bands found in the  $950 - 850 \text{ cm}^{-1}$  region.

As seen in Fig. 2, namely, in the spectra of  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Mn}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  only one of the components of the doublet appearing here is intense and broad, whereas both bands have almost equal intensity and appearance in the spectra of the compounds of cobalt and iron.

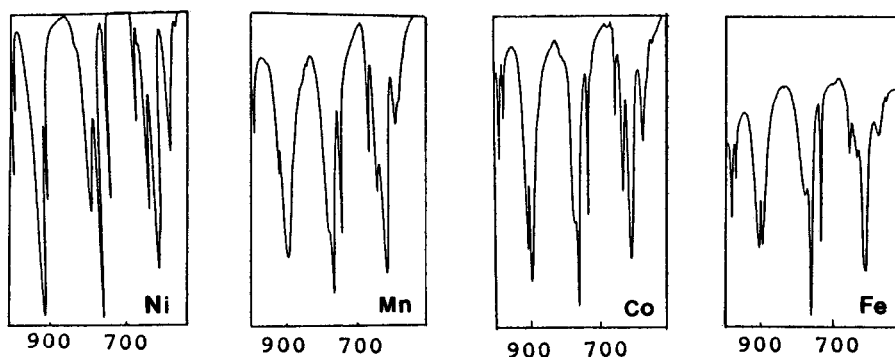


Fig. 2. LNT spectra of  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Co}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Fe}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$

The differences can readily be explained if an interaction of the water libration with one of the bipyridine bands is assumed. The coupling will obviously be stronger if the frequencies of the two interacting modes are closer together. On the basis of this interpretation and the appearance of the spectra it can be deduced that the frequency of the water libration in question is *highest* in the case of the nickel compound, *intermediate* in  $\text{Co}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and its iron analogue and *lowest* for the manganese compound. This order, it should be noted, is that of *increase* of the ionic radii and *decrease* of the effective charges (the charge-to-radius ratios) of the divalent ions.

The combination of low-temperature studies and of studies of deuterated samples makes it possible to attribute to water librations the bands whose LNT frequencies in the spectra of the protiated samples are : 920, 785 and 575  $\text{cm}^{-1}$  for  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ; 925, 775 and 575  $\text{cm}^{-1}$  for its selenate analogue;  $\approx 900$ , 775 and 580  $\text{cm}^{-1}$  for the dihydrate of cobalt(bipyridine) sulfate;  $\approx 905$ , 760 and 580  $\text{cm}^{-1}$  for the corresponding selenate;  $\approx 900$ , 765 and 575  $\text{cm}^{-1}$  for  $\text{Fe}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ; 890, 775 and 575  $\text{cm}^{-1}$  for  $\text{Mn}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and finally  $\approx 905$ , 760 and 575  $\text{cm}^{-1}$  for the selenate compound of manganese. As can be seen, the frequencies within each pair of corresponding bands are quite close to each other, the small differences probably reflecting the small variations in the hydrogen-bond strength.

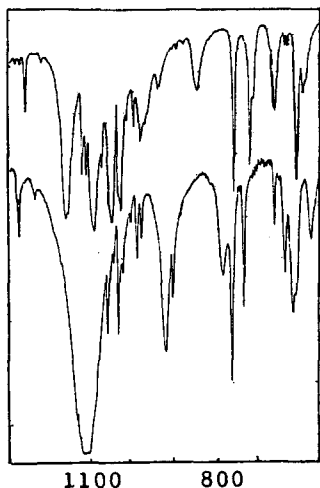


Fig. 3. Comparison of the spectra of  $\text{Cu}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$

The librational bands in the spectrum of  $\text{Cu}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (980, 850 and 670  $\text{cm}^{-1}$ ) are *appreciably higher* than in those of the nickel analogue (Fig. 3). It is unlikely that these frequency differences are caused by the metal-to-water interactions. The ionic radius of  $\text{Cu}^{2+}$ , namely, is *larger* than that of  $\text{Ni}^{2+}$ , the effective charge of the former ions should be less than that of the latter ones and, if anything, the *opposite* trend should be present. On the other hand, the hydrogen bonds which are formed by the water molecules are stronger in the structure of  $\text{Cu}(\text{bpy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$  than in the Ni compound [4,5] and this must be the main factor causing the differences in the frequencies of the water librational bands in the spectrum of the copper compound as compared with those in the spectrum of its nickel analogue.

It should be noted that the location of the bands in each of the above-treated compounds is possible without resorting to the study of the isomorphous analogues.

*Cu(bpy)SeO<sub>4</sub> · 2H<sub>2</sub>O*

The situation is much less favorable in the case of the dihydrate of copper(2,2'-bipyridine) selenate (the spectrum of this compound is discussed in more detail in [3]).

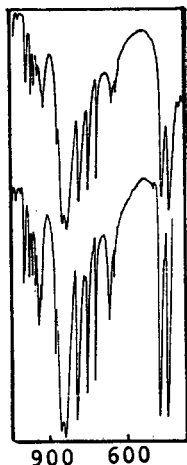


Fig. 4. RT and LNT infrared spectra of *Cu(bpy)SeO<sub>4</sub> · 2H<sub>2</sub>O*

As seen in Fig. 4, namely, the comparison of the RT and LNT spectra of *Cu(bpy)SeO<sub>4</sub> · 2H<sub>2</sub>O* makes it possible to locate *only two* of the librational bands, those around 990 and 665  $\text{cm}^{-1}$ . The frequencies, it should be noted, are close to those found in the spectrum of the corresponding sulfate.

However, in the 900 - 800  $\text{cm}^{-1}$  region (where the third librational band is found in the spectrum of the supposedly isomorphous sulfate compound) hardly any change is observed as the temperature is lowered. The reason for this is simple: the selenate antisymmetric stretchings appear in this spectral region and the resulting intense bands hide the one which is due to water libration. In the spectrum of *Cu(bpy)SeO<sub>4</sub> · 2D<sub>2</sub>O*, however, a new band is found around 635  $\text{cm}^{-1}$  and is interpreted [3] as the D<sub>2</sub>O analogue of the band hidden under the selenate bands which is found around 880  $\text{cm}^{-1}$ . The intensity of this new band is rather low

and it may have been overlooked were it not for the knowledge (based on the study of the isomorphous sulfate compound) that a H<sub>2</sub>O librational band is expected around 880  $\text{cm}^{-1}$ .

*Monohydrates of CuSO<sub>4</sub> and CuSeO<sub>4</sub>*

According to Giester [7], *CuSO<sub>4</sub> · H<sub>2</sub>O* and *CuSeO<sub>4</sub> · H<sub>2</sub>O* are triclinic (space group  $\bar{P}1$ ,  $Z = 2$ ) and closely related to the kieserite-family of compounds with the general formula *M*SO<sub>4</sub> · H<sub>2</sub>O ( $M = \text{Mg, Ni, Co, Zn, Fe, Mn}$ ). Since the space group is centrosymmetric, three librations and three modes of translational origin are expected to appear.

The interpretation of the infrared spectrum of *CuSO<sub>4</sub> · H<sub>2</sub>O* (Fig. 5) is not straight-forward and the complete analysis will be postponed until later [8]. On the basis of the comparison of the RT and LNT spectra, the intense bands around 880 and 795  $\text{cm}^{-1}$  (LNT values) are assigned to water librations and the almost equally strong band found around 475  $\text{cm}^{-1}$  - to mode(s) also having librational character.

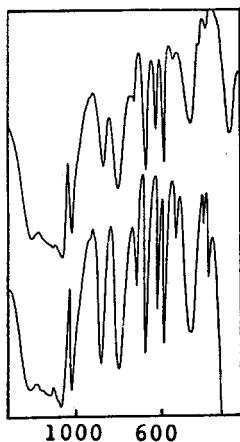


Fig. 5. RT and LNT spectra of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$

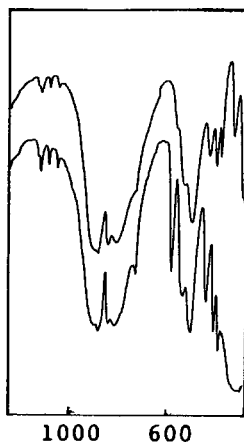


Fig. 6. RT and LNT spectra of  $\text{CuSeO}_4 \cdot \text{H}_2\text{O}$

In the spectrum of the corresponding selenate, on the other hand, the selenate stretches are expected in the former and the selenate bendings in the latter region. The comparison of the RT and LNT spectra (Fig. 6) shows that hardly anything happens in the region around  $880 \text{ cm}^{-1}$ . More pronounced changes are, on the other hand, observed in the region above  $450 \text{ cm}^{-1}$ . Thus, the location of a water librational band above  $800 \text{ cm}^{-1}$  in the spectrum of the selenate is possible only if the results of the study of the sulfate are available and only then the subtle changes produced by lowering the temperature in the region above  $800 \text{ cm}^{-1}$  become obvious.

#### REFERENCES

1. V. P. Tayal, B. K. Srivastava and P. P. Khandelwal, *Appl. Spectrosc. Rev.*, **16** (1980) 48.
2. H. D. Lutz, *Structure and Bonding*, **69** (1988) 97.
3. M. Trpkovska and B. Šoptrajanov, *Croat. Chem. Acta* (submitted for publication).
4. J. C. Tedenac and E. Philippot, *Acta Crystallogr.*, **B30** (1974) 2288.
5. J. C. Tedenac and E. Philippot, *J. Inorg. Nucl. Chem.*, **37** (1975) 846.
6. M. Trpkovska, *MS Thesis*, Cyril and Methodius University, Skopje, 1980.
7. G. Giester, *Mineral. Petrol.*, **38** (1988) 277.
8. M. Trpkovska and B. Šoptrajanov, to be published.