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PHASE TRANSITION IN METAL HEXAMMINE COMPLEXES

I. THE INFRARED SPECTRA OF  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ \*

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## ABSTRACT

Far i.r. spectra of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  were recorded above and below the order-disorder phase transition at  $T_c = 243$  K. The results are compared to the spectra of the isomorphous crystal  $\text{NiCl}_2 \cdot 6\text{NH}_3$ , which has no transition in the same temperature range. The antisymmetric stretching vibration of the ammonias shows a broken degeneracy below  $T_c$  for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ . No broken degeneracy was observed in the nickel-nitrogen vibration of the  $[\text{Ni}(\text{NH}_3)_6]^{++}$  clusters. The discussion of our results lends support to the assumption that the phase transition is due to the collective freezing of the degrees of rotation of the ammonias.

## I - INTRODUCTION

This article is the first of a series of papers on the phase transition properties of some metal hexammine complexes. We report here the infrared spectra of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ . Optical, EPR and NMR spectra and thermal measurements will be the subject of future communications.

The phase transition of the hexammine nickel halide complexes ( $\text{NiX}_2 \cdot 6\text{NH}_3$ , X = Cl, Br, I) has been largely studied in the last years. The ammonia cooperative transition induces a separation of the EPR line of  $\text{Ni}^{++}$  below the transition temperature in the magnetic diluted crystals<sup>1</sup> and a broadening of the isotropic single line in undiluted crystal.<sup>2</sup> Specific heat<sup>3,4</sup> and magnetic susceptibility<sup>5</sup> measurements show an antiferromagnetic transition in these crystals at liquid He temperatures.

The  $\text{NiCl}_2 \cdot 6\text{NH}_3$  has a phase transition at 76 K characterized by a sudden broadening<sup>6</sup> of the EPR line. Magnetic susceptibility measurements show that this transition is not of magnetic nature<sup>2</sup>. Bates and Stevens<sup>7</sup> and Bates<sup>8</sup> proposed a theoretical model to explain the broadening of the EPR line in the undiluted complexes. It was proposed that the ammonia ordered cooperatively by electrostatic interaction between nearest neighbor clusters of  $[\text{Ni}(\text{NH}_3)_6]^{++}$ . The critical temperature  $T_c$  depends only on the lattice parameter.  $T_c$  is

approximately 76 K for  $\text{NiCl}_2\text{6NH}_3$  ( $a=10.09 \text{ \AA}$ ), 45K for  $\text{NiBr}_2\text{6NH}_3$  ( $a=10.48 \text{ \AA}$ ) and 24K for  $\text{NiI}_2\text{6NH}_3$  ( $a=11.01 \text{ \AA}$ ).

The isomorphous complex  $\text{Ni}(\text{NO}_3)_2\text{6NH}_3$  would have the same properties of the halides, but the presence of the  $\text{NO}_3^-$  anion makes the analysis more complex.

The crystal structure of  $\text{Ni}(\text{NO}_3)_2\text{6NH}_3$  was initially studied by Wyckoff<sup>9</sup>. The nickel atoms occupy a f.c.c. lattice with  $a=10.96 \text{ \AA}$ . Each Ni is in the center of an octahedral environment of six ammonias, forming a cluster  $[\text{Ni}(\text{NH}_3)_6]^{++}$ . This cluster is placed at the center of a cube with edge  $a/2$  whose vertices are occupied by  $\text{NO}_3^-$ . Wyckoff attributes paramorphic hemihedral symmetry  $m3(T_h)$  to the complex. This structure was later contested by Kracek et al<sup>10</sup>, whose conclusions from investigations of others nitrate crystals showed that the  $\text{NO}_3^-$  group is rotating in the unit cell, with spherical symmetry. Yu<sup>11</sup> investigated the crystalline structure from 80K to 300K with powder and oscillation photographic techniques. His results show that the  $\text{Ni}(\text{NO}_3)_2\text{6NH}_3$  crystal has the holohedral symmetry  $m3m(O_h)$ , and that triangular planes of  $\text{NO}_3^-$  are oscillating with large amplitudes. One of the oxygens oscillates about the line which passes through the average positions of the other two.

Specific heat measurements<sup>12</sup> exhibit a  $\lambda$  type peak at 243 K, which was initially attributed to an order-disorder changing in the orientations of the  $\text{NO}_3^-$  group with respect to the crystal axes. It was also observed an anomaly at 90 K<sup>13</sup>. EPR measurements in the undiluted complexes<sup>14</sup> show a line broadening at 243 K, which is quite similar to the one observed

for the isomorphous halides. Moreover the observed line width between the antiferromagnetic phase transition ( $T_N = 1.35\text{K}$ )<sup>15</sup> and the order-disorder transition ( $T = 243\text{K}$ ) does not exhibit considerable variations. Hysteresis of about 5 K was observed through the transition, in good agreement with the results from dilatometric measurements<sup>16</sup>. The magnitude of the entropy of transition for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  is of the same order as the observed one for  $\text{NiCl}_2 \cdot 6\text{NH}_3$ <sup>17</sup>. This lends support to the suggestion that the transition in  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  is entirely due to the ammonia, and that the order-disorder model involving the radical  $\text{NO}_3^-$  is not good.

We have two models to be considered if we assume that the phase transition is due to the ammonias: (1) the mechanical brake model<sup>17</sup>, i.e., the unit cell is distorted through the transition and the triangles of the hydrogens overlap with the anions, (2) the Bates and Stevens model, i.e., a cooperative freezing of the degrees of freedom of rotation of the ammonias. The X-Ray data show large amplitudes of oscillation of the  $\text{NO}_3^-$  groups, which are possible if the  $\text{NO}_3^-$  groups are subjected to a very broad potential. This observation rules out the use of the mechanical brake model. On the other hand, the critical temperature of the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  complex is larger than the expected one from the Bates and Stevens's model. The  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  complex has the lattice parameter of the order of the one observed for  $\text{NiI}_2 \cdot 6\text{NH}_3$ . From the Bates and Stevens's model we would expect  $T_c = 20\text{K}$ , which is about 12 times lower than the observed value.

As the vibrational spectra can give insights on the hypothesis discussed above, we recorded infrared spectra of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  above and below  $T_c$ , using  $\text{NiCl}_2 \cdot 6\text{NH}_3$  as a reference.

## II - SAMPLE AND APPARATUS

The  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  and  $\text{NiCl}_2 \cdot 6\text{NH}_3$  crystals were prepared by reactions of  $\text{NiCO}_3$  with solutions of nitric and chloridric acids, respectively. The crystals of about 1mm of size were grown at room temperature and dried in an ammonia atmosphere to prevent decomposition by ammonia loss. An analysis made by distillation process gave an approximate value of 99% for the ammonia content in both samples.

The infrared spectra with mulled samples (Nujol) were recorded with a IR-180 Perkin Elmer spectrometer, using CsI and polyethylen windows. The low temperature measurements were made in a low temperature cell. Windows of CsI were mounted in a cold finger kept in vacuum and cooled by liquid nitrogen and other cryogenic substances. The minimal temperature obtained by us was about 110 K. The contact between the windows and the cold finger was not perfect and the i.r. radiation absorbed was enough to prevent lower temperatures in the windows. So, it was not possible to observe the region, at about 90 K where an anomaly in the specific heat was observed<sup>13</sup>.

III - RESULTS AND DISCUSSION

The absorption lines are given in Table 1. The free ammonia molecules have  $C_{3v}$  symmetry and two lines of  $A_1$  and E

INSERT TABLE 1

species assigned to the stretching vibrations of  $NH_3$ . The spectra obtained by us show a broad band with two poorly resolved lines. That is, the ammonias of the crystals behave as free molecules, except by the fact that the lines are broad. The absorption lines at  $3365\text{ cm}^{-1}$  and  $3340\text{ cm}^{-1}$  for the  $Ni(NO_3)_2 \cdot 6NH_3$  and the  $NiCl_2 \cdot 6NH_3$  were assigned to the mainly antisymmetric vibrations, because they appear as the head of the lines. The lines at  $3280\text{ cm}^{-1}$  and  $3240\text{ cm}^{-1}$  for  $Ni(NO_3)_2 \cdot 6NH_3$  and  $NiCl_2 \cdot 6NH_3$  were assigned to the mainly symmetric vibrations. The lines of very small intensity at  $3220$  and  $3495\text{ cm}^{-1}$  for  $Ni(NO_3)_2 \cdot 6NH_3$ , and at  $3290\text{ cm}^{-1}$  for  $NiCl_2 \cdot 6NH_3$ , were assigned to traces of water.

The stretching frequencies of the free ammonias are larger than those observed in crystals. This was also observed in other  $MX_2 \cdot 6NH_3$  crystals, and attributed to small interactions (like hydrogen bonds, electrostatic interactions, etc.) between the ammonias and X<sup>18,21</sup>. The frequencies of the  $Ni(NO_3)_2 \cdot 6NH_3$  lines are greater than those observed for  $NiCl_2 \cdot 6NH_3$ . So, it is

reasonable to suppose that the interaction between  $\text{NO}_3^-$  and the ammonias is lower <sup>than</sup> between  $\text{Cl}^-$  and the ammonias. This is supported by the large amplitude of oscillation observed in the  $\text{NO}_3^-$  groups.

At 110 K the stretching frequencies of both  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  and  $\text{NiCl}_2 \cdot 6\text{NH}_3$  crystals show displacements to higher values. On the other hand, at 243 K the frequency assigned to the mainly antisymmetric stretching vibration shows a broken degeneracy only for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ . This effect was observed just below  $T_c$ . In figure 1, we show the stretching model of

INSERT FIGURE 1

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  at room temperature and 110K. The broken degeneracy of the antisymmetric model through the transition, show the lowering of the symmetry of the ammonias at  $T_c$ .

If the ammonia molecule is treated as a single entity, the  $[\text{Ni}(\text{NH}_3)_6]^{++}$  cluster can be regarded as possessing at room temperature the symmetry  $O_h$ . Two infrared absorption lines of species  $F_{1u}$  are expected. The line assigned to the mainly nickel nitrogen stretching vibration was observed at  $325 \text{ cm}^{-1}$  for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  and at  $330 \text{ cm}^{-1}$  for  $\text{NiCl}_2 \cdot 6\text{NH}_3$ . At temperatures below  $T_c$  for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ , and at 110 K for  $\text{NiCl}_2 \cdot 6\text{NH}_3$ , these lines show displacements to higher values only. However, the line at  $330 \text{ cm}^{-1}$  for  $\text{NiCl}_2 \cdot 6\text{NH}_3$ , recorded after a brief exposure to humid air, in a closed bottle, shows a single sharp absorption



line at room temperature and a broken degeneracy at 110 K ( see figure 2 ) . This observation shows that the distortion may

INSERT FIGURE 2

be due to the loss of a small amounts of ammonia in the crystal and probable substitution by water. On the other hand, we observe that the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  crystals are more stable than the  $\text{NiCl}_2 \cdot 6\text{NH}_3$  ones. A brief exposure to humid air, in a closed bottle does not alter the recorded spectra of the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  crystals.

The relation between the intensities of the lines assigned to the skeleton,  $I\{\nu(\text{NiN})\}/I\{\sigma(\text{NNiN})\}$  is smaller than 1 for  $\text{NiCl}_2 \cdot 6\text{NH}_3$  and larger than 1 for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  (see figure 3). The region of observation is the same for

INSERT FIGURE 3

both crystals. So, we say that the line assigned to the mainly metal-ammonia bending vibration has larger intensity for the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  crystals than for the  $\text{NiCl}_2 \cdot 6\text{NH}_3$  crystal. The lattice vibrations of the nitrate observed for  $\text{M}(\text{NO}_3)_2$  ( $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$ ) crystals<sup>22</sup> have frequencies below  $200 \text{ cm}^{-1}$ . If we put  $\text{M} = |\text{Ni}(\text{NH}_3)_6|^{++}$ , the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  crystal has the same structure of these crystals and analogous lattice vibrations are expected.

8

So, there is a possible coupling of the vibrations at  $220 \text{ cm}^{-1}$  for the  $[\text{Ni}(\text{NH}_3)_6]^{++}$  cluster and the lattice vibrations of the nitrate. This coupling increases the intensity of the line at  $220 \text{ cm}^{-1}$  for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ .

The two lines of  $F_{1u}$  species assigned to the  $[\text{Ni}(\text{NH}_3)_6]^{++}$  clusters show that they have  $O_h$  symmetry, both above and below  $T_c$ . That is, the symmetry of the clusters is not modified through the phase transition. This result differs from the situation reported for  $\text{CoCl}_2 \cdot 6\text{NH}_3$ , where broken of the degeneracy of the line at  $330 \text{ cm}^{-1}$  was observed.

#### IV - CONCLUSIONS

The present data do not support the mechanical brake model to explain the phase transition in  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ . In this model the distortion of the unit cell causes the overlapping of the triangles of hydrogens with the anions. This increases the interaction between the nitrate and the ammonia and will lead to a decrease of the strength of the N-H bond, with a shifting of the frequencies to lower values. Such a shifting was not observed in the spectra. On the other hand, if the unit cell suffers a distortion, it is reasonable to expect the distortion of the symmetry of the  $[\text{Ni}(\text{NH}_3)_6]^{++}$  clusters. This was also not observed.

The Bates and Stevens model has two restrictions. The first is the large value of  $T_c$ . The second is the lowering of symmetry of the ammonia molecules. The triangles of hydrogens

are at the faces of a cube in center of which is the  $\text{Ni}^{++}$ . The axes perpendicular to the faces of this cube pass through the  $\text{Ni}^{++}$ , the nitrogen and the center of the triangles. This model is not compatible with the broken of degeneracy observed in figure 1. The above considerations would be accounted for by the following arguments:

(1) Each ammonia molecule is supposed to be in a rotational potential well due to the eletrostatic interactions between its hydrogen triangle and the hydrogen and oxygen triangles of the other ammonias and nitrates.

(2) There is a small non axial component in the rotational ground state of the rotational potential well. Above  $T_c$  the ammonia molecules are in an excited rotational state and the non axial component of the rotational potential is averaged out.

Itens (1) and (2) are going to be subjected to new experimental tests and theoretical calculations.

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TABLE 1

INFRARED SPECTRA OF  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  AND  $\text{NiCl}_2 \cdot 6\text{NH}_3$  ( $\text{cm}^{-1}$ )

	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$		$\text{NiCl}_2 \cdot 6\text{NH}_3$		
	T=300 K	T=110 K	T=300 K	T=300 K	T=110K
	—	3495	—	—	—
$\nu_e(\text{NH}_3)$	3365	3375 3360	3340	3370*	3340
$\nu_a(\text{NH}_3)$	3280	3280	3240	—	3240
	3220	3220	3190	—	3190
	2390	2385	—	—	—
	1755	1750	—	—	—
$\sigma_d(\text{NH}_3)$	1620	1620	1600	1607*	1600
$\nu(\text{NO}_3)$	1355	1355	—	—	—
$\sigma_s(\text{NH}_3)$	1210	1195	1200	1175*	1200
$\sigma_d(\text{NO}_3)$	830	835	—	—	—
$\rho_n(\text{NH}_3)$	660	670	670	680*	670
$\nu(\text{NiN})$	325	335	330	334**	335
$\sigma(\text{NNiN})$	220	230	215	215**	—

\* From ref. 20

\*\* From ref. 19

FIGURE CAPTIONS

FIGURE 1. IR absorption of NH antisymmetric stretching mode of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  at room and low temperatures.

FIGURE 2. IR absorption of  $F_{1u}$  mode assigned to nickel-ammonia of: A)  $\text{NiCl}_2 \cdot 6\text{NH}_3$ ; B)  $\text{NiCl}_2 \cdot 6\text{NH}_3$  propositely exposed to humid air. The arrow indicates a beginning of separation.

FIGURE 3. IR SPECTRA of  $F_{1u}$  modes at room temperature of:  
A)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ ; B)  $\text{NiCl}_2 \cdot 6\text{NH}_3$ .







