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FOURIER-TRANSFORM INFRARED SPECTRA OF TETRAAMMINE-COPPER(II) CHROMATE : COMPARISON WITH THE SPECTRA OF TETRAAMMINECOPPER(II) SELENATE[1]

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ABSTRACT

Analyzed were the Fourier-transform infrared (FTIR) spectra of tetraamminecopper(II) chromate recorded at room-temperature (RT) and at the boiling temperature of liquid nitrogen (LNT). Also analyzed were the spectra of a partially deuterated analogue of the title compound. The similarities between the infrared spectra of $[Cu(NH_3)_4]CrO_4$ and $[Cu(NH_3)_4]SeO_4$ indicate that structural similarities between the two compounds exist as well. The hydrogen bonds formed between the ammonia molecules and the chromate anions are not appreciably different in strength from those formed in the case when the selenate ions play the role of proton-acceptors.

INTRODUCTION

Continuing our work on the vibrational spectra of potentially isomorphous pairs of sulfate–selenate and sulfate–tetrafluoroberyllate compounds and, in that context, on the spectra of tetraamminecopper(II) compounds with oxoanions (SO_4^{2-} and SeO_4^{2-}) as well as with the BeF_4^{2-} anion [1-4], we now report data on the infrared spectra of $[Cu(NH_3)_4]CrO_4$ and compare them with the spectra of the corresponding selenate which has the same overall composition.

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[1] Dedicated to the memory of Dr. Marko Razinger.

To be sure, the fact that two given compounds are isotypic does not necessarily mean that they are isomorphous. Thus, sulfate–selenate or sulfate–tetrafluoroberyllate pairs of compounds of the same type *are* known to often be isomorphous, but the monohydrates of tetraamminecopper(II) sulfate and tetraamminecopper(II) tetrafluoroberyllate which not only are of the same overall composition but even crystallize in the same, orthorhombic, system [5,6] can not be strictly isomorphous if only because of the fact that the unit cell of the tetrafluoroberyllate compound is approximately four times that of the sulfate (other differences are also present).

As far as the structure of the presently studied chromate compound is concerned, it is only known [7] that it is not cubic. On the other hand, the structure of the corresponding selenate has been fully determined. It was found [6] that this compound crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. Four non-equivalent types of ammonia molecules with twelve non-equivalent hydrogen atoms are present in the unit cell.

Data on the infrared spectra of $[Cu(NH_3)_4]CrO_4$ have already been reported [7,8] but apparently only the RT spectra of the protiated compound have been studied. We have already given a brief account of the presently studied problem [9] but feel that a more detailed discussion is in order.

The main aim of the present study was to see whether a detailed indication of the structural relationship between the two studied compounds could be obtained from the analysis of the infrared spectra since it is generally accepted that the similarity of the spectra of two compounds could serve as an indication of structural resemblance (not necessarily isomorphism). In addition, we wanted to compare the strength of the hydrogen bonds formed in the structures of the two investigated compounds, assuming that the lower frequencies of the NH_3 stretching modes indicate stronger hydrogen bonds and *vice versa.*

EXPERIMENTAL

The two investigated compounds were prepared following, essentially, the method out-lined by Morosin [5] but applied with a small modification (in order to incite crys-tallization, dioxane was added instead of ethanol). The partially deuterated analogue of $[Cu(NH_3)_4]CrO_4$ was prepared by crystallization from solutions of the protiated com-pound in H_2O/D_2O mixtures of appropriate composition ($w_D \approx 5$ %).

The Fourier-transform infrared (FTIR) spectra were recorded on a Perkin-Elmer System 2000 FT-IR (resolution – 2 cm^{-1}, OPD velocity – 0.2 cm/s, 16 background and 32 sample scans; the abbreviation OPD stands for optical path difference) from powders dispersed in sodium chloride pellets. For the low-temperature work, a P/N 21525 low-temperature cell (Graseby Specac) with a temperature controller was used. Liquid nitrogen was employed as a cooling agent. The software package GRAMS 2000 [10] was used for the spectra acquisition, and GRAMS/386 [11] was used to analyze the spectra.

RESULTS AND DISCUSSION

The infrared spectra of $[Cu(NH_3)_4]CrO_4$ recorded at RT and LNT are shown in Fig. 1. The assignment is not difficult to make and the observed bands can be roughly divided into those originating from modes localized mainly within the ammonia molecules, bands belonging to vibrations of the anions and, finally, bands corresponding to motions of the complex cations as a whole.

Internal ammonia modes

According to the work of Schmidt and Müller [8,12], it is easy to assign the bands which are due to the internal NH_3 modes. Thus, the complex feature above 3000 cm^{-1} is unquestionably due to the antisymmetric and symmetric N-H stretchings, the bands appearing around 1625 cm^{-1} are attributed to the antisymmetric NH_3 bendings and the bands found around 1240 cm^{-1} to the symmetric NH_3 bending modes. It should be

pointed out that the frequency of the band originating from the antisymmetric NH_3 bending vibrations (≈ 1624 cm^{-1} at RT) in our spectra is slightly lower than that reported by Müller *et al.* [7] while the two values for the $\delta_s(NH_3)$ bands are practically identical. We are unable to explain the observed inconsistency of our results with those reported previously [8,12] but believe that the present frequencies (recorded on a superior instrument) are correct.
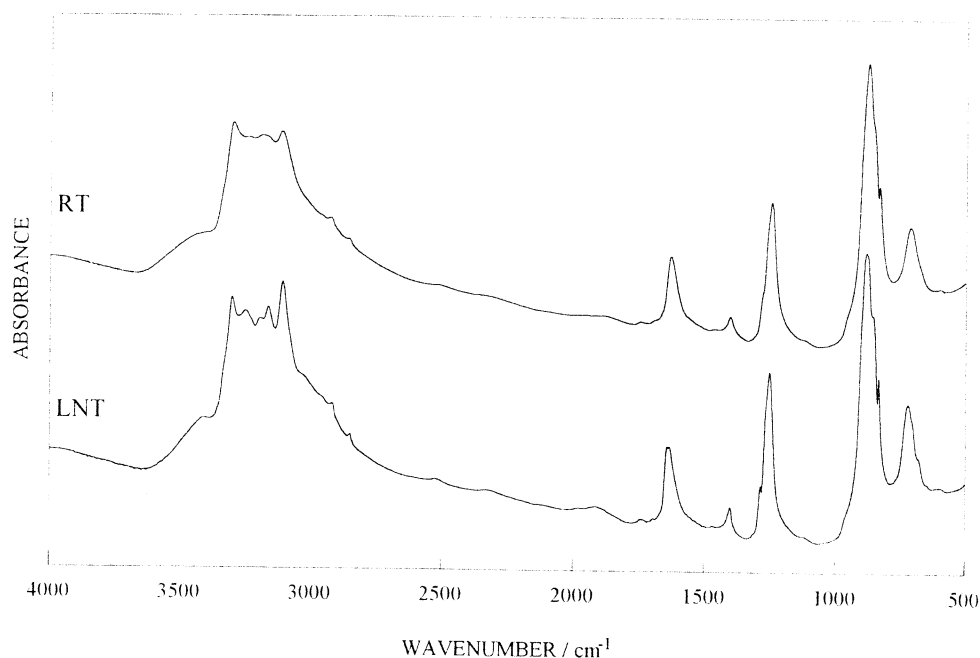

Fig. 1. The RT and LNT FTIR spectra of $[Cu(NH_3)_4]CrO_4$

As expected, the overlapping of the bands detected at room-temperature (RT) is more pronounced than those found in the LNT spectrum. It should also be noted that the NH_3 bending modes are shifted towards higher wavenumber values on going from RT to LNT (the values are 1640, 1284 and 1250 cm^{-1} at LNT and 1628, and 1244 cm^{-1} in the RT spectrum) whereas the temperature-induced band shifts in the stretching region are more difficult to determine. Moreover, these shifts do not seem to be the same for all infrared bands (in the LNT spectrum the maxima have frequencies of 3304, 3252, 3165, 3110 and 2849 cm^{-1} whereas the RT frequencies are 3301, 3189, 3116 and 2926 cm^{-1}).

Chromate modes

The bands appearing in the 900-800 cm^{-1} region are certainly due to the antisymmetric and symmetric stretching modes of the chromate anions. We agree with Müller *et al.* [7] that the high-frequency components of the complex feature originate from the antisymmetric stretching vibrations of the "tetrahedral" anion and that the sharp and relatively weak band found around 833 cm^{-1} in the RT infrared spectrum and at about 834 cm^{-1} in the LNT spectrum is a more likely candidate for assignment to the symmetric stretch than the much stronger bands at higher frequencies (883 and $\approx$ 857 cm^{-1}), notwithstanding the earlier suggestion [13] for a reverse assignment.

Vibrations of the complex cations

The bands below 750 cm^{-1} are certainly due to vibrations of the complex cations [8,12]. Among these, the band at around 700 cm^{-1} has already been assigned [8] to the rocking mode of the coordinated ammonia. The presently measured band frequencies (712 cm^{-1} at RT and 720 cm^{-1} at LNT) are higher than the value of 701 cm^{-1} given by Müller and Baran [8] but there is little doubt that we are dealing with the same band. The temperature sensitivity of this band and its negative temperature coefficient $d\tilde{v}/dT$ are in full agreement with such an assignment. Because of the use of NaCl pellets, we were unable to study the region where the remaining modes of the complex cation and the bending modes of the "tetrahedral" anions are expected to appear. Therefore we will not discuss the assignments of the low-frequency modes until we are able to obtain far-infrared spectra of better quality.

Structural inferences

In Fig. 2 the LNT spectrum of [Cu(NH$_3$)$_4$]CrO$_4$ is compared with that of the corresponding selenate. As seen, the similarities between the two spectra are considerable so that it can be concluded that the two structures must be similar although an outright claim of isomorphism may not be warranted. It should be noted that in the selenate spectrum the bands in the N-H stretching region are clearly arranged into two groups which may indicate that the structural differences between the NH$_3$ ligands in the complex cation

are more pronounced for $[Cu(NH_3)_4]SeO_4$ than for $[Cu(NH_3)_4]CrO_4$. A similar explanation could be given for the differences in the appearance of the $\delta_s(NH_3)$ bands in the spectra of the presently considered compounds (they are clearly visible in Fig. 3).
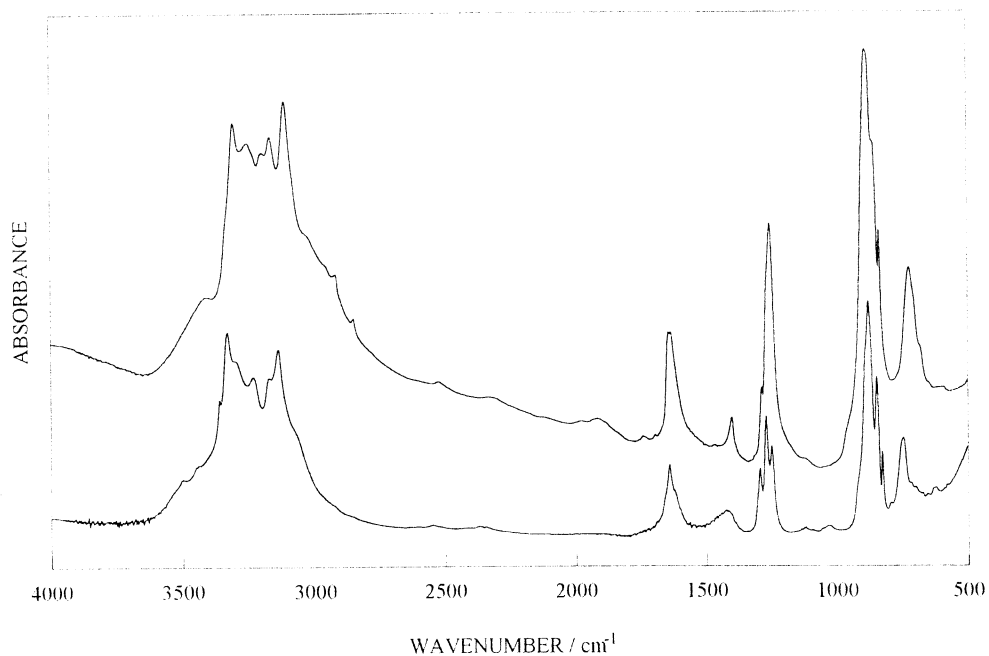

Fig. 2. The LNT FTIR spectra of $[Cu(NH_3)_4]CrO_4$ (upper curve) and $[Cu(NH_3)_4]SeO_4$

If $[Cu(NH_3)_4]CrO_4$ is isomorphous or, at least, structurally similar to the corresponding selenate, four non-equivalent ammonia molecules and twelve non-equivalent hydrogen atoms would be present in both structures. Even if the maximal symmetry of the ammonia molecules is maintained (for example, as a result of a practically unrestricted rotation), at least eight bands would be expected in the N-H stretching region. As seen, however, even in the LNT spectra the number of $v(NH_3)$ bands in both spectra is smaller than expected (Fig. 2) so that the suspected isomorphism could not either be confirmed or rejected on this basis alone.
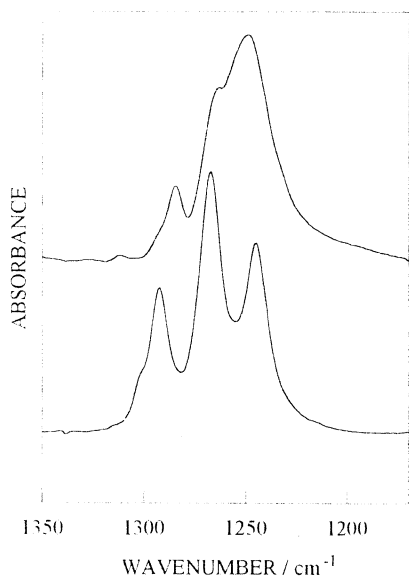
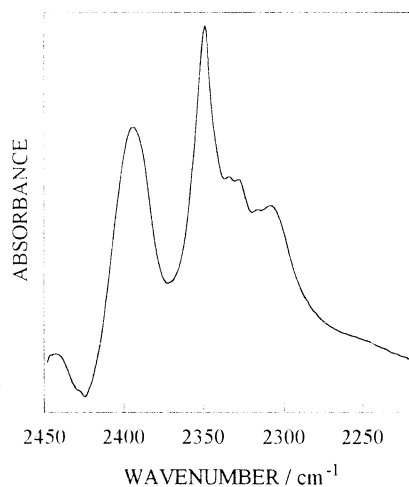Fig. 3. The $\delta_s(NH_3)$ region in the deconvoluted spectra of $[Cu(NH_3)_4]CrO_4$ (upper curve) and of $[Cu(NH_3)_4]SeO_4$

Fig. 4. The N-D stretching region in the spectrum of slightly deuterated $[Cu(NH_3)_4]CrO_4$

In order to study this problem further, we decided to analyze the spectra of the partially deuterated analogue of $[Cu(NH_3)_4]CrO_4$. The N–D stretching region in the spectra of the isotopically isolated NH_2D molecules are shown[1] in Fig. 4. As seen, the bands are overlapped and only seven absorption maxima or shoulders are observed in the deconvoluted spectrum. Among them, the highest-frequency band is much weaker than that at ≈ 2393 cm^{-1} or than the bands forming the complex feature whose main maximum is found at 2349 cm^{-1} where the overlap is particularly pronounced (ill-resolved peaks are observed at its low-frequency side around 2337, 2330, 2317 and 2308 cm^{-1}). In any case, the actual number of overlapped components must be far greater than the number of observed bands (or shoulders). Furthermore, the number of stronger hydrogen bonds must exceed that of the weaker ones. It is important to add that the situation is similar in the corresponding region of the spectrum of the selenate [15] although the separation between the components in the latter case is more noticeable. Thus, the structural similarity between the two compounds is again indicated but the structures seem to be far from being identical.

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[1] In order to eliminate the influence of the bands which are present in the same region of the spectrum of the protiated compound, the latter has been subtracted from the spectrum of the partially deuterated $[Cu(NH_3)_4]CrO_4$. Finally, the difference spectrum has been deconvoluted using the GRAMS/386 routine.

Another point is worth mentioning. As seen in Fig. 2, the centroid of the feature in the N-H stretching region in the spectrum of the chromate compound appears at slightly lower frequencies than in that of the corresponding selenate, indicating that a slightly stronger over-all hydrogen bonding exists in the former case. This is unexpected since on the basis of the conventional (Pauling's) electronegativities a notably higher electron density around the oxygen atoms in the CrO_4^{2-} would be intuitively anticipated than within the SeO_4^{2-} ions. The electronegativity value for Cr (1.66) is, namely, much smaller than that for Se (2.55) and it would appear that the difference between the electronegativities of the chromium and oxygen atoms should be much greater than that between the electronegativities of the selenium and oxygen atoms. As a consequence of that, the chromate ions would be expected to be considerably better proton-acceptors than the selenate ones. As pointed out above, this is *not* in agreement with the experimental data obtained from the spectra. This contradiction is resolved if the electronegativity value for Cr(VI) (3.37) given by Sanderson [14] is taken into account. This value is much greater than the conventional one and even bigger than the corresponding one (3.014) for selenium(VI). As a consequence, according to this model, the difference in the electronegativity between Cr and O is much closer to that between Se and O and this may explain the observed *slight* difference in the frequency of the N-H stretching bands in the spectra of the two investigated compounds.

The NH_3 rocking frequency in the spectra of ammine complexes is also considered to be a good indicator for the strength of the hydrogen bonds formed by the ammonia molecules. When the hydrogen-bond strength is assessed from the $\rho(NH_3)$ frequency it is expected that the increase in the hydrogen bond strength would give rise to higher ammonia rocking frequencies. In our spectra the corresponding band is found at *lower* frequencies in the chromate than in the selenate spectra (Fig. 2) although on the basis of the analysis of the N-H stretching region, one would expect the opposite to be true. Since the frequency difference is not large, this result is in agreement with the assumption that the hydrogen bonds formed with CrO_4^{2-} anion as proton-acceptor are not, on

the average, significantly different in strength from those formed with the oxygens of the SeO_4^{2-} anion serving as proton-acceptors. Nevertheless, the unexpected trend (lower frequency of the rocking NH_3 mode in the chromate than in the selenate spectrum) indicates that this frequency is determined by a number of factors and not solely by the strength of the hydrogen bonds formed by the ammonia molecules. On the other hand, the fact that the N-H stretching frequencies are not higher than for the selenate must be a consequence of the fact that these frequencies depend on all the structural peculiarities and not only on the expected electron density around the acceptor atoms.

Conclusions

To summarize, it is clear that the conclusions based only on the conventional electronegativity values do not always agree with the experimental data and a more sophisticated treatment should be adopted. In the present case, the use of electronegativity values different from the commonly used ones explained the observed controversies but we have found examples where such a substitution did not change the trends in the electronegativity differences and yet the spectra did not support the conclusions based on these differences. For example, the electronegativity of fluorine is considerably higher than that of oxygen and that of beryllium is much lower than that of sulfur irrespective of the scale (Pauling's, Mulliken's or that proposed by Sanderson), but the spectra of sulfate–tetrafluoroberyllate isomorphous pairs [1-3,15,16] nevertheless show that when BeF_4^{2-} anions serve as proton–acceptors, the hydrogen bonding is not appreciably stronger than that in the case where the sulfate oxygens are acceptors. In fact, a preliminary *ab-initio* calculation showed [16] that the partial electric charge on the sulfate oxygen atoms was *higher* than that of the fluorine atoms of the BeF_4^{2-} anions.

As far as the structural similarity between the chromate and the selenate is concerned, the comparison of the spectra strongly indicates that the two structures are similar, although apparently they are not strictly isomorphous. The symmetry of the complex tetraamminecopper(2+) ions seems to be higher in the former case, a conclusion based

mainly on the fact that the NH_3 stretching bands in the spectrum of $[Cu(NH_3)_4]CrO_4$ are closer together than those in the spectrum of $[Cu(NH_3)_4]SeO_4$.

ACKNOWLEDGMENTS

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POVZETEK

Analizirani so Fourier-transformirani infrardeči (FTIR) spektri tetraaminbakrovega(II) kromata(VI) posneti pri sobni temperaturi in temperaturi vrelišča tekočega dušika. Analizirani so tudi spektri deloma devterirane spojine. Podobnost med infrardečimi spektri [Cu(NH3)4]CrO4 in [Cu(NH3)4]SeO4 kaže na strukturno sorodnost med obema spojinama. Vodikove vezi med amonijevimi molekulami in kromatnim anionom niso bistveno različne v moči kot kadar je proton akceptor selenatni anion.