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**AN INFRARED ABSORPTION STUDY
OF THE PHASE TRANSITION IN HEXAMMINE
CADMIUM (II) CHLORIDE**

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IN HEXAMINE CADMIUM (II) CHLORIDE

BADANIE PRZEJŚCIA FAZOWEGO W $\text{Cd}(\text{NH}_3)_6 \text{Cl}_2$ METODĄ ABSORPCJI
W PODCZERWIENI

ИССЛЕДОВАНИЕ ФАЗОВОГО ПЕРЕХОДА В $\text{Cd}(\text{NH}_3)_6 \text{Cl}_2$ МЕТОДОМ
ИНФРАКРАСНОГО ПОГЛОЩЕНИЯ

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The infra-red absorption spectra of the $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ compound were obtained in the $80 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$ frequency range as a function of temperature from 90 K to 300 K. Two additional bands appeared at the phase transition temperature $T_0 = 175 \text{ K}$ in the far-infrared range. They were assigned as the torsional modes of the NH_3 groups. The phase transition was also observed in the middle infrared region: two bands connected with the internal deformation of the NH_3 groups split into two components each below T_0 . These results confirm the Bates and Stevens theory of the dynamic character of the phase transition for hexammine metal (II) halides.

Otrzymano widma absorpcyjne w podczerwieni dla związku kompleksowego $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ w przedziale częstości $80 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$ w zakresie temperatur od 90 K do 300 K. W temperaturze przejścia fazowego $T_0 : 175 \text{ K}$ zaobserwowano pojawienie się dwóch dodatkowych pasm w obszarze dalekiej podczerwieni, które zinterpretowano jako pochodzące od drgań torsyjnych grup NH_3 . W obszarze średniej podczerwieni przejście fazowe jest również widoczne, a mianowicie pasma drgań deformacyjnych dla grup NH_3 rozszczepiają się w temperaturze T_0 . Otrzymane wyniki potwierdzają teorię Bates'a i Stevens'a o dynamicznym charakterze przejścia fazowego w sześciocamminowych halogenkach metali (II).

Получены спектры инфракрасного поглощения для комплексного соединения $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ в диапазоне частот $80 - 4000 \text{ см}^{-1}$ при температурах $90 - 300 \text{ К}$. В температуре фазового перехода $T_c = 175 \text{ К}$ обнаружено возникновение двух добавочных полос в области дальнего инфракрасного диапазона, которые объясняются как результат торсионных колебаний NH_3 групп. В области среднего инфракрасного диапазона фазовый переход тоже обнаруживается благодаря расщеплению в T_c некоторых полос связанных с деформационными колебаниями NH_3 групп. Полученные результаты подтверждают теорию Бейтса и Стивенса об динамическом характере фазового перехода в шестиаминохлориде кадмия.

1. INTRODUCTION

Hexammine metal (II) halides of a general formula $M(NH_3)_6 X_2$ have face - centred cubic structure at room temperature /1/. When the temperature is lowered to T_c (which depends on the metal M and the halide X) the phase transition occurs. This is not only connected with a reducing of the symmetry of the unit cell but also with a critical slowing down of NH_3 groups /2/. The structures of the low - temperature phase are known only for some of these compounds; e.g.: $Fe(NH_3)_6 Cl_2$ and $Ir(NH_3)_6 Cl_2$ are monoclinic /3/, whereas $Ni(NH_3)_6 I_2$ is trigonal below T_c /3/.

A theoretical model to explain the mechanism of the phase transitions in hexammine metal (II) halides was suggested by Bates and Stevens /2,4/. According to it the NH_3 groups in each cation reorientate collectively between eight equivalent low-energy arrangements in the high-temperature phase. At a phase transition temperature T_c the reorientations of the NH_3 groups become frozen as one of these arrangements becomes preferred. This critical slowing down of the NH_3 reorientation leads to a trigonal unit cell. One may expect that the effect of a structural distortion below T_c will be visible in a skeleton vibration range of the complex cation i.e. in the range from 100 cm^{-1} to 400 cm^{-1} .

The Raman spectra presented by Bates et al. /3/ for the $Cd(NH_3)_6 Cl_2$ and $Cd(ND_3)_6 Cl_2$ compounds reflect indeed the dynamic changes at the phase transition temperatures (175 K and 185 K respectively). Bands which in the high-temperature phase have T_{2g} symmetry split or become asymmetric in the low-temperature phase. Apart from that one or two additional bands appear in the low frequency region. These additional bands are connected with the torsional modes of the NH_3 groups. Bates et al. /3/ discuss on the basis of the group-theory analysis the changes observed in the Raman spectra and they suggest the C_{2h} symmetry for the structure of the low-temperature phase in the $Cd(NH_3)_6 Cl_2$ case.

In this paper the infrared spectra obtained by us for $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ in the frequency range from 80 cm^{-1} to 4000 cm^{-1} are presented and discussed.

2. EXPERIMENTAL

2.1. Preparation of the $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ sample

The $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ sample was obtained from $\text{CdCl}_2 \cdot \frac{5}{2}\text{H}_2\text{O}$. The latter was placed in a glass tube through which dry gaseous ammonia was blown. Ammonia was dried by passing through several vessels which were filled with ascarite and finally with barium oxide. At first, the glass tube containing the $\text{CdCl}_2 \cdot \frac{5}{2}\text{H}_2\text{O}$ with ammonia passing through it was heated for several hours to ca. 90°C in order to remove water from the sample. In the later stage the tube was cooled down to about 0°C in order to stabilize the $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ sample (sensitive to NH_3 losing).

The whole process of obtaining $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ sample lasted several days without any break.

In order to measure the ammonia and cadmium ions contents, the final product was submitted to chemical analysis /5/ which gave the following content of NH_3 and Cd^{++} :

% NH_3	= 35.63% \pm 0.24%	(theoret. % NH_3 = 35.79%)
% Cd	= 39.42% \pm 0.07%	(theoret. % Cd = 39.37%)

2.2. Far-infrared measurements

The absorption spectra in the 80 cm^{-1} - 400 cm^{-1} region were obtained using the Grubb Parsons Fourier spectrometer IRIS. The measurements were performed in the temperature range from 90 K to 300 K with the temperature stabilization accuracy of ca. 1 K. The resolution was 4 cm^{-1} . The sample was prepared in the form of a suspension of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ with nujol.

2.3. Infrared measurements

The absorption spectra in the 400 cm^{-1} - 4000 cm^{-1} region were obtained using the Carl Zeiss-Jena spectrometer UR-10.

The measurements were carried out in the temperature range from 80 K to 300 K. The resolution was ca. 5 cm^{-1} . The sample was prepared in the form of a nujol suspension as for the far-infrared measurements. Apart from the nujol suspension spectra we obtained the absorption spectra of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ in KBr pressed discs. In this case however the sample was unstable and decomposed, probably during pressing. So we believe that for the KBr disc samples we obtained spectra of $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ rather than those of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ as the $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ complex is the more stable compound than $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ one /6/.

3. RESULTS

3.1. The spectra in the $80 \text{ cm}^{-1} - 400 \text{ cm}^{-1}$ frequency range

The absorption spectra of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ in the far infrared region are shown in Fig. 1. The high-temperature phase spectra are quite similar to those obtained earlier for the $\text{Ni}(\text{NH}_3)_6\text{X}_2$ compounds /7/. All infrared-active vibrations have T_{1g} symmetry and are connected with the lattice vibration, the deformation vibration $\delta(\text{NCdN})$ and the stretching vibration $\nu(\text{CdN})$ respectively. The $\delta(\text{NCdN})$ mode overlaps with a broad additional band later on referred to as the A band. This additional band which shows up between the lattice and the deformation mode was observed before in both far-infrared and Raman spectra of complexes with simple anions X /7,8/. We believe that the band A is connected with a quasi-free (low barrier) rotation of NH_3 groups in the high-temperature phase /8/.

In our measurements the phase transition for $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ was clearly visible in the far-infrared region. At the phase transition temperature 175 K the band A disappears and two sharp peaks emerge in the same frequency range. This phenomenon is similar to that observed by Bates et al. /3/ in the Raman spectra of $\text{Cd}(\text{NH}_3)_6\text{X}_2$ and $\text{Cd}(\text{ND}_3)_6\text{X}_2$. These new bands are obviously connected with the torsional vibrations of the NH_3 groups.

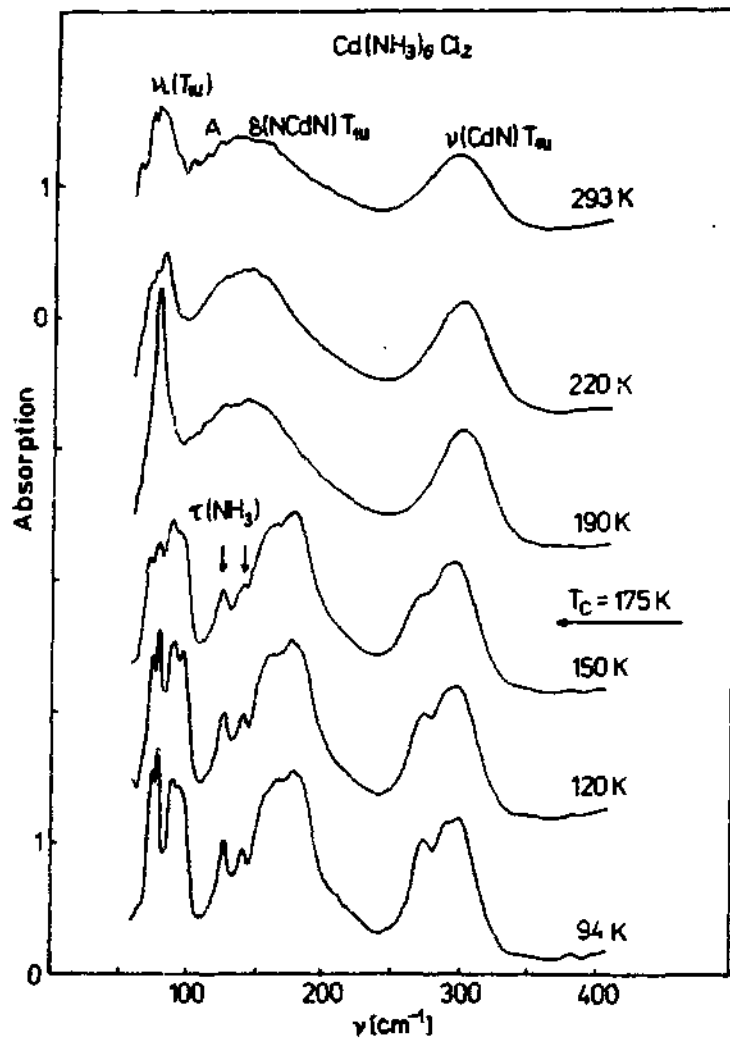


Fig. 1. IR spectra of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ in the 80 - 400 cm^{-1} frequency range

Moreover, the bands corresponding to high-temperature phase T_{1u} modes split in the low-temperature phase into at least two components, as the result of removing the degeneracy of modes. The frequencies of the modes observed in the far-infrared spectra of the high and of the low-temperature phases are given in Table 1.

3.2. The spectra in the 400 cm^{-1} - 4000 cm^{-1} frequency range

The absorption spectrum of the high-temperature phase in this frequency range consists of five bands connected with: the rocking vibration $\rho(\text{NH}_3)T_{1u}$, two deformation vibrations: $\xi_g(\text{HNH})T_{1u}$, $\xi_g(\text{HNH})T_{1u}$ and two stretching vibrations: $\nu_g(\text{NH})T_{1u}$, $\nu_g(\text{NH})T_{1u}$ respectively. The best spectrum of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ obtained at room temperature is shown in Fig. 2. Two bands which are connected with the stretching vibrations $\nu(\text{NH})T_{1u}$ are very broad and overlap partially. Two NH_3 deformation vibrations have the frequencies of 1090 cm^{-1} and 1600 cm^{-1} respectively. The additional band at 1200 cm^{-1} we interpret as a band which is connected with the deformation vibration of the NH_3 group in the $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ compound /10/. As it was mentioned above, $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ is more stable than $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ hence we suppose that all the absorption spectra in the medium infrared range have some admixture of $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ bands.

The phase transition is visible in the now discussed frequency range, especially in the range of the deformation vibrations of the NH_3 groups. The band at 1090 cm^{-1} shifts toward higher frequencies by ca. 40 cm^{-1} and splits into two components below T_c (Fig. 3). The second band connected with the deformation vibrations of the NH_3 groups i.e. that at ca 1600 cm^{-1} also splits into two components in the low-temperature phase (Fig.3).

The infrared active vibrations for the $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ compound are given in Table 1 for both the high-temperature and the low-temperature phases.

Table 1. The frequencies of the IR active modes observed above and below T_0 in the 80 cm^{-1} - 4000 cm^{-1} range for $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$. (All frequencies in cm^{-1})

temp.	ν_L	$\nu(\text{NH}_3)$	$\delta(\text{NCdN})$	$\nu(\text{CdN})$	$\rho(\text{NH}_3)$	$\delta_B(\text{HNH})$	$\delta_0(\text{HNH})$	$\nu_0(\text{NH})$	$\nu_B(\text{NH})$
room temp.	78	broad band A 100-166		297	615	1100	1585	3220	3350
				298 ^a	613 ^a	1091 ^a	1585 ^a		
190 K	76	broad band A 100-166		301	615	1090	1600	3220	3320
$T_0=175 \text{ K}$									
150 K	72	125	162	271	620	1130	1580	3230	3320
	78	141	178	295		1150	1600		
	88								
	96								

a - data reported in ref. /9/

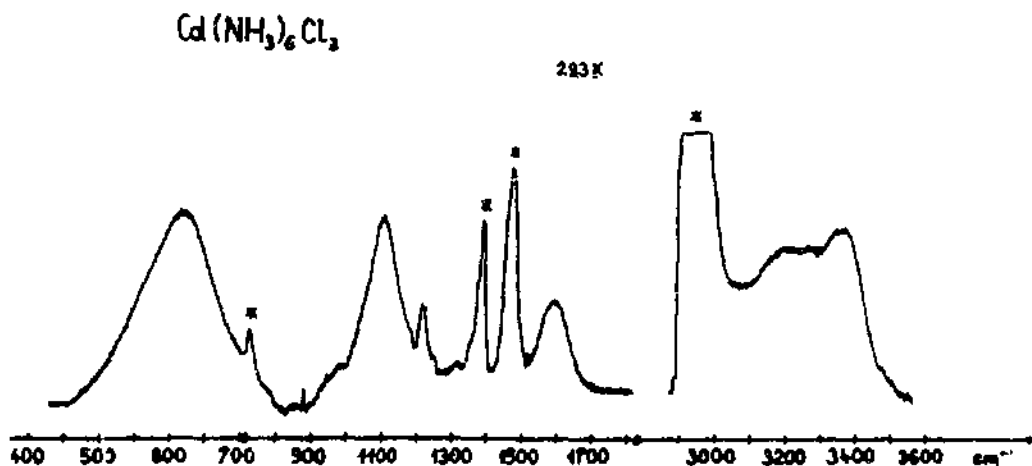


Fig. 2. IR spectrum of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ at room temperature in the 400 - 4000 cm^{-1} frequency range. The asterisks indicate bands connected with nujol

4. DISCUSSION

The 69 internal modes of the $\text{M}(\text{NH}_3)_6^{++}$ cation should be divided via the group theory (for space group $\text{Fm}\bar{3}\text{m}$) into following species:

$$\Gamma_{\text{int}} = 3A_{1g} + 3E_g + 4T_{1g} + 4T_{2g} + A_{1u} + E_u + 7T_{1u} + 4T_{2u}$$

Six of them are connected with the torsions of the NH_3 groups:

$$\Gamma_{\text{tors}} = A_{1u} + E_u + T_{1g}$$

All these and also the modes of T_{2u} symmetry are both infrared- and Raman-inactive.

If we assume, according to Bates et al. /3/ that the low-temperature point group of $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ is C_{2h} we obtain the following correlation diagram for the inactive modes:

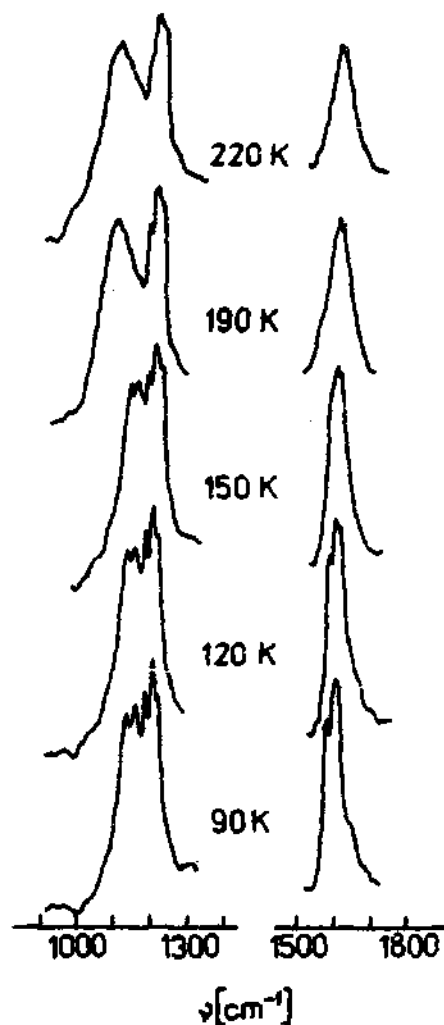
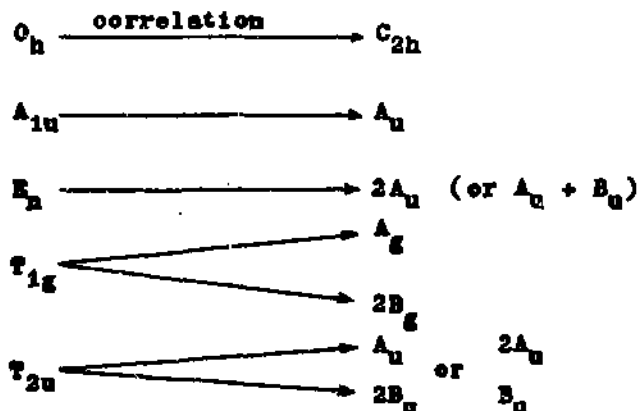


Fig. 3. The temperature evolution of the $\delta_g(\text{HNH})$ at ca. 1100 cm^{-1} and $\delta_e(\text{HNH})$ at ca. 1600 cm^{-1} bands in $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$. The phase transition temperature is equal to 175 K . The band at ca. 1200 cm^{-1} , discussed in the text, corresponds to an admixture of $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ in the sample.



A_g and B_g modes are now Raman - active while A_u and B_u modes are infrared active. So, the reducing of the unit cell symmetry from cubic to monoclinic one, should be connected with showing up of six new bands which correspond to torsions of the NH_3 groups. Three of them should be visible in the infrared spectrum and the other three in the Raman spectrum. In the IR we observe only two torsional bands. A similar situation is reported by Bates et al. /3/ for the Raman spectrum. According to their /3/ explanation this may be caused by the fact that the rotations about two axes are equivalent in C_{2h} group, and thus the $Cd(NH_3)_6^{++}$ cation has an axial symmetry for the low-temperature phase.

Moreover, as it can be seen from the correlation diagram, the infrared-inactive modes of the T_{2u} symmetry for O_h point group should become infrared-active for C_{2h} point group. There are four internal modes of T_{2u} symmetry for the high-temperature phase of $M(NH_3)_6X_2$. They are connected with: the deformation vibration of the cation - $\delta(NHN)$, the rocking vibration of the NH_3 groups - $\rho(NH_3)$, the angle deformation in the NH_3 group - $\xi_0(HNH)$, and the stretching vibration in the NH_3 group - $\nu_0(NH)$. Thus one may expect that additional bands arising from these modes will appear in the low-temperature phase spectra. However, we do not observe them, although it may be that the splittings which we observe for the deformation

vibrations in the whole infrared range are in fact not splittings but vibrations arising from those of T_{2u} symmetry which became active. For example the maximum at 178 cm^{-1} (Fig. 1) could be connected with the deformation of cation which became active in the low-temperature phase but, rather, we suppose that this maximum is connected with the T_{1u} deformation vibration observed in the high-temperature phase which shifts toward higher frequencies and splits into two components at the phase transition temperature.

An obvious possibility to explain the fact that we do not observe a proper number of bands in our low-temperature phase spectra may be connected with the poor resolution of the spectra. All bands visible in the absorption spectrum are rather broad and it may very well be that some of them remain unresolved. It is also possible that some of the additional bands are too weak to be detected.

It is worthwhile to notice that the width of the $\delta_0(\text{ENE})$ band at 1600 cm^{-1} decreases when the temperature decreases to T_c . This may be connected with a slowing down of NH_3 reorientations in agreement with the Bates and Stevens model /2/. This corroborates the observed replacement of the broad A band by the two torsional peaks in the far-infrared when passing from the high - to the low temperature phase.

5. CONCLUSIONS

The infrared measurements for $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ presented in this paper were carried out in order to complete the Bates et al. /3/ Raman investigation of the hexammine cadmium (II) halides.

The phase transition in $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ is distinctly visible in the infrared absorption spectra. Two new bands connected with the torsions of the NH_3 groups appear in the low-temperature phase in the far infrared region. Two bands connected with the internal deformation of the NH_3 groups split into two components each below the phase transition temperature in the medium infrared frequency range. It confirms the Bates and

Stevens theory /2/ of the dynamic changes which take place at the phase transition temperature for hexamine metal (II) halides. This transition arises from the critical slowing down of the NH_3 reorientation. The freezing of the reorientation can thus be observed both in the infrared and in the Raman spectra of these compounds /3/.

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