

COMPARATIVE ANALYSIS OF THE INFRARED SPECTRA OF SOME TETRAAMMINECOPPER(II) COMPOUNDS

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Abstract

Subjected to a comparative analysis were the infrared spectra of four tetraamminecopper(II) complexes: two anhydrous compounds ($[\text{Cu}(\text{NH}_3)_4]\text{SeO}_4$ and $[\text{Cu}(\text{NH}_3)_4]\text{CrO}_4$) and two monohydrates ($[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{NH}_3)_4]\text{BeF}_4 \cdot \text{H}_2\text{O}$). The spectra were recorded at room temperature and at the boiling temperature of liquid nitrogen. Particular attention was paid to the bands which are indicative of the strength of the hydrogen bonds formed by the ammonia and (when present) water molecules. The electronegativity difference between the chromium and oxygen, and beryllium and fluorine atoms, on the one hand, is much larger than the difference between the sulphur (or selenium) and oxygen atoms. Nevertheless, the hydrogen bonds in each pair of isomorphous compounds do not differ considerably in their strength. A more sophisticated approach in predicting the relative proton-acceptor ability of different anions is therefore needed.

Keywords: *Infrared spectroscopy, Tetraamminecopper(II) compounds, Tetraamminecopper(II) selenate, Tetraamminecopper(II) chromate, Tetraamminecopper(II) sulphate monohydrate, Tetraamminecopper(II) tetrafluoroberyllate monohydrate, Hydrogen bonding*

Introduction

Continuing our work on the infrared (IR) spectra of various copper(II) compounds, especially of those containing moieties which could act as proton donors (water or ammonia molecules, ammonium ions) [1-6], we now report the results of our comparative study of the IR spectra of four tetraamminecopper(II) complexes: two anhydrous compounds ($[\text{Cu}(\text{NH}_3)_4]\text{SeO}_4$ and $[\text{Cu}(\text{NH}_3)_4]\text{CrO}_4$) and two monohydrates ($[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{NH}_3)_4]\text{BeF}_4 \cdot \text{H}_2\text{O}$). The compounds were selected to test the relative proton-acceptor abilities of the four investigated anions.

It should be noted that the IR spectra of tetraamminecopper(II) compounds have already been analyzed by other authors [7-10]. A particularly thorough study was the analysis of Schmidt and Müller [11] who studied the spectra of

tetraamminecopper(II) sulfate and its fully deuterated analogue while Acevedo and Diaz [12] performed a normal-coordinate analysis of the complex cation. However, we are not aware of any comparative research on the compounds we have studied: neither the anhydrous compounds nor the two monohydrates. In fact, the infrared spectra of the tetrafluoroberyllate and of the chromate compounds do not seem to have been analyzed in detail, except for our own works [1, 6].

The crystal structures of all the studied compounds except for the chromate compound have been published. It was shown [13] that $[\text{Cu}(\text{NH}_3)_4]\text{SeO}_4$ crystallized in the monoclinic space group C_{2h}^5 , whereas the sulphate and the tetrafluoroberyllate compounds are orthorhombic and crystallize in the space group D_{2h}^{16} [13, 14]. It seems that the only crystallographic data on $[\text{Cu}(\text{NH}_3)_4]\text{CrO}_4$ are those found in ref. [15] where

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it is only stated that the compound is not cubic.

In all four compounds, the ammonia molecules are hydrogen-bonded and act as proton donors. The reported N...Y distances range from 297.8 pm to 318.3 pm in the case of the sulfate [13], from 275.7 to 344.0 pm in the structure of the selenate [13] (in both cases $Y = O$) and from 297 to 307 pm for the tetrafluoroberyllate [14] where $Y = F$. Hydrogen bonds are also formed by the water molecules (when present). Those in the sulfate are 277.7 pm long, whereas the reported O...F distances in the case of $[\text{Cu}(\text{NH}_3)_4]\text{BeF}_4$ are 265, 268, 269 and 273 pm. The comparison of proton-to-acceptor distances should be made with caution since the acceptor atoms are not the same (oxygen in the structures of the sulfate and selenate, fluorine in that of the tetrafluoroberyllate) and the differences in the van der Waals radii should be taken into account.

The water molecules in the two monohydrates are coordinated to the Cu^{2+} ions, whereas the selenate anions enter the coordination sphere of copper in $[\text{Cu}(\text{NH}_3)_4]\text{SeO}_4$.

Experimental

The studied compounds were prepared by methods found in the literature [13-16], slightly modified when necessary. The deuterated analogues were prepared by evaporating the solutions of the studied compounds in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of appropriate composition.

The infrared spectra were recorded, from NaCl pellets, at room temperature (RT), at boiling temperature of liquid-nitrogen (LNT), as well as at intermediate temperatures on a Perkin Elmer (USA) 580 infrared spectrophotometer.

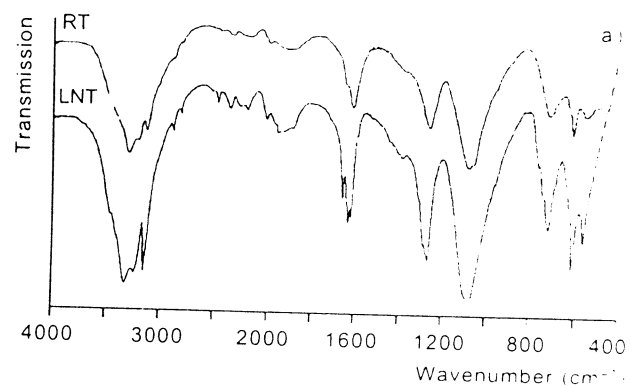
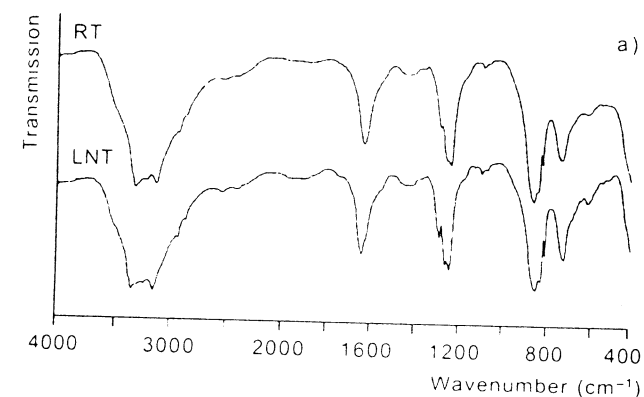


Fig. 1. Infrared spectra of tetraamminecopper(II) selenate (a) and tetraamminecopper(II) chromate (b)

Fig. 2. Infrared spectra of tetraamminecopper(II) sulphate monohydrate (a) and tetraamminecopper(II) tetrafluoroberyllate monohydrate (b)

Results and Discussion

The infrared spectra of $[\text{Cu}(\text{NH}_3)_4]\text{SeO}_4$ and $[\text{Cu}(\text{NH}_3)_4]\text{CrO}_4$ are shown in Fig. 1 and those of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{NH}_3)_4]\text{BeF}_4 \cdot \text{H}_2\text{O}$ are given in Fig. 2. Since the assignment of most bands originating from the vibrations of the complex cations is a rather straightforward task, it will not be dealt with in unnecessary details. Instead we shall concentrate only on those bands which can provide information about the hydrogen bonding in the studied compounds. Such bands are, of course, those which originate from the stretching vibrations of the ammonia and, when present, water molecules and also those which are due to the librational NH_3 and H_2O modes. These latter bands are relatively easy to locate when the RT spectra are compared with those recorded at LNT since the librational bands are temperature-sensitive and have a negative temperature coefficient $d\bar{\nu}/dT$, that is why they shift towards *higher* frequencies when the temperature is *lowered*.

In principle, the N–D and/or O–D stretching bands in the spectra of the isotopically isolated NH_2D and/or HDO molecules should be even more indicative. However, because bands belonging to the spectra of the protiated compounds (the upper curves in Fig. 3 and Fig. 4) are present in the same region, it is

difficult to correlate individual hydrogen bonds with bands in the N–D/O–D stretching region of slightly deuterated samples of the selenate (Fig. 3) or of the sulfate compound (Fig. 4).

Thus, for the time being, we abandoned the detailed analysis of this region and reverted to the analysis of the bands found in the N–H/O–H stretching region of the protiated compounds. As seen in Fig. 1 and Fig. 2, the frequencies of the bands in the above mentioned region of the chromate spectrum are not significantly different from those in the spectrum of the selenate and the situation is similar in the case of the spectra of the $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ – $[\text{Cu}(\text{NH}_3)_4]\text{BeF}_4 \cdot \text{H}_2\text{O}$ pair. Such a situation is rather unexpected if the electronegativity difference between the X and Y atoms of the *tetrahedral* XY_4^{2-} anions is taken into account. Since this difference is incomparably larger between the chromium and oxygen than between selenium and oxygen atoms, one would expect the partial electric charge on the oxygen atoms in CrO_4^{2-} to be larger than in SeO_4^{2-} . A similar reasoning leads to the conclusion that the partial electric charge should be larger on the fluorine atoms in BeF_4^{2-} than on the oxygen atoms in SO_4^{2-} . Consequently, the hydrogen bonds in the case of the chromate and tetrafluoroberyllate would be expected to be stronger than in the re-

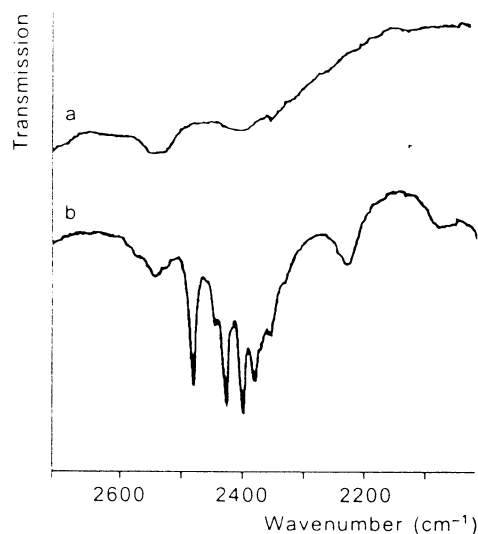


Fig. 3. The N–D stretching region in the infrared spectra of protiated (a) and slightly deuterated (b) tetraamminecopper(II) selenate

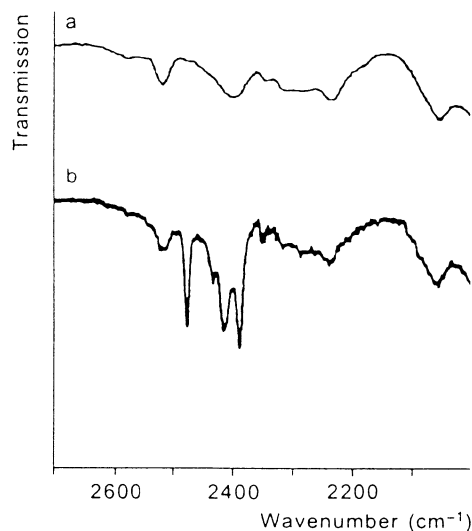


Fig. 4. The N–D/O–D stretching region in the infrared spectra of protiated (a) and slightly deuterated (b) tetraamminecopper(II) sulphate monohydrate

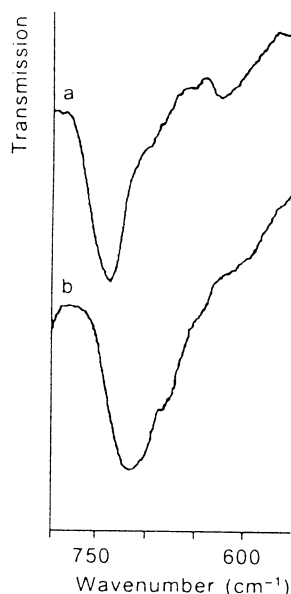


Fig. 5. The NH_3 rocking bands in the infrared spectra of tetraamminecopper(II) selenate (a) and tetraamminecopper(II) chromate (b)

maining two compounds. However, as Figs. 1 and 2 clearly show, this is *not* the case.

Since the NH_3 rocking frequencies are also considered to be indicative of the strength of the hydrogen bonds in which the ammonia molecules take part, the region below 1000 cm^{-1} in the spectra of the two anhydrous compounds was analyzed in more details (a similar comparative analysis of the two monohydrates was hampered by the occurrence of intense bands in the above region, due to the stretching vibrations of the BeF_4^{2-} anions). As seen in Fig. 5, the $\nu(\text{NH}_3)$ band frequency in the chromate spectrum is not appreciably different from the respective frequency in the selenate spectrum. Thus, contrary to the expectations, it must be concluded that the hydrogen bonds formed with the CrO_4^{2-} or BeF_4^{2-} anions as proton-acceptors are not significantly different in strength from those in which the proton-acceptor role is played by the SeO_4^{2-} or SO_4^{2-} anions.

The analysis presented above shows beyond doubt that the conclusions based on the simple electronegativity concept do not agree with the experimental data and that some more sophisticated approach should be adopted. We intend to continue our

work in this field and publish additional results in due time.

Acknowledgements

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