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The Thermal Decomposition of Hexamminenickel(II) Complexes

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From the thermogravimetric analysis, hexamminenickel(II) complexes were confirmed to decompose in two or three steps through lower ammine intermediates $NiX_m \cdot nNH_3$: $n=2$, 1 and $m=2$ for $X=Cl$; $n=2$ and $m=2$ for $X=I$, Br; $n=4$ and $m=2$ for $X=NO_3$ and $n=2$, 1/2 and $m=1$ for $X=SO_4$. The diffuse reflectance spectra of these intermediates have been measured in a range between 5000 to 27000 cm^{-1}, and they suggested that these intermediates may be polymers in which nickel ions were octahedrally coordinated with ammonia molecules and bridging halogen atoms. The infrared absorption spectra of these intermediates obtained in a range between 5000 and 60 cm^{-1} are also reported.

There have been several papers on the relative thermal stability, the stoichiometry of the decomposition process and other thermal properties of hexamminenickel(II) complexes.[1-4] In addition, the kinetics of the decomposition process and the structures of the intermediates have been reported recently.[5-10] Nevertheless, the effects of the heating rate on the processes and the structures of the intermediates in the thermal decomposition of hexamminenickel(II) complexes do not seem to be satisfactorily clear yet.

In the present study, the decomposition processes of various salts of hexamminenickel(II) have been reexamined by the methods of thermogravimetric analysis under the condition of smaller heating rates and by the chemical analysis of the intermediates. The structures of the intermediates have also been investigated by the measurements of the diffuse reflectance spectra and the infrared absorption spectra.

Experimental

Preparation of Complexes. Chloride, bromide, iodide, sulfate and nitrate of hexamminenickel(II) were precipitated from the strongly ammoniacal solution of nickel sulfate with appropriate ammonium salts. Only the sulfate was precipitated with ethanol because of its greater solubility in water. These compounds were recrystallized from concentrated ammonia, washed with ethanol and ether, and dried in air. They were identified by the measurements of their infrared absorption spectra.

Apparatus and Procedure. Thermogravimetric curves were recorded with a recording thermobalance, Shimadzu Thermano Balance RT-2, with 400 mg of sample at about 3°C/min of heating rate in nitrogen atmosphere of the flow rate of about 300 ml/min.

Hitachi infrared spectrometers EPI-2G and FIS-1 were used for the measurement of the infrared absorption spectra in the regions from 5000 to 400 cm^{-1} and from 500 to 60 cm^{-1}, respectively. Nujol mull method was adopted; in potassium bromide disk an absorption band due to ammonium ions was observed at 1400 cm^{-1}, which were considered to be formed by the reaction between ammonia of a complex or an intermediate and a trace of water contained in potassium bromide.

The diffuse reflectance spectra were recorded for magnesium oxide as a reference with a standard integrating sphere attached to a Hitachi spectrophotometer Type EPU-2 and a recording EPS-3T.

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2) F. Ephraim and F. Muller, *Ber.*, **54**, 973 (1921).

3) T. D. George and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **25**, 395 (1963).

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5) T. Flora, *Acta Chim. Acad. Sci. Hung.*, **48**(3), 225 (1966).

6) I. G. Murgulescu, E. Segal and D. Fătu, *Rev. Roumaine Chim.*, **11**(3), 291 (1966).

7) I. G. Murgulescu and E. Segal, *Acad. Rep. Polulare Romine, Studii Cercetari Chim.*, **10**, No. 1, 39 (1962).

8) I. G. Murgulescu and E. Segal, *Rev. Roumaine Chim.*, **11**(1), 13 (1966).

9) S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, **1965**, 3276.

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The chemical analysis was carried out as follows: Nickel and sulfate contents were determined by the gravimetric method by precipitating nickel ions with dimethylglyoxime and sulfate ions with barium chloride. The determination of halogens was followed by Fajans' method after removing nickel ions with a cation exchanger Dowex-50W-X8 in Na-form. Ammonia was analyzed in the following way. After a sample was dissolved into a known amount of excess standard hydrochloric acid, the unreacted acid was determined by the back titration with a standard sodium hydroxide solution. The mixed indicator, *i. e.,* the alcoholic solution of bromocresol green and methyl red, was used to detect the end-point (pH 5.5). Its color is gray or colorless at the end-point, pink in an acid and green in an alkaline region. It was found from the preliminary experiments carried out with synthetic samples that the color of nickel ions did not interfere with the detection of the end-point and the result was not affected by the amount of ammonium ions present in the solution. After removing nickel ions by using a cation exchanger in the potassium form, the nitrate content was determined with spectrophotometric method using absorption band at 200 mμ which is due to the charge transfer between a nitrate ion and a water molecule.

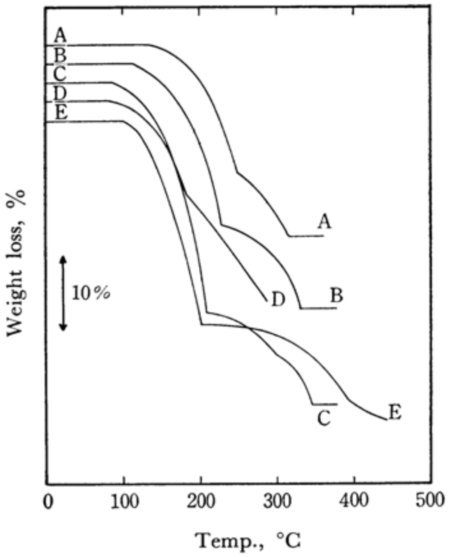

Fig. 1. Thermogravimetric curves of (A) $[Ni(NH_3)_6]I_2$, (B) $[Ni(NH_3)_6]Br_2$, (C) $[Ni(NH_3)_6]Cl_2$, (D) $[Ni(NH_3)_6](NO_3)_2$ and (E) $[Ni(NH_3)_6]SO_4$.

Results and Discussion

Thermogravimetric and Chemical Analyses. Figure 1 shows the thermogravimetric curves of hexamminenickel(II) complexes. The values of weight loss determined by the measurement of the thermogravimetric curves were well agreed with the calculated values, when the weight loss was assumed to be due to only the loss of ammonia. The analytical data of the intermediates are given in Table 1.

Hexamminenickel(II) chloride decomposed in three steps. On the thermogravimetric curves, the first one corresponding to the reaction

$$[Ni(NH_3)_6]Cl_2 \rightarrow NiCl_2\cdot 2NH_3 + 4NH_3$$

proceeded in a temperature range from 85 to 211°C, the second one corresponding to the reaction

$$NiCl_2\cdot 2NH_3 \rightarrow NiCl_2\cdot NH_3 + NH_3,$$

from 211 to 303°C and the third one corresponding to the reaction

$$NiCl_2\cdot NH_3 \rightarrow NiCl_2 + NH_3,$$

from 303 to 350°C. Since a small amount of NH_4Cl was formed above 300°C, the results of chemical analyses of $NiCl_2\cdot NH_3$ and $NiCl_2$ somewhat deviated from the calculated values. However, the diffuse reflectance spectra and the infrared absorption spectra of these two intermediates

Table 1. Analytical data of intermediates

	Ni, %		NH$_3$, %		Anion, %	
	Found	Calcd	Found	Calcd	Found	Calcd
$[Ni(NH_3)_6]Cl_2$	25.4	25.3	43.8	44.1	30.6	30.6
$NiCl_2\cdot 2NH_3$	35.6	35.9	20.6	20.8	43.4	43.3
$[Ni(NH_3)_6]Br_2$	18.3	18.3	32.0	31.9	49.9	49.8
$NiBr_2\cdot 2NH_3$	23.0	23.2	13.4	13.5	63.2	63.3
$NiBr_2$	26.4	26.9			71.3	73.1
$[Ni(NH_3)_6]I_2$	14.0	14.2	24.5	24.6	61.1	61.2
$NiI_2\cdot 2NH_3$	16.6	16.9	9.8	9.8	72.6	73.2
NiI_2	18.3	18.8			80.1	81.2
$[Ni(NH_3)_6]SO_4$	22.0	22.8	37.4	39.8	36.1	37.4
$NiSO_4\cdot 2NH_3$	30.5	31.1	17.6	18.0	51.2	50.9
$NiSO_4\cdot \frac{1}{2}NH_3$	35.4	36.0	5.0	5.2	58.6	58.8
$NiSO_4$	36.5	37.9			59.7	62.1
$[Ni(NH_3)_6](NO_3)_2$	20.5	20.6	35.9	35.9	43.9	43.5
$Ni(NO_3)_2\cdot 4NH_3$	23.4	23.4	27.1	27.2	48.2	45.4

indicated that the greater parts of these intermediates were $NiCl_2 \cdot NH_3$ and $NiCl_2$, respectively.

The formation of $NiCl_2 \cdot NH_3$ is considered to depend greatly on the experimental condition, especially on the heating rate. For example, according to George and Wendlandt,[3] $NiCl_2 \cdot NH_3$ was not found in the process of decomposition at the larger heating rate, 7°C/min.

Hexamminenickel(II) iodide and bromide decomposed to NiX_2 (X=Br, I), obviously in two steps through $NiX_2 \cdot 2NH_3$. The first step,

$$[Ni(NH_3)_6]X_2 \rightarrow NiX_2 \cdot 2NH_3 + 4NH_3$$

proceeded at 109 to 231°C for X=Br and at 131 to 252°C for X=I. The second step,

$$NiX_2 \cdot 2NH_3 \rightarrow NiX_2 + 2NH_3$$

took place at 231 to 335°C for X=Br and at 252 to 318°C for X=I. Although the formation of $NiBr_2 \cdot NH_3$ had been reported,[1,5] it was not observed in this experiment.

Hexamminenickel(II) sulfate also decomposed to anhydrous $NiSO_4$ in three steps through $NiSO_4 \cdot 2NH_3$ and $NiSO_4 \cdot \frac{1}{2}NH_3$. The reaction,

$$[Ni(NH_3)_6]SO_4 \rightarrow NiSO_4 \cdot 2NH_3 + 4NH_3$$

proceeded at 100 to 205°C, the reaction,

$$NiSO_4 \cdot 2NH_3 \rightarrow NiSO_4 \cdot \tfrac{1}{2}NH_3 + \tfrac{3}{2}NH_3$$

at 205 to 397°C, and the reaction,

$$NiSO_4 \cdot \tfrac{1}{2}NH_3 \rightarrow NiSO_4 + \tfrac{1}{2}NH_3$$

at 397 to 455°C. $NiSO_4 \cdot \frac{1}{2}NH_3$ was not found at the heating rate 7°C/min,[3] whereas it was found at the heating rate 5°C/min.[4]

Hexamminenickel(II) nitrate was changed to $Ni(NO_3)_2 \cdot 4NH_3$ in a temperature range from 78 to 181°C by the reaction,

$$[Ni(NH_3)_6](NO_3)_2 \rightarrow Ni(NO_3)_2 \cdot 4NH_3 + 2NH_3 .$$

Upon further heating, it decomposed violently leaving a black residue. The ratio of ammonia to nickel contents in this intermediate was confirmed to be exactly 4 : 1 by the chemical analysis. George and Wendlandt,[3] and Viltange[4] have reported that the intermediate which was formed at the first step had ammonia less than 4 mol. This disagreement is considered mainly due to the difference in heating rate. The smaller heating rate employed in this experiment may be the main cause of the formation of the tetrammine intermediate, similarly to the fact that $NiCl_2 \cdot \frac{1}{2}NH_3$ has been demonstrated by Murgulescu *et al.*[6] at the smaller heating rate, 2°C/min.

The thermal stability or the decomposition temperature of hexamminenickel(II) complexes at which a complex begins to decompose increased in order of the nitrate<the chloride<the sulfate<the bormide<the idodide. Especially, the order of the halides is the same as the increasing order of the size of halide ions, *i. e.*, $Cl^- < Br^- < I^-$. This may indicate a possibility that the dissociation of ammonia of hexamminenickel(II) complexes occurs after an outer-sphere ion enters into the coordination sphere (S_N2 mechanism), because, if the bond breaking between ammonia and nickel takes place before the bond formation between nickel and outer-sphere ion, the decomposition temperature is expected to be independent of the kind of outer-sphere ion.

Diffuse Reflectance Spectra. The wave numbers of the band maxima of diffuse reflectance spectra of hexamminenickel(II) complex and the intermediates are given in Table 2. The measurement of NiI_2 was not successful.

The diffuse reflectance spectra of nickel(II) chloride and nickel(II) bromide have been analyzed in the field of octahedral symmetry,[11] and these halides are reported to have a polymeric structure similar to cadmium chloride.[11] The reflectance spectra of $NiCl_2 \cdot 2NH_3$, $NiBr_2 \cdot 2NH_3$ and $NiI_2 \cdot 2NH_3$ obtained in the region above 10000 cm^{-1} have also been reported.[9,10] These compounds

TABLE 2. WAVE NUMBERS OF BAND MAXIMA OF DIFFUSE REFLECTANCE SPECTRA (in 10^3 cm^{-1})

Complex	Assignment*					
	$^3T_{2g}$ (F)		$^3T_{1g}$ (F)			$^3T_{1g}$ (P)
$[Ni(NH_3)_6]Cl_2$	—		17.9			
$NiCl_2 \cdot 2NH_3$	7.7		14.3	19.8 w	23.0 sh	24.9
$NiCl_2 \cdot NH_3$	—	12.5 sh	13.3			22.7
$NiCl_2$	—	12.2 sh	13.0	9.0 sh		22.2
$[Ni(NH_3)_6]Br_2$	11.1		17.9			
$NiBr_2 \cdot 2NH_3$	7.3		13.9	18.9 w	22.2 sh	24.1
$NiBr_2$	7.0		11.9	16.5 w	18.2 sh	20.7
$[Ni(NH_3)_6]I_2$	11.1		17.9			
$NiI_2 \cdot 2NH_3$	7.3		13.9			23.3

* Assignment is for O_h symmetry. sh means shoulder; w means weak. — not measured.

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[11] A. Ludi and W. Feitknecht, *Helv. Chim. Acta*, **46**(3), 2226 (1963).

are considered to have polymeric pseudo-octahedral symmetry; the absorption band, $^3A_{2g} \rightarrow {}^3T_{2g}$ (F), was confirmed in this experiment. Their configurational structure is assumed to be not similar to $CdCl_2$ but similar to $NiCl_2 \cdot 2py$ (py= pyridine). In $NiX_2 \cdot 2NH_3$ (X=halogens), each nickel ion is considered to be surrounded by four bridging halogens arranged in a square planar configuration and two ammonia molecules located in trans position. Some spin-forbidden bands were observed because the symmetry of their ligand field was lower than the octahedral one.

It may be concluded from these results that the nickel ion keeps the coordination number 6 in whole thermal decomposition process when ammonia molecules are replaced stepwise by halogen ions. The fact that ammonia molecules and halogens are coordinated to a nickel ion is important for the band assignment of the infrared absorption spectra of these intermediates.

Although a nickel(II) ion of monoammine compound, $NiCl_2 \cdot NH_3$, is considered to be also six-coordinated because its spectrum has a great resemblance to that of $NiCl_2$ or $NiCl_2 \cdot 2NH_3$, its configurational structure has not been known yet.

Nelson and Shepherd[9] were successful in explaining the well-known fact that $NiX_2 \cdot 4py$ could be prepared whereas $NiX_2 \cdot 4NH_3$ has not been found yet. According to their discussion, in the case of $NiX_2 \cdot 4py$, the excess negative charge on nickel caused by the electron transfer from coordinated halogen could be reduced with the presence of a π-electron acceptor capacity of coordinated pyridine molecule; the "electroneutrality principle" holds. This seems to be the most probable cause of the stabilization of $NiX_2 \cdot 4py$. This consideration explains the instability of $NiX_2 \cdot 4NH_3$, because an NH_3 molecule does not have such a π-electron acceptor capacity and, consequently, if the compound were formed, negative charges must be localized on nikel. Since bridging halogens have a smaller capacity of electron transfer, $NiX_2 \cdot 2NH_3$ may exist in stable form though it has four halogens coordinated to nickel ion. The discussion cited above may be one of the important examples in which the process of the thermal decomposition is attempted to be explained from the considerations of the electronic structure.

Infrared Absorption Spectra. Figure 2 shows the infrared absorption spectra of the chloride, and Table 3 gives the wave numbers and the assignment of the absorption bands of the hexamminenickel(II) halides and their thermal decomposition products.

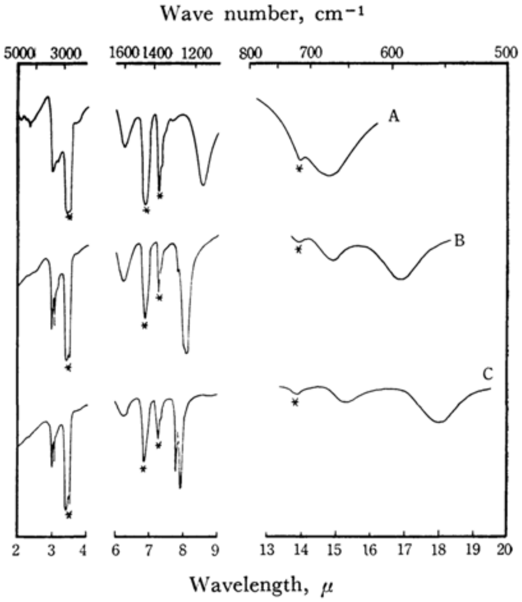

Fig. 2. The infrared absorption spectra of (A) $[Ni(NH_3)_6]Cl_2$, (B) $NiCl_2 \cdot 2NH_3$ and (C) $NiCl_2 \cdot NH_3$ in the range from 5000 cm^{-1} to 500 cm^{-1}. Optical density scale displaced arbitrarily.
* Indicates the Nujol band.

TABLE 3. THE WAVE NUMBERS OF THE MAIN INFRARED ABSORPTION BANDS OF $[Ni(NH_3)_6]X_2$ AND THE RELATED COMPOUNDS

	ν(NH)	$\delta_{deg}(NH_3)$	$\delta_s(NH_3)$	$\rho_r(NH_3)$	ν(NiN)	ν(NNiN)	Lattice
$[Ni(NH_3)_6]Cl_2$	3344 s	1607m	1176 s	683.2sb	334 s	220 s	120 s
$[Ni(NH_3)_6]Br_2$	3344 s	1607m	1187 s	673.1sb	327 s	216 s	95 s
$[Ni(NH_3)_6]I_2$	3322 s	1597m	1203 s	655.2sb	321 s	214 s	85 s

	ν(NH)		$\delta_{deg}(NH_3)$	$\delta_s(NH_3)$		$\rho_r(NH_3)$		ν(NiN)	ν(NiX)		
$NiCl_2 \cdot 2NH_3$	3344 s	3268 s	1607m	1243 s		674.0w	590.3m	435 s	216sb	189 s *	150 s *
$NiBr_2 \cdot 2NH_3$	3344 s	3268 s	1610m	1249 s		674.0w	603.1m	—	191 s	156 s *	135 s *
$NiI_2 \cdot 2NH_3$	3322 s	3236 s	1597m	1243 s		—	618.4m	—	178 s	130 s	116 s *
$NiCl_2 \cdot NH_3$	3344 s	3268 s	1604m	1287 s	1264 s		555.6m	—	250sb	206sb*	130w*
$NiCl_2$									292m	235sb*	193m*
$NiBr_2$									229 s	163 s *	140 s *
NiI_2									183 s	161 s *	118 s *

s, strong; m, medium; w, weak; sb, strong and broad.
— not observed. * not assigned.

TABLE 4. THE WAVE NUMBERS OF THE INFRARED ABSORPTION BANDS OF $[Ni(NH_3)_6]SO_4$ AND $[Ni(NH_3)_6](NO_3)_2$ AND THE RELATED COMPOUNDS (cm^{-1})

	ν(NH)		$\delta_{deg}(NH_3)$	$\delta_s(NH_3)$	$\rho_r(NH_3)$	SO_4^{2-}				
$[Ni(NH_3)_6]SO_4$	3344 s	3185 m	1636 m	1219 mb	683.7 sb	1082 sb	971.0 w	610.5 sb		
$NiSO_4\cdot 2NH_3$	3378 s	3356 s	1617 m	1226 m	590.4* s	1202 m	1116 s	1062 s	984.3 m	719.4 m
						669.2 m	509.4 m	590.4* s		
						NO_3^-				
$[Ni(NH_3)_6](NO_3)_2$	3356 s	3268 m	1620 m	1196 s	653.5** sb	1349 s	831.9 m	653.5** sb		
$Ni(NO_3)_2\cdot 4NH_3$	3378 s	3300 m	1620 m	1207 s	645.6*** sb	1404 s	1323 s	1047 m	814.3 m	645.6*** sb

*, **, and ***, may overlap each other, respectively.

The assignment of the absorption bands of hexamminenickel(II) halides has been reported previously.[4,12] It is interesting to know how the absorption bands due to ammonia are affected by the structure change which occurs when the monomeric structure in the hexammine complex is changed to the polymeric one bridged with halogen ions in the lower ammine intermediates.

In the case of the diamminenickel(II) chloride, for example, the ν(NH) split into two peaks, whereas $\delta_{deg}(NH_3)$ neither split nor shifted, compared with those of hexamminenickel(II) chloride. The $\delta_s(NH_3)$, being affected by the structure change, shifted to higher wave numbers. Ammonia is considered to coordinate to nickel ion from the diffuse reflectance spectra, which suggests that the absorption band due to the $\rho_r(NH_3)$ must appear. A weak absorption band, however, was observed in the usual rocking region, while a strong absorption band appeared at 590.3 cm^{-1} and a new band at 435 cm^{-1}. This phenomenon has been recently reported on various kinds of diammine complexes by Clark and Williams,[10] who assigned the former two bands to $\rho_r(NH_3)$ and the latter to the ν(NiN). Although $\delta_s(NH_3)$, $\rho_r(NH_3)$ and ν(NiN) are generally expected from their modes of vibration to shift to the same direction, the experimental results did not agree with this expectation. However, since ammonia and halogen must be coordinated to nickel ion, this assignment is considered as reasonable. Especially, the $\rho_r(NH_3)$ of the diammine complexes shifted to higher wave numbers in order of the iodide$>$the bromide$>$ the chloride, which was the reverse of the order in the hexammine compounds. This change may be explained by considering that the effect of outer-sphere ions[12] disappears as the halogen ion is coordinated to nickel. The ν(NiN) of the diammine complexes was observed at higher wave numbers by 100 cm^{-1} than that of hexamminenickel(II). The reason why, in the case of the diammine complexes, the $\delta_s(NH_3)$ and ν(NiN) shift to higher wave numbers in the opposite direction of the $\rho_r(NH_3)$ has not been understood yet. The strong absorption band observed at 216 cm^{-1} may be assigned to ν(NiCl). However, other absorption bands observed at 189 cm^{-1} and 150 cm^{-1} were not assigned yet. The same was also observed with the bromides and the iodides.

Nickel chloride, bromide and iodide gave the same type of absorption bands. The absorption bands at 292 cm^{-1} for nickl chloride, at 229 cm^{-1} for nickel bromide and at 183 cm^{-1} for nickel iodide may be assigned to ν(NiCl), ν(NiBr) and ν(NiI), respectively. Other absorption bands were not assigned.

As to monoamminenickel(II) chloride, $NiCl_2\cdot NH_3$, the $\delta_s(NH_3)$ split and shifted to higher wave numbers than that of diamminenickel(II), whereas the $\rho_r(NH_3)$ shifted to lower wave numbers, 555.6 cm^{-1}. It is interesting that the $\rho_r(NH_3)$ was observed in a region of such lower wave numbers.

The infrared absorption spectra of $[Ni(NH_3)_6]SO_4$ and its diammine intermediate are given in Table 4. In the diammine compound, the ν(NH), the $\delta_{deg}(NH_3)$ and the $\delta_s(NH_3)$ due to ammonia showed the same behavior as the diamminenickel(II) chloride. The SO_4^{2-} absorption band may be explained with C_{2v} symmetry, though it is not clear whether the SO_4^{2-} ion behaves as a simple bidentate or a bridging bidentate. As for the hemiammine compound, it was difficult to deduce whether the SO_4^{2-} ion is coordinated to a nickel(II) ion or not, because the band at 1130 cm^{-1} did not split and that at 977 cm^{-1} was strong; the former is characteristic of a free SO_4^{2-} ion and the latter is characteristic of a coordinated one. These may be attributed to the distortion of the SO_4^{2-} ion which was caused by heating.

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[12] J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956).

The wave numbers of the absorption bands of hexamminenickel(II) nitrate and its intermediate are also given in Table 4. The measurement was made by both nujol and HCB mull methods. The NO_3^- ion was considered to be coordinated to nickel ion in the tetrammine compound from its spectral change from a D_{3h} symmetry in the hexammine complex to a C_{2v} symmetry in the dinitratotetrammine complex. The structure of the tetramminenickel(II) nitrate may be monomeric because the shift of the $\rho_r(NH_3)$ to lower wave numbers was not observed.

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