ground state $Ru(NH_3)_6^{2+}$. Thus, both the excess Franck–Condon energy and the high-spin–low-spin energy difference in $Co(NH_3)_6^{3+}$ are likely to account for our estimated difference in the CT excitation energies in the $Ru(NH_3)_6^{3+},X^-$ and $Co(NH_3)_6^{3+},X^-$ ion pairs.

In conclusion, one may say that the absence of absorption lines in the visible region in the spectrum of the $Ru(NH_3)_6^{3+}$ free ion and the relatively low excitation energies for the CT transitions of its ion pairs make this complex an excellent ion for spectrophotometric investigations of ion pairs.

Registry No. $Ru(NH_3)_6^{3+},Cl^-$, 53293-35-9; $Ru(NH_3)_6^{3+},Br^-$, 53293-36-0; $Ru(NH_3)_6^{3+},I^-$, 53293-37-1.

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Cryogenic Excited-State Fine Structure of $[Ni(NH_3)_6]A_2$ and Magnetic Circular Dichroism Temperature Dependence of $^3T_{1g}(t_{2g}^5e_g^3)$[1]

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Seven compounds of hexaamminenickel(II), $[Ni(NH_3)_6]A_2$, or the deuterated d_{18} analogs, $[Ni(ND_3)_6]A_2$, where A^- = Cl^-, Br^-, I^-, ClO_4^-, or PF_6^-, were studied by means of electronic absorption and magnetic circular dichroism (MCD) techniques at several temperatures (*ca.* 12–300°K). The absorption spectra in the d–d excitation region of six parity-forbidden bands permitted the observation of numerous vibronic progressions of the (NiN_6) skeletal normal modes and the symmetric stretching mode, $\nu_s(N-H)$, which are modes of the electronic excited states. These are progressions of a_{1g} or e_g built on t_{1u} and t_{2u} modes. The temperature-dependent MCD spectra through $^3T_{1g}(t_{2g}^5e_g^3)$ experimentally confirm the earlier suggestion that second-order spin–orbit coupling is important in the ground state $^3A_{2g}(t_{2g}^6e_g^2)$ so as to give this state angular momentum from the excited state $^3T_{2g}(t_{2g}^5e_g^3)$. Finally, the band position of $^3A_{2g} \rightarrow {}^1A_{1g}(t_{2g}^6e_g^2)$ is an excellent probe for the interaction between the lattice counterion and the complex ion $[Ni(NH_3)_6]^{2+}$.

Introduction

The most recent report[2] dealing with the nature of electronic excited states of the important parent complex ion hexaamminenickel(II), or $[Ni(NH_3)_6]^{2+}$, contained descriptions of vibronic structural features on two d–d excitations, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^1A_{1g}$, between *ca.* 600 nm (16,670 cm^{-1}) and 430 nm (23,260 cm^{-1}). This was observed at 80°K for the Cl^- and ClO_4^- salts of the complex ion and complemented ambient room-temperature solution spectra measured previously by others.[3] The present paper reports on newly observed vibronic structure, measured between 12 and 80°K, with distinct vibronic progressions on $^3T_{2g}(t_{2g}^5e_g^3$; $^3F)$, $^3T_{1g}(t_{2g}^5e_g^3$; $^3F)$, $^1E_g(t_{2g}^6e_g^2$; $^1D)$, $^1A_{1g}(t_{2g}^6e_g^2$; $^1G)$, $^1T_{2g}(t_{2g}^4e_g^4$; $^1D)$, and $^1T_{1g}(t_{2g}^5e_g^3$; $^1G)$ which represent intra- as well as interconfigurational excitations. Some of the identifications of vibronic progressions were substantiated by preparing and studying the deuterated d_{18} complex, $[Ni(ND_3)_6](PF_6)_2$. In all, seven salts were studied, and the counterions were Cl^-, Br^-, I^-, PF_6^-, and ClO_4^-.

It was also possible experimentally to substantiate some suggestions made by Harding, Mason, Robbins, and Thomson[4] about the MCD spectrum of $[Ni(NH_3)_6]^{2+}$; *i.e.*, we measured the MCD spectra at 18 and 27°K of $[Ni(NH_3)_6]Cl_2$. The latter data contribute importantly to the understanding of excited-state structure of the hexaammine.

Experimental Section

1. Instrumentation. MCD spectra were obtained with a JASCO spectropolarimeter (Model ORD/UV/CD-5 with the SS-20 electronics modification). Low temperatures for MCD were attained by throttling vapors from a liquid helium reservoir past the sample. Near-ir, far-ir, and Raman spectra were measured on Perkin-Elmer 521, Perkin-Elmer FIS-3, and Jarrell-Ash 25-100 instruments (4880-Å Ar laser line), respectively. Low-temperature electronic absorption spectra were obtained by using an all-glass exchange-gas dewar and an all-glass dewar whose internal compartment and sample are cooled by throttling vapors from a liquid helium reservoir into it. Au–Co *vs.* Cu and constantan *vs.* copper thermocouples were used following their calibration. The matrices of the crystalline samples were either KBr disks or Kel-F mulls.

2. Compounds. The syntheses of $[Ni(NH_3)_6]A_2$ complexes, where A^- = Cl^-, Br^-, I^-, and ClO_4^-, are well known.[5] The syntheses of $[Ni(NH_3)_6](PF_6)_2$ and its d_{18} deuteration analog were devised as follows. $[Ni(NH_3)_6](PF_6)_2$ was prepared by the metathetical replacement reaction between $[Ni(NH_3)_6]Cl_2$ (in an ammoniacal

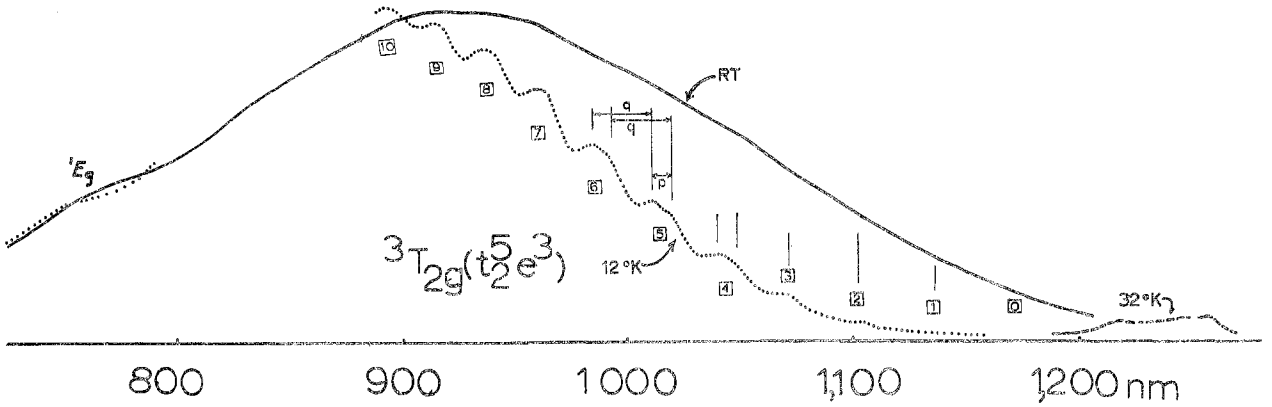

Figure 1. Electronic absorption bands, $^3T_{2g}(t_{2g}^5e_g^3)$ and $^1E_g(t_{2g}^6e_g^2)$, at ambient room temperature, 32°K, and 12°K, of $[Ni(NH_3)_6]Cl_2$ (KBr disk).

solution) and NH_4PF_6. The deep blue precipitate appeared immediately, was filtered, and then washed several times with a *ca.* 3% ammonia solution to remove any remaining chloride salts. This step is followed by two washes, each with absolute ethanol and diethyl ether. The reaction is nearly quantitative.

The deuterated analog, $[Ni(ND_3)_6](PF_6)_2$, was prepared from anhydrous $NiCl_2$, KPF_6, and ND_4OD as follows. Anhydrous $NiCl_2$ (0.01 mol), prepared *in situ* from $[Ni(H_2O)_6]Cl_2$ by heating, was dissolved in a minimum amount of D_2O. This solution was filtered into a previously filtered and saturated solution of KPF_6 (0.02 mol, 3.683 g) in D_2O. To this cloudy, yellow-green solution 7 ml of 25% ND_3–D_2O in D_2O was added dropwise with stirring to produce an almost transparent, blue suspension of $[Ni(ND_3)_6](PF_6)_2$. The reaction mixture was allowed to cool on ice for 25 min and was then filtered. The supernatant was nearly colorless, indicating the completeness of the reaction. The precipitate was carefully washed with 2 ml of 25% ND_4OD followed by two 5-ml portions of 2.5% ND_4OD. Finally, the precipitate was washed twice, each time with absolute ethanol and diethyl ether. The reaction was nearly quantitative, and the product was at least 90% deuterated on the basis of the vibrational spectra in the N–H and N–D stretching regions, *i.e.*, 3400 and 2450 cm^{-1}, respectively. The product was stored in an inert atmosphere (absence of H_2O).

Results and Discussion

The spectral data will be discussed in the order of increasing energy of d–d bands, which is believed[2,6] to be $^3T_{2g}(t_{2g}^5e_g^3) < {}^1E_g(t_{2g}^6e_g^2) < {}^3T_{1g}(t_{2g}^5e_g^3) < {}^1A_{1g}(t_{2g}^6e_g^2) < {}^1T_{2g}(t_{2g}^4e_g^4) < {}^1T_{1g}(t_{2g}^5e_g^3)$. We refer to these as bands 1, 2, 3, 4, 5, and 6, respectively. Of these bands, the first three ($^3T_{2g}$, ^1E_g, $^3T_{1g}$) were previously observed,[3] $^1A_{1g}$ and $^1T_{2g}$ were observed[2] in 1973, and $^1T_{1g}$ is reported here for the first time.[13]

Band 1, or $^3A_{2g}(t_{2g}^6e_g^2) \rightarrow {}^3T_{2g}(t_{2g}^5e_g^3)$. This band is the lowest energy spin-allowed, one-electron d–d excitation of the interconfigurational type where an electron is excited from a nonbonding to an antibonding orbital, and its maximum is at *ca.* 900 nm (~11,100 cm^{-1}) for $[Ni(NH_3)_6]Cl_2$ (Figure 1), as measured in a KBr disk. The band of the complex with this particular Cl^- counterion will be discussed, because it showed the most vibronic structure. On lowering the temperature from ambient room temperature to 12°K there is a severe loss of intensity in the red tail, *i.e.*, from *ca.* 1200 nm (~8330 cm^{-1}) to 900 nm (~11,100 cm^{-1}), and the spectra of both temperatures are given in Figure 1. It is also quite interesting that at 12°K an extended 10-member progression develops between 1150 nm (~8700 cm^{-1}) and 920 nm (~10,900 cm^{-1}). The members are separated by an average of *ca.* 280 cm^{-1}, for which reason they are assigned as advanced members of the a_{1g}' skeletal NiN_6 mode, where the prime symbolizes that it is the vibration in the $^3T_{2g}$ electronic excited state. The reduction from the value (360 cm^{-1}) of the fundamental a_{1g} skeletal frequency[2] of the electronic ground state, $^3A_{2g}$, is attributed to the more antibonding nature of the excited configuration, $t_{2g}^5e_g^3$.

This progression has another very interesting feature; *i.e.*, the progression members at 990 nm (10,100 cm^{-1}), 1015 nm (9850 cm^{-1}), and perhaps 1045 nm (9570 cm^{-1}) are composed of two components each with a separation, p, of 80 cm^{-1}. Since this value is approximately the difference in energy between NiN_6 skeletal vibrational fundamentals $t_{1u}{}'^a$ and $t_{1u}{}'^b$ of the excited state $^3T_{1g}(t_{2g}^5e_g^3)$, or band 3 (*vide infra*), which is of the same antibonding excited configuration, we also attribute these pairs to $t_{1u}{}'^a$ and $t_{1u}{}'^b$ modes of the $^3T_{2g}$ excited state. The consequence, then, of the presence of these two-component members is that the a_{1g}'' progression giving rise to the ten members is actually originating at two ungerade, single-quantum origins. The $0 \rightarrow 0'$ origin of these progressions can be estimated by observing the positions of the hot bands which develop in the spectrum as the sample temperature is raised from 12 to 32°K (Figure 1); these are the bands at *ca.* 1215 nm (8230 cm^{-1}) and 1255 nm (7970 cm^{-1}), the former being broad and the latter having two components which are separated by *ca.* 80 cm^{-1}. We note parenthetically that this last separation is about the difference between the $t_{1u}{}'^a$ (215 cm^{-1}) and $t_{1u}{}'^b$ (336 cm^{-1} estimate; *vide infra*) NiN_6 skeletal fundamental modes. From these hot bands we estimate that the $0 \rightarrow 0'$ position of $^3A_{2g} \rightarrow {}^3T_{2g}$ is near 11,700 ± 5 nm (Figure 1). More detailed spectral refinements must await the measurements on single crystals of this solid. Finally, the absorption band of Figure 1 near 750 nm (13,330 cm^{-1}), or ^1E_g, will be discussed next.

Band 2, or $^3A_{2g}(t_{2g}^6e_g^2) \rightarrow {}^1E_g(t_{2g}^6e_g^2)$. This excitation at about 750 nm (13,330 cm^{-1}) (Figures 1 and 2) is spin forbidden and parity forbidden by electric dipole selection rules, but it can become allowed *via* spin–orbit coupling plus vibronic coupling to NiN_6 skeletal (or N–H) vibrational modes of the excited state, *e.g.*

$$\langle \Gamma_{5g}(^3A_{2g})|\Gamma_{4u}|\Gamma_{3g}(^1E_g)\cdot t_{1u}{}'^v)\epsilon\Gamma_{1g}$$

$$\langle \Gamma_{5g}(^3A_{2g})|\Gamma_{4u}|\Gamma_{3g}(^1E_g)\cdot t_{2u}{}'^v)\epsilon\Gamma_{1g}$$

where Γ_{1g}, the totally symmetric representation must be contained in the direct product of the integrand, and, for example, $\Gamma_{3g}\cdot t_{1u}{}'^v$, symbolizes the symmetry product of the Γ_{3g} electronic state and a t_{1u} vibration of that state. Furthermore, one expects that the energies of the vibrational modes of this excited state, ^1E_g, should differ very little from those of the electronic ground state because both states arise from the same spatial electron configuration, $t_{2g}^6e_g^2$. The distinct f progression observed (Figure 2) on ^1E_g at 750 nm (13,330 cm^{-1}) is composed of eight members when the PF_6^- salt is studied, and it appears at 80°K. The progression was not present in the chloride salt (Figure 1). These progression members are separated by approximately 245 ± 10 cm^{-1}. Our laser Raman spectrum of this powdered complex has a strong band at 220

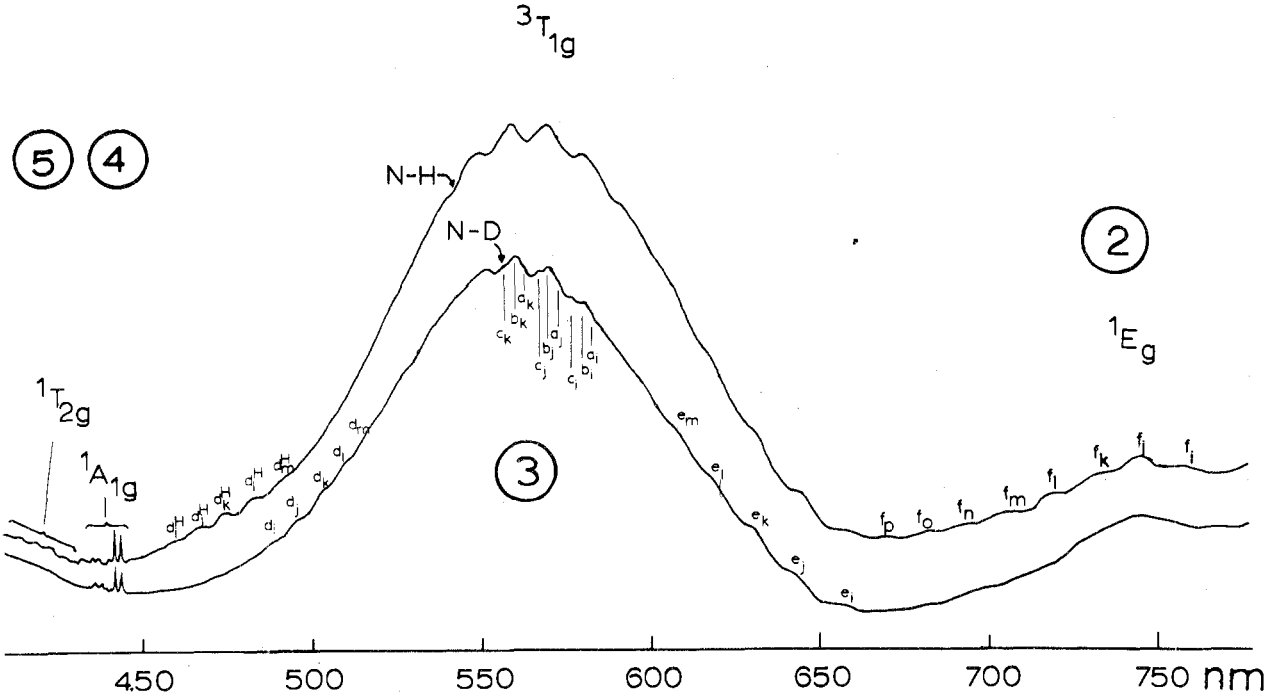

Figure 2. Electronic absorption of ^1E_g (band 2), $^3T_{1g}(t_{2g}^5e_g^3)$ (band 3), and band 4 at 80°K of $[Ni(NH_3)_6](PF_6)_2$ and the deuterated d_{18} analog (mull).

cm^{-1}, which we assign to the e_g fundamental mode of the NiN_6 skeleton. For this reason one associates the eight-member progression on $^1E_g(t_{2g}^6e_g^2)$ with this e_g skeletal mode. This is an unusual event, since progressions on electronic absorption bands of the g → g type conventionally display a_{1g} progressions. We make the assignments as shown for the f progression (k = integer). It cannot be determined at this stage upon which ungerade vibration, $t_{1u}'^a$, $t_{1u}'^b$, or t_{2u}', the progression is built.

f_i	13,193 cm^{-1} (758 nm)	$t_u' + ke_g'$
f_j	13,423 cm^{-1} (745 nm)	$t_u' + (k+1)e_g'$
f_k	13,661 cm^{-1} (732 nm)	$t_u' + (k+2)e_g'$
f_l	13,937 cm^{-1} (717.5 nm)	$t_u' + (k+3)e_g'$
f_m	14,184 cm^{-1} (705 nm)	$t_u' + (k+4)e_g'$
f_n	14,440 cm^{-1} (692.5 nm)	$t_u + (k+5)e_g'$
f_o	14,684 cm^{-1} (681 nm)	$t_u' + (k+6)e_g'$
f_p	14,925 cm^{-1} (670 nm)	$t_u' + (k+7)e_g'$

Band 3, or $^3A_{2g}(t_{2g}^6e_g^2) \rightarrow {}^3T_{1g}(t_{2g}^5e_g^3)$. The spin-allowed, but parity-forbidden band at *ca.* 560 nm (~18,000 cm^{-1}) is the result of exciting an electron from a nonbonding t_{2g} orbital to an antibonding e_g orbital. It was found that at 80°K $[Ni(NH_3)_6](PF_6)_2$ and its d_{18} analog gave the best resolved structure (Figure 2) of the hexaammine salts studied, which included the counterions PF_6^-, ClO_4^-, Cl^-, Br^-, and I^-. Five vibronic progressions are clearly visible in the spectrum of this PF_6^- salt (Table I, Figure 2). For example, on the band maximum of the d_{18} complex, the members of the b progression are most intense, and they have an average spacing of 311 ± 10 cm^{-1}. Since the excited state, $^3T_{1g}$, is of a more antibonding configuration, $t_{2g}^5e_g^3$, as is $^3T_{2g}$ (band 1), than the ground-state configuration, $t_{2g}^6e_g^2$, these members are assigned to vibronic combination levels of one quantum of an excited state $t_{1u}'^b$ NiN_6 skeletal mode and multiple quanta of the a_{1g}' skeletal mode, which in the ground state we found to be at 348 cm^{-1} in the laser Raman spectrum; the Raman and electronic spectra were each recorded in the powdered crystalline state. The observation of relative magnitudes, a_{1g}' (311 cm^{-1}: $^3T_{1g}$) < a_{1g} (348 cm^{-1}: $^3A_{2g}$), is quite reasonable, and we assign (*vide infra*) the b progression as shown (see Table I).

Table I. Vibronic Progressions[a] on $^3T_{1g}(t_{2g}^5e_g^3)$ of $[Ni(ND_3)_6](PF_6)_2$ at 80°K

Resolved progressions	Position, cm^{-1} (nm)	Broad progressions	Position, cm^{-1} (nm)
a_i	17,153 (583)	d_m	19,608 (510)
a_j	17,452 (573)	d_l	19,908 (502.3)
a_k	17,778 (562.5)	d_k	20,202 (495)
b_i	17,227 (580.5)	d_j	20,502 (487.75)
b_j	17,535 (570.3)	d_i	20,777 (481.3)
b_k	17,849 (560.3)	e_i	15,221 (657)
c_i	17,331 (576.3)	e_j	15,552 (643)
c_j	17,637 (567)	e_k	15,860 (630.5)
c_k	17,963 (556.7)	e_l	16,155 (619)
		e_m	16,447 (608)

[a] Average spacing: a, 313 cm^{-1}; b, 311 cm^{-1}; c, 316 cm^{-1}; d, 339 cm^{-1}; e, 302 cm^{-1}; with an approximately 10 cm^{-1} experimental uncertainty.

$$b_i \quad t_{1u}'^a + na_{1g}'$$
$$b_j \quad t_{1u}'^a + (n+1)a_{1g}'$$
$$b_k \quad t_{1u}'^a + (n+2)a_{1g}'$$

The members of progression c (Table I, Figure 2) are on the average about 105 cm^{-1} higher in energy than the members of progression b. However, the members of progression c are separated from each other by 316 cm^{-1} which, within the experimental uncertainty, is the same spacing as between the members of progression b (311 cm^{-1}). Therefore, the a_{1g}' NiN_6 skeletal mode of this electronic excited state, $^3T_{1g}$, is con-

tributing to this c progression too. Also, it is known that the higher energy t_{1u} skeletal vibration, $t_{1u}{}^{b}$ ($\sim$330 cm^{-1}), of the ground state is $\sim$115 cm^{-1} higher than the one at lower energy, $t_{1u}{}^{a}$ ($\sim$215 cm^{-1}). For this reason the c-progression is assigned to be based on one quantum of $t_{1u}{}'^{b}$, where the prime signifies the vibrational mode in the $^3T_{1g}$ excited state (Table I).

$$c_i \quad t_{1u}{}'^{b} + n a_{1g}'$$
$$c_j \quad t_{1u}{}'^{b} + (n+1) a_{1g}' \quad .$$
$$c_k \quad t_{1u}{}'^{b} + (n+2) a_{1g}'$$

The members of the third, or a progression, near the $^3T_{1g}$ maximum, are weakest of the three progressions. They lie on the average 76 cm^{-1} to lower energy than members of the most intense b progression. First, we find that the members of this a progression are separated (313 cm^{-1}) by the same distance within the approximate 10 cm^{-1} experimental uncertainty as found for progressions b and c, so that a_{1g}' is operative again. Furthermore, it is known for similar octahedral complex ions that t_{2u} ν(ML$_6$) skeletal modes are at lower energy than the lowest energy t_{1u} skeletal mode. For example, we have the data shown here.

	$t_{1u}{}^{a}$	t_{2u}	Ref
$[Cr(NH_3)_6]^{3+}$	264 cm^{-1}	212 cm^{-1}	7a, 12
$[Ni(H_2O)_6]^{2+}$	268 cm^{-1}	124 cm^{-1}	7b
$[Co(H_2O)_6]^{2+}$	261 cm^{-1}	133 cm^{-1}	7b

This prompts us to assign the base of the origin of the a progression to t_{2u}'. Additional and more direct evidence for t_{2u} is that we find a band at 160 cm^{-1} in the far-infrared spectrum of $[Ni(NH_3)_6](ClO_4)_2$; this position is 62 cm^{-1} to lower energy of the $t_{1u}{}^{a}$ far-infrared band. This difference compares very favorably with the experimental difference of 76 cm^{-1} between progression members b_i ($t_{1u}{}'^{a}$) and a_i (t_{2u}'). This vibronic structure, then, leads to the interesting conclusion that in the $^3T_{1g}(t_{2g}{}^5e_g{}^3)$ excited state the t_{2u}' NiN$_6$ skeletal mode occurs about 76 cm^{-1} below that of the $t_{1u}{}'^{a}$ skeletal mode (Table I).

$$a_i \quad t_{2u}' + n a_{1g}'$$
$$a_j \quad t_{2u}' + (n+1) a_{1g}'$$
$$a_k \quad t_{2u}' + (n+2) a_{1g}'$$

The question of where one of the $0(^3A_{2g}) \rightarrow 0'(^3T_{1g})$ positions (there can be more than one since the spin–orbit manifold of $^3T_{1g}$ is composed of Γ_1, Γ_3, Γ_4, Γ_5) ought to be can be answered with somewhat reasonable certainty by analyzing the d progression (Figure 2) in the blue tail of $^3T_{1g}$ along with the apparent beginning of progressions a, b, and c. Regarding the d progression observed at 80°K, it should be noted that the first observed member, d_i, at 481.3 nm (20,777 cm^{-1}) in d_{18} $[Ni(NH_3)_6]^{2+}$, or $[Ni(ND_3)_6](PF_6)_2$, is measured to be *ca.* 880 cm^{-1} lower in energy than the first component, $d_i{}^{H}$, at 21,657 cm^{-1} (Figure 2) of the undeuterated complex, $[Ni(NH_3)_6](PF_6)_2$; d^H and d symbolize analogous progression members of $[Ni(NH_3)_6](PF_6)_2$ and $[Ni(ND_3)_6](PF_6)_2$. In fact each member between 460 and 500 nm (21,750 and 20,000 cm^{-1}) of the d^H progression of $[Ni(NH_3)_6](PF_6)_2$ shifts to lower energy by *ca.* 900 cm^{-1} upon deuterating the complex to $[Ni(ND_3)_6](PF_6)_2$, *i.e.*, $d_i{}^{H} - d_i$ = 880 cm^{-1}, $d_j{}^{H} - d_j$ = 900 cm^{-1}, etc. Indeed, this is the shift expected if the vibronic d progression consists of a symmetric N–H (N–D) stretching mode being built upon one quantum of an allowing mode $t_{1u}{}'^{a}$, $t_{1u}{}'^{b}$, or t_{2u}' within $^3T_{1g}$.

In order to shed additional light on this possibility we obtained the following vibrational data. We find $\nu_s{}^{H}(NH_3)$ 3310 cm^{-1} for $[Ni(NH_3)_6](PF_6$ and $\nu_s{}^{D}(ND_3)$ 2410 cm^{-1} for the d_{18} analog from ambient room-temperature Raman spectra. This difference, $\nu_s{}^{H} - \nu_s{}^{D}$, is 900 cm^{-1} and our average vibronic shift, $d^H - d$, of 890 cm^{-1} compares quite favorably with this.

The second point of interest is that the members of the d progression of $[Ni(ND_3)_6](PF_6)_2$ are separated by an average of 300 $\pm$ 10 cm^{-1}. Since this is also the amount by which the members within the a, b, and c progressions are separated, it is concluded that progression members d_i to d_m are multiply excited quanta of the a_{1g}' ν(NiN$_6$) skeletal vibrations. Therefore, one is led to make the assignments for the d progression as shown (Table I), where Λ is an integer.[8]

$$d_m \quad 1t_u' + \nu_s'(ND_3) + \Lambda a_{1g}'(NiN_6)$$
$$d_l \quad 1t_u' + \nu_s'(ND_3) + (\Lambda+1) a_{1g}'(NiN_6)$$
$$d_k \quad 1t_u' + \nu_s'(ND_3) + (\Lambda+2) a_{1g}'(NiN_6)$$
$$d_j \quad 1t_u' + \nu_s'(ND_3) + (\Lambda+3) a_{1g}'(NiN_6)$$
$$d_i \quad 1t_u' + \nu_s'(ND_3) + (\Lambda+4) a_{1g}'(NiN_6)$$

Using converse reasoning one can now look for the t_u' level on which the $\nu_s{}^{D}(ND_3)$ mode might be built; *i.e.*, if one adds $\nu_s{}^{D}(ND_3)$ 2410 cm^{-1} to the most prominent member, or $t_{1u}{}'^{a}$, at 580.5 nm (17,227 cm^{-1}), one obtains 509 nm (19,637 cm^{-1}), which indeed is the position of the mth member (510 nm) of the d progression! This then leads to the reasonable conclusion that the $0 \rightarrow 0'$ origin of progressions a, b, and c *may be* one fundamental vibrational mode of $t_{1u}{}'^{a}$ toward the red side of 580.5 nm (17,227 cm^{-1}). An estimate of this position is obtainable by reducing the $\nu(t_{1u}{}^{a})$ ground-state skeletal fundamental by the amount (13%) that a_{1g} of the ground state is reduced compared to a_{1g}' of the excited state, $^3T_{1g}$. Based on this reasoning, the $0 \rightarrow 0'$ position is at 586.8 nm (17,040 cm^{-1}). We attribute this origin to the forbidden transition from $[\Gamma_5(^3A_{2g})]$ to $[\Gamma_3(^3T_{1g})]$ or $[\Gamma_5(^3T_{1g})]$, or to both, because we previously ascertained, by computation[2] as did Liehr and Ballhausen,[6] that they are separated by only about 100 cm^{-1}. However, this origin is speculative at present because there is another origin near about 660 nm (Figure 2) which is too far from the Γ_3,Γ_5 position; *i.e.*, a $\Gamma_1(^3T_{1g})$ origin near 670 nm would require the unorthodox postulate that $\zeta_{3d}(Ni^{2+})$ of the complex be sizably larger than the free-ion value of 630 cm^{-1}. Thus, locating the Γ_3,Γ_5 origin with greatest firmness must await the single-crystal data.

The vibronic e progression on the red tail of $^3T_{1g}$ of $[Ni(ND_3)_6](PF_6)_2$ has its members (Table I) separated by an average of 300 cm^{-1}, and it starts at about 15,220 cm^{-1} (657 nm). Each of these e members is broad, so that it is not possible to establish onto which of the ungerade fundamental modes, t_{1u}' or t_{2u}', it is built. However, this 300 cm^{-1} interval prompts us to assign the members to multiply excited quanta of a_{1g}' as found for the other four progressions (Table I) where

$$e_i \quad 1t_u' + \nu a_{1g}' \qquad e_l \quad 1t_u' + (\nu+3) a_{1g}'$$
$$e_j \quad 1t_u' + (\nu+1) a_{1g}' \qquad e_m \quad 1t_u' + (\nu+4) a_{1g}'$$
$$e_k \quad 1t_u' + (\nu+2) a_{1g}'$$

ν is an integer. The $0 \rightarrow 0'$ spin-orbit parentage position of this progression is difficult to estimate since it is strongly forbidden, but the spin–orbit parent ought to be $\Gamma_1(^3T_{1g})$ on the basis of previous ligand field computations.[2,6]

From Figure 2 it is evident that the general features of the vibronic structure of this $^3T_{1g}$ band of $[Ni(ND_3)_6](PF_6)_2$, as discussed in the preceding paragraphs, are also present in the undeuterated complex, $[Ni(NH_3)_6](PF_6)_2$. However, most members of the progressions are broader in the latter complex, and the d progression is blue shifted for the reason given above.

The ambient room-temperature MCD solution spectrum of $[Ni(NH_3)_6]^{2+}$ was measured by Harding, Mason, Robbins, and Thomson.[4] The excitation under discussion here, $^3A_{2g} \rightarrow {}^3T_{1g}$, was found to have residual integrated MCD activity.

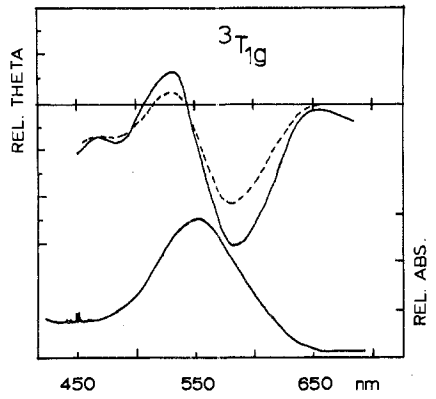

Figure 3. MCD of $^3T_{2g}(t_{2g}^5e_g^3)$ at 18°K (solid line) and 27°K (dashed line) of $[Ni(NH_3)_6]Cl_2$ (KBr disk). Electronic spectrum at 38°K.

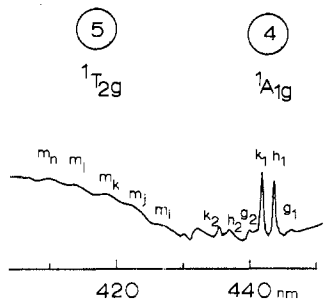

Figure 4. Electronic absorption of $^1A_{1g}$ and $^1T_{2g}$ (bands 4 and 5) at 80°K of $[Ni(NH_3)_6](PF_6)_2$ (mull).

If the residual activity could be shown to be the result of Faraday *C* terms,[9] one could conclude that the ground state, $^3A_{2g}$, contains angular momentum (after spin–orbit coupling) from primarily the first excited state, $^3T_{2g}(t_{2g}^5e_g^3)$.[10] The temperature dependence of the MCD of this $^3T_{1g}$ band (*ca.* 550 nm) of $[Ni(NH_3)_6]Cl_2$, which we measured at 18 and 27°K (Figure 3), provides the necessary experimental verification that second-order spin–orbit coupling indeed mixes angular momentum from excited state (probably $^3T_{2g}$) into ground state, $^3A_{2g}$. It is also quite interesting to note that the negative MCD band at about 480 nm (20,830 cm^{-1}) demonstrates that the vibronic d progression, which involves the symmetric N–H stretching motion, of this $^3T_{1g}$ state has its own distinct MCD activity.

Band 4, or $^3A_{2g}(t_{2g}^6e_g^2) \rightarrow {}^1A_{1g}(t_{2g}^6e_g^2)$. This high-energy intraconfigurational d–d band is at about 445 nm (22,470 cm^{-1}). Its intensity at 80°K is rather weak (Figures 2, 4) relative to its large and broad neighbor, $^3T_{1g}$ (550 nm), or band 3 (toward the red), so that a rapid spectral scan can almost lead to the loss of this very interesting structure (also see Figure 5). However, the fine structure persists distinctly for seven compounds studied, *i.e.*, $[Ni(NH_3)_6]A_2$, where $A^- = Cl^-$, Br^-, I^-, ClO_4^-, and PF_6^-, and in the deuterated complex cation with counterions $A^- = Cl^-$ and PF_6^- (see Figures 2–5). By having obtained the spectra for the deuterated and undeuterated Cl^- and PF_6^- salts, it is clear that the progressions near 445 nm (22,470 cm^{-1}) are to be associated with skeletal NiN_6 vibrations and not with N–H stretching or NH_3 distortion modes. Two vibronic progressions, h and k, are of dominant intensity in the low-temperature (≤80°K) spectra of the seven complexes mentioned above (Figure 5 and Table II). In two of these undeuterated complexes, however, *i.e.*, the ClO_4^- and Cl^-, and in the deuterated version of the latter, a third progression, g, is observed (Figure 5, Table II). In view of the magnitudes of the separations between the first components, g_1, h_1, k_1, of the three progressions and because of the fact that each is the

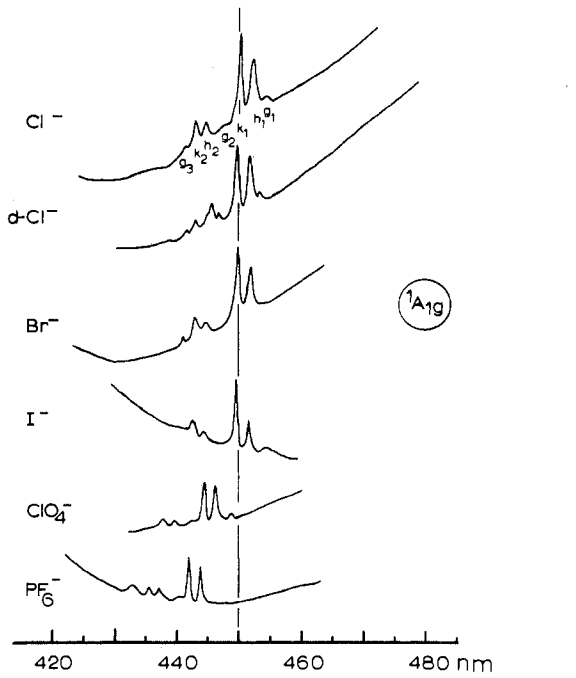

Figure 5. Electronic absorption of band 4 at 80°K of $[Ni(NH_3)_6]A_2$ (mull). "*d*-Cl" is $[Ni(ND_3)_6]Cl_2$.

Table II. Vibronic Progressions on $^1A_{1g}(t_{2g}^6e_g^2)$ of $[Ni(NH_3)_6]A_2$ at 80°K

Member of progression	Position, cm^{-1} (nm)				
	Cl^-	Br^-	I^-	ClO_4^-	PF_6^-
g_1	22,022 (454.1)			22,280 (448.8)	
h_1	22,112 (452.25)	22,130 (451.9)	22,153 (451.4)	22,410 (446.5)	25,530 (443.8)
k_1	22,209 (450.15)	22,230 (449.0)	22,247 (449.5)	22,500 (444.4)	22,620 (442.1)
g_2	22,346 (447.5)		22,318 (448.1)	22,619 (442.2)	22,727 (440)
h_2	22,471 (445.0)	22,490 (444.7)	22,490 (444.6)	22,760 (439.3)	22,870 (437.3)
k_2	22,578 (442.9)	22,580 (442.8)	22,580 (442.8)	22,840 (437.8)	22,960 (435.6)
g_3	22,676 (441.0)	22,681 (440.9)	22,648 (441.5)	22,940 (435.9)	23,094 (433)

start of an approximate 350-cm^{-1} progression, we make the assignments (Table II)

g_1	$^1A_{1g} + t_{2u}' \equiv \delta$	h_1	$^1A_{1g} + t_{1u}'^a \equiv \gamma$
g_2	$\delta + a_{1g}'$	h_2	$\gamma + a_{1g}'$
g_3	$\delta + 2a_{1g}'$	k_1	$^1A_{1g} + t_{1u}'^b \equiv \epsilon$
		k_2	$\epsilon + a_{1g}'$

where all vibrations are skeletal NiN_6 modes, and the positions of these bands are shown in Figure 5 (also see Table II). Also, from comparing the spectra of Figure 5 it seems the t_{2u} NiN_6 skeletal mode plays an intensity role only in the case of the Cl^- and ClO_4^- salts.

It is another point of interest that the energy position of the $^1A_{1g}$ band depends almost linearly on the size of the unit cell of these cubic complexes. For example, Figure 6 shows our plot of the energy of the first component, h_1, of the h progression of $^1A_{1g}$ as a function of the magnitude of the length of the unit cell; *i.e.*, the energy is directly proportional to the length of the unit cell. The most hydrogen-bonding halide ion, Cl^-, deviates from the linearity. It is at first sight perplexing that the energy of an intraconfigurational $t_{2g}^6e_g^2$ excitation, such as this $^3A_{2g} \rightarrow {}^1A_{1g}$ transition, should vary (Figure 6)

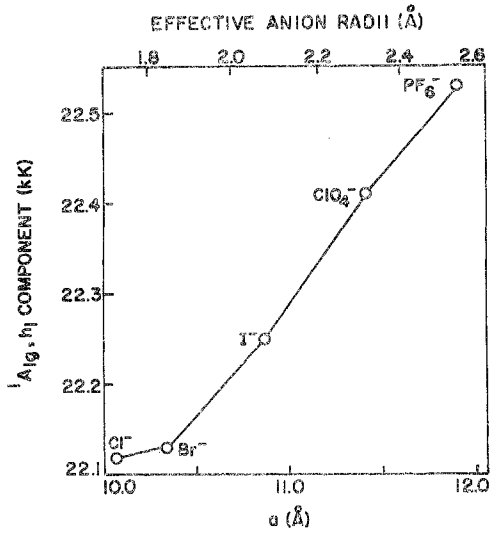

Figure 6. Variation of the position of band 4 (first component of h progression) as a function of the lengths of (cubic) unit cells and effective radii of anions.

several hundred kaysers as one changes the counterion. However, Flint and Greenough[12] found a similar effect in their emission spectra of $[Cr(NH_3)_6](PF_6)_3$ and $[Cr(NH_3)_6](ClO_4)_3$; *i.e.*, the intraconfiguration t_{2g}^3 emission energies from ^2E_g to the $^4A_{2g}$ ground state were 15,291 and 15,221 cm^{-1}, respectively. In the present study it is found, for example, that $^1A_{1g}$ of the PF_6^- salt is also at higher energy than the ClO_4^- salt (22,530 and 22,410 cm^{-1}), and by the same order of magnitude. *We conclude that this intraconfiguration $t_{2g}^6e_g^2$ excitation, $^3A_{2g} \rightarrow {}^1A_{1g}$ near 445 nm (22,470 cm^{-1}) is an excellent means of ascertaining the extent of interaction between the crystalline lattice and the complex ion* $[Ni(NH_3)_6]^{3+}$. While the mechanism of interaction (hydrogen bonding or electrostatic) is less certain, hydrogen bonding appears to be a reasonable suggestion. Furthermore, if the electrostatic interaction between the lattice ion and the Ni^{2+} were dominant, then the order of energies should be $Cl^- > Br^- > I^-$, which contradicts our experimental order, $Cl^- < Br^- < I^-$.

The Fifth and Sixth Bands, $^3A_{2g} \rightarrow {}^1T_{2g}$ and $^3A_{2g} \rightarrow {}^1T_{1g}$, Respectively. These two bands, at about 415 nm (24,100 cm^{-1}) and about 390 nm (25,640 cm^{-1}), became apparent in all our low-temperature spectra (≤80°K) of $[Ni(NH_3)_6]^{2+}$ and deuterated analogs; *e.g.*, see Figures 2 and 7. The assignment of the order, $^1T_{2g} < {}^1T_{1g}$, was made on the basis of the ligand field computation ($-Dq$ = 1100 cm^{-1}, B = 890 cm^{-1}, C = 3290 cm^{-1}, $-\zeta$ = 400 cm^{-1}) which predicts $^1T_{2g}$ (23,905 cm^{-1}) to be below $^1T_{1g}$ (28,281 cm^{-1}). These computed energies can certainly be in error, since the computation does not mix the close and immensely intense charge-transfer band(s) (<350 nm) with the d–d bands. At the temperature of this work only the low-energy band, or $^1T_{2g}$, showed any evidence of vibronic fine structure (Figures 2, 4). Thus, in the spectrum of $[Ni(NH_3)_6](PF_6)_2$ at 80°K the following reasonably regularly spaced peaks are present

m_i	427.5 nm (23,392 cm^{-1})	m_l	414.5 nm (27,125 cm^{-1})
m_j	423 nm (23,641 cm^{-1})	m_m	410.5 nm (24,360 cm^{-1})
m_k	419 nm (23,866 cm^{-1})		

Since this state, $^1T_{2g}$, derives from the severely antibonding configuration $t_{2g}^4e_g^4$, it is reasonable to associate this spacing (*ca.* 245 cm^{-1}) with an a_{1g}' progression of the excited state.

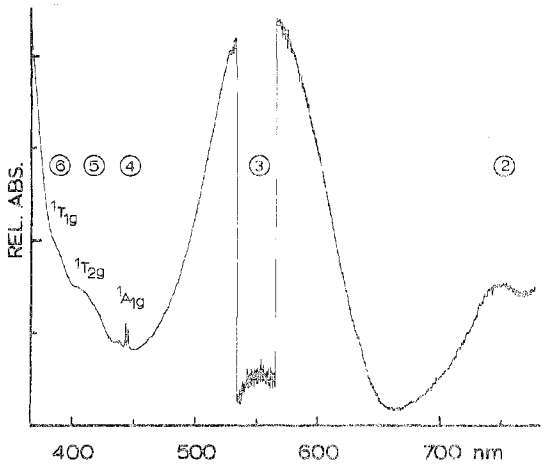

Figure 7. Electronic absorption spectrum of $[Ni(ND_3)_6](ClO_4)_2$, obtained at 79°K, which shows bands 5 and 6 (mull).

Summary

The low-temperature electronic absorption spectra of salts of $[Ni(NH_3)_6]^{2+}$ reveal two vibronic progressions on $^3T_{2g}(F)$, five progressions on $^3T_{1g}(F)$, one progression on $^1E_g(D)$, three progressions on $^1A_{1g}(G)$, and one on $^1T_{2g}(D)$. The members of these progressions variously involve excitations of a_{1g}, e_g, t_{1u}^a, t_{1u}^b, and t_{2u} NiN_6 skeletal modes and the symmetric N–H stretching mode of coordinated NH_3. It is also found that the position of the $^3A_{2g} \rightarrow {}^1A_{1g}$ intraconfigurational excitation is a good indicator of the interaction of the lattice ions and the complex ion $[Ni(NH_3)_6]^{2+}$. Finally, the MCD spectra as measured at two temperatures through the $^3T_{1g}(F)$ establish that the Faraday C term activity of this band and the presence of the residual MCD activity verify experimentally that the ground state, $^3A_{2g}$, obtains angular momentum by second-order spin–orbit coupling, probably with the $^3T_{2g}(F)$ excited state.

Registry No. $[Ni(NH_3)_6]Cl_2$, 10534-88-0; $[Ni(NH_3)_6]Br_2$, 13601-55-3; $[Ni(NH_3)_6]I_2$, 13859-68-2; $[Ni(NH_3)_6](ClO_4)_2$, 14322-50-0; $[Ni(NH_3)_6](PF_6)_2$, 18445-50-6; $[Ni(ND_3)_6](PF_6)_2$, 53385-37-8; $[Ni(ND_3)_6](ClO_4)_2$, 53385-38-9; $[Ni(ND_3)_6]Cl_2$, 14286-01-2.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.
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